Table of Contents

Plenary Sessions

1A Fine and Coarse Particle Mass and Composition: Spatial and Temporal Variability - I

1B Application of Continuous Methods

1C Organic Speciation: Ambient - I

2A Fine and Coarse Particle Mass and Composition: Spatial and Temporal Variability - II

2B Emissions Estimates: Methods and Measurements - I

2C Organic Speciation: Ambient - II

3A Fine and Coarse Particle Mass and Composition: Spatial and Temporal Variability - III

3B Emissions Estimates: Methods and Measurements - II

3C Organic Speciation: Gas-Particle Partitioning

4A Source Apportionment - I

4B PM Composition / Precursor Gases: PM Cation and Anion Field Measurements

4C OC Speciation Methods

5A Source Apportionment - II

5B PM Composition / Precursor Gases: PM Composition Methods & QA

5C Carbonaceous Aerosols: Organic and Elemental Carbon

6A Source Apportionment - III

6B PM Composition / Precursor Gases : Gas and Gas/Particle Species Methods and Measurements

6C PM and Visibility: Regional Haze

7PA Measurements and Methods - I

7PF Source Apportionment - I

7PG Models and Modeling

8A Policy-Relevant Findings at Global, National, and Local Scales

8B Local and Regional Aerosols and Their Influence on Rural and Urban PM Levels - I

8C Ultrafine PM Methods

9A Particle Mass Spectrometer Methods

9B Local and Regional Aerosols and Their Influence on Rural and Urban PM Levels - II

9C Ultrafine PM - Spatial and Temporal Variability

10A Particle Mass Spectrometer Methods - Organic Carbon

10B Estimating Uncertainties in Measurements and Modeling

10C Model Performance Evaluation - I

11A Identifying the Impact of Fires - I

11B Emissions Inventory Verification

11C Model Performance Evaluation - II

12PA Measurements and Methods - II

12PD Measurements and Characterization - I

12PF Source Apportionment - II

13A Identifying the Impact of Fires - II

13B Ammonia Emissions Estimates

13C Model Performance Evaluation - III

14A Size Distribution Measurements and Assumptions

14B Source Apportionment - IV

14C Deposition

15A Influence of Fogs and Clouds on PM Concentrations

15B Source Apportionment - V

15C PM Mass Closure and Assumptions

16A PM Mass Measurements: PM Mass Methods

16B Source Apportionment - VI

16C Optical and Remote Sensing Methods and Measurements

17PB Emissions

17PD Measurements and Methods - II

17PE Atmospheric Processes and Chemistry

17PH Policy Implications

17PI Health and Exposure

17PJ Late Breaking Results

18A Atmospheric Processes and Aerosol Formation

18B Measurement of Toxic Particulate Pollutants

18C Organic Aerosol Chemistry

19A Comparison of Data Among National Networks and Measurement Representativeness - I

19B Role of Acidity in Organic Aerosol Formation

19C Aerosol Water Measurements

20A Comparison of Data Among National Networks and Measurement Representativeness - II

20B Observational Based Modeling Methods and Results

20C PM Mass Measurements: Semivolatiles & Intercomparisons

PLENARY

UNDERSTANDING THE HEALTH EFFECTS OF PM: ARE WE THERE YET?

DANIEL GREENBAUM, Health Effects Institute, MA

In the wake of the promulgation of new NAAQS for PM in 1997, a wave of new research funding and initiatives, guided by the National Research Council Committee on Research Priorities for Airborne Particulate Matter and by a NARSTO workshop in July 1998, were undertaken to attempt to answer key uncertainties about sources, exposure, and effects. Much exposure, epidemiology and toxicology work has now been completed and the NRC Committee has issued its final report. This presentation will summarize what we needed to know in 1997, the progress we have made, and the continuing key questions looking forward.

PLENARY

GLOBAL CLIMATE CHANGE: AEROSOLS AND THEIR LINKAGES,

JEFFREY S. GAFFNEY, Argonne National Laboratory, Argonne, IL

Global climate change is usually associated with increasing greenhouse gas levels in the troposphere, which can lead to changes in Earth's heat balance and global warming. Increased carbon dioxide levels in the troposphere have received the major attention, along with trace gas species including methane, nitrous oxide, ozone, and chlorofluorocarbons. Aerosols are another species that can change the radiative balance of the atmosphere, either by scattering incoming shortwave radiation from the sun or by absorbing radiation. Of the potentially absorbing aerosols, black carbon absorbs most strongly; it was recently identified as a potentially important climate change agent. In addition to their direct effects, aerosols can also act indirectly to increase or decrease cloud formation, depending on their ability to act as cloud condensation nuclei (CCN). The uptake of water vapor on aerosol surfaces is critical to aerosols' growth, removal, and ability to act as CCN. The ability to act as CCN also depends on an aerosol's chemical composition, size distribution, and concentration. Both primary and secondary aerosols can have both direct and indirect radiative effects. Because of the complexity of aerosol processes, aerosols' effects on climate forcing are among the largest uncertainties in prediction of global climate change. Concerns related to natural aerosols include (1) the formation of increased secondary organic aerosols through oxidation of monoterpenes and (2) emissions of sesquiterpene from biota. Megacities (cities with populations greater than 10 million) and mini-megacities (cities with population 5-10 million, which are currently on the rise) are major anthropogenic sources of both primary aerosols and secondary aerosol precursors. This presentation will summarize current issues related to aerosol effects in global climate change and will also examine the linkages between aerosol radiative forcing and related environmental issues. Linkages discussed will include health and air quality, visibility loss, and ecosystem impacts due to direct and indirect aerosol effects. The need for a better fundamental understanding of fine aerosols and their surface chemical and physical natures in regional- and global-scale models will be stressed.

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PLENARY

THE US-EPA SUPERSITES PROGRAM: ELUCIDATING SPATIAL VARIABILITY IN PARTICULATE MATTER SIZE AND COMPOSITION,

JAY TURNER, Washington University, St. Louis, MO

Several of the USEPA Supersites conducted studies at multiple locations in their respective study domains. A variety of measurement platforms were used depending on the specific study objectives. In some cases, integrated sampling for fine particulate matter mass and composition was performed under routine- or intensive-studies scenarios, while in other cases relatively sophisticated batteries of semicontinuous monitors for aerosol chemical and physical properties were deployed. This data can be used to describe how particulate matter size and composition varies across the local, neighborhood, urban, and regional scale within a given Supersites study domain. This presentation provides a brief synthesis of the studies conducted under the USEPA Supersites program towards elucidating spatial variability in particulate matter size and composition. Selected examples will be provided to demonstrate how such studies have supported the development of conceptual models for aerosol behavior.

PLENARY

ATMOSPHERIC PROCESSES AND REDUCTION OF PM2.5 CONCENTRATIONS,

SPYROS PANDIS, Carnegie Mellon University, Pittsburgh, PA

The major precursors of secondary aerosol (sulfates, nitrates, secondary organic PM) are sulfur dioxide, nitrogen oxides, selected VOCs and ammonia. The concentrations of these secondary components are also affected by the presence of primary components (primary organic PM, dust, etc.). Establishment of the relationship between the emissions of the above precursors and the aerosol concentrations in a given area is a necessary first step for the design of a PM2.5 control strategy. Insights into these relationships for inorganic and organic PM components are discussed using examples from the Pittsburgh and other PM Supersite programs. The responses of the major inorganic PM components to changes in emissions of their precursors can be nonlinear and in some extreme cases counterintuitive (e.g. increase of the PM concentration even if the emission of one precursor is reduced). In other cases the system has a limiting reactant: the inorganic PM responds readily to changes to its concentration while at the same time it does not respond to changes in the concentrations of other precursors. The use of both observation-based approaches (thermodynamic models, models combining thermodynamics and removal processes) and 3D Chemical Transport Models for the investigation of these responses will be discussed. The results for Pittsburgh suggest that reductions of sulfur dioxide will result in reductions of PM in all seasons. However, some of the sulfate will be replaced by ammonium nitrate. This ammonium nitrate can be reduced by controlling NOx especially during the winter but also by reducing ammonia throughout the year (Vayenas et al., 2005) The response of the organic component of atmospheric PM to emission changes is complicated by its dual origin. The primary component (direct emission of organic PM from combustion sources, etc.) is expected to respond practically linearly to its emission changes. However, the secondary component is linked to the VOC emissions (and also NOx) emissions through strongly non-linear chemical and thermodynamic processes. The secondary organic component was found to be highly variable during the year in Pittsburgh contributing from almost zero to up to 70% of the organic aerosol concentration on a daily basis (the maximum was observed during the most polluted days) and around 20 -30% on an annual basis. The secondary organic aerosol (SOA) is expected to respond only weakly to change in emissions of the smaller (less than five carbon atoms) VOCs. However, a superlinear reduction (35% reduction of SOA for a 30% reduction of emissions) was estimated for the larger VOCs. The potential changes in organic aerosol because of changes in sulfur dioxide and nitrogen oxide emissions will also be discussed.

References Takahama S., D. Vayenas, S. N. Pandis, and C. Davidson (2004) Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study, J. Geophys. Res., in press. Vayenas D., S. Takahama, C. Davidson, and S. N. Pandis (2005) Simulation of the thermodynamics and removal processes in the sulfate-ammonia-nitric acid system: Implications for PM2.5 control strategies, J. Geophys. Res., in press.

PLENARY

COMPARISON OF PM MASS AND CHEMICAL SPECIES MEASUREMENT TECHNOLOGIES: IMPLICATIONS FOR NETWORK MONITORING,

KENNETH L. DEMERJIAN, J. Schwab, O. Hogrefe, Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY; D. Felton, Division of Air Resources, New York State Department of Environmental Conservation; S. Pandis, Carnegie Mellon University. Pittsburgh, PA; J. Turner, Washington University. St. Louis, MO; J. Froines, University of California at Los Angeles, Los Angeles, CA; J. Ondov, University of Maryland, College Park, MD; J. Watson, Desert Research Institute, Reno, NV; D. Allen, University of Texas at Austin, Austin, TX

U.S. EPA “PM Supersite” programs, in addition to having focused specialized themes regarding PM characterization and formation processes, have each considered the evaluation and performance of traditional and advanced PM measurement technologies. These efforts have included the evaluation of new commercially available semi-continuous PM mass and speciation measurement technologies in field and laboratory environments using a compliment of advanced research instrumentation. The studies, performed with collocated traditional PM measurement technologies, have identified outstanding issues and observed biases among the measurement methods and have provided insights to data harmonization and processing methodologies for establishing equivalency across measurement platforms and networks. The findings from these studies are summarized and their implications for current and future network monitoring systems discussed.

PLENARY

NEW POSSIBILITIES FOR AEROSOL MEASUREMENTS AND SOURCE APPORTIONMENT,

Dr. John Watson, Desert Research Institute, Reno, NV

Several new continuous measurement methods have been demonstrated as part of the Supersites Program than can assist in source apportionment studies. Some of these, such as in situ single particle mass spectrometers, have great potential for the future, but they are currently costly and require special expertise. However, additional measurements on existing filter samples can fill in the gap for source apportionment purposes by taking advantage of new technologies that are applicable to the same types of samples that are taken in long-term networks such as IMPROVE and STN. Thermally-desorbed carbon fractions detected by GCMS have been shown to yield equivalent results to those obtained from extracted samples, with only small slivers of a filter being necessary for analysis. Lead isotopic abundances can be determined along with other elements by ICPMS. The spectral transmission properties through a filter have been shown to vary with wavelength for vehicle exhaust and wood smoke. These and other emerging technologies can be used to address source contribution questions regarding relative contributions from local and distant dust sources, contributions from diesel and gasoline vehicle exhaust, and other primary contributions from burning and cooking.

1A-1

SEASONAL PATTERNS IN AEROSOL COMPOSITION AT LOOK ROCK: IMPLICATIONS FOR HAZE CONTROL, ROGER L. TANNER, Myra L. Valente, Solomon T. Bairai, Kenneth J. Olszyna, and Ralph J. Valente, Tennessee Valley Authority, Environmental Technologies, Muscle Shoals, AL; Jim Renfro, National Park Service, Gatlinburg, TN

Continuous measurements of aerosol composition have been made since mid-March, 2003 at the Look Rock site, collocated with an IMPROVE network site bordering Great Smoky Mountains NP. This work is part of VISTAS RPO focus site monitoring in the Southeast region for haze modeling validation. In connection with previous TVA and National Park Service (NPS) monitoring at the site, an all-season record of hourly-resolved PM2.5 aerosol composition has been acquired. This data shows strong season patterns in both the levels and composition of fine particles at a regionally representative background site. This has implications for the long-term reduction of haze in the region as well as for strategies for meeting the fine particle NAAQS. We have confirmed that high sulfate levels exist only in the summer season or under summer-like conditions (low wind speed, non-precipitating stagnant air masses). For example, monthly means of hourly sulfate data averaged 7.4 µg/m3 for June-July, 2003, but only 2.6 µg/m3 in Dec. 2003-Jan. 2004; for the remaining months through June, 2004, sulfate monthly means were 3.6 ±<0.5 µg/m3. In contrast, under clean conditions, i.e., days with lowest 20% extinction, which occur predominantly from mid-autumn through mid-spring, organic aerosols (corrected for non-carbon mass contributions) are the largest constituent of fine mass at this regional site. Diurnal patterns of hourly PM2.5 aerosol composition are weak in all seasons, and the variability in both mass levels and composition is generally dominated by synoptic air mass changes and precipitation scavenging. Urban and transportation impacts can be seen at the site, but the largest sources of organic aerosols derive from “modern carbon” sources in all seasons. Inter-annual variation in mass and levels of individual constituents can be significant, as indicated by the lower levels observed in the cooler and wetter summer of 2004 (compared to 2000-2003 levels), but do not significantly change the conclusions noted above.

1A-2

COMPARISON OF TWO WINTER AIR QUALITY EPISODES DURING THE CALIFORNIA REGIONAL PARTICULATE AIR QUALITY STUDY, KAREN MAGLIANO, Kasia Turkiewicz, Theresa Najita, California Air Resources Board, Sacramento, CA

The duration, strength, spatial extent, and chemical makeup of particulate matter are compared for two winter air quality episodes in central California. Each episode, from the beginning of the buildup through the dissolution, lasted about three weeks. The first episode occurred from December 14, 1999 through January 1, 2000, with peak 24-hr average PM2.5 concentrations reaching 129 ug/m3. The second episode occurred almost a year later, from December 18, 2000 through January 8, 2001, with peak 24-hr average PM2.5 concentrations reaching 179 ug/m3. Although similar in duration, each episode had unique characteristics. One of the most significant differences was the episode buildup rate, which was rapid during the December 1999 episode, but was slow and steady during the December 2000/January 2001 episode. The rapid buildup of the first episode resulted in more days with PM2.5 concentrations above the 24-hr federal standard while the slow and steady increase of the second episode produced higher peaks. The spatial extent and progress was also different among the two episodes. The first episode was centered over the northern and central San Joaquin Valley and later expanded into the southern Valley. The second episode was centered over the central and southern Valley and by the end of the episode reached into the northern Valley. The differences carried over into the chemical composition. In a rather atypical manner, ammonium nitrate dominated the PM2.5 mass throughout the San Joaquin Valley during the December 1999 episode. The second episode reflected a dichotomy typical to the San Joaquin Valley, with Fresno concentrations dominated by organic and elemental carbon and the rest of the Valley concentrations dominated by ammonium nitrate.

1A-3

CONTINUOUS ANALYSIS OF FRESNO AEROSOLS BY SIZE, TIME, AND ELEMENTAL COMPOSITION, MARCH - DECEMBER, 2001, THOMAS A. CAHILL, Steven S. Cliff, Michael Jimenez-Cruz, DELTA Group, UC Davis, and Kevin D. Perry, Meteorology Dept., U. Utah

In response to the need to get a wide variety of aerosol types as a function of size and time to support short term medical data from the Fresno Asthmatic Children's Environment Study (FACES), the DELTA Group designed and implemented continuous sampling in 8 size modes from 10 µm to 0.09 µm from March 10 to December 21, 2001, using a PM10 modified DELTA Group slotted DRUM impactor. Time resolution was set by the analysis techniques, originally 6 hr, but reduced to 3 hr in July in response to the presence of sharp spikes in the concentrations of many transition metals. Elemental analysis of elements from sodium through molybdenum plus some heavy elements was performed by synchrotron-induced x-ray fluorescence (S-XRF) at the Advanced Light Source, Lawrence Berkeley NL, routinely achieving < 0.1 ng/m3 sensitivity. Extensive quality assurance tests were performed versus standard Dichotomous samples and ARB XRF analysis, with excellent agreement for metals, 1.02 ± 0.11, but highly correlated differences in fine soils associated with the sharper cut point of the impactor and possible sizing differences near the 2.5 µm cut point. Over 1500 sampling periods were examined, with 8 size modes and 32 elements recorded in each, for a total of over 1/3 million data points. Major differences were seen in almost time scales and all species, from seasonal, summer versus winter, to synoptic, diurnal, and short term, with most transition metals showing order of magnitude concentration changes in time scales of a few hours. Summer fine aerosols were dominated by organics (mostly smoke), ammonium sulfate, and soil, with significant soil finer than 2.5 µm. Sharp peaks were seen in time and concentration of transition metals such as zinc (in spring) and copper (in summer), possibly with origins in agriculture despite the distance of the residential sampling site from farming operations. The highest levels of very fine aerosols in summer for many metals were associated with the 4th of July fireworks both local and from sources nearer the Bay Area. More than ½ of winter aerosols were ammonium nitrate, with organic matter and ammonium sulfate the next largest components. High levels of very fine (0.26 > Dp > 0.09 µm) automotive particulates (diesel and smoking cars) were seen in winter months, usually in sharp peaks during nighttime hours, while the anticipated wood smoke signatures were generally weak. These results show that 24 hr average PM10 and PM2.5 data were not adequate at Fresno for short time impacts such as asthmatic responses. We gratefully acknowledge funding from the California Air Resources Board FACES Program and the support of the DOE Advanced Light Source, LBNL.

1A-4

AEROSOL CLIMATOLOGY AT THE ST. LOUIS – MIDWEST SUPERSITE, JAY TURNER, Washington University, St. Louis, MO; George Allen, NESCAUM, Boston, MA; Tina Bahadori, American Chemistry Council, Washington DC; Judith Chow, John Watson, Desert Research Institute, Reno, NV; D. Alan Hansen, EPRI, Palo Alto, CA; Petros Koutrakis, Harvard School of Public Health; Peter McMurry, University of Minnesota, Minneapolis, MN; John Ondov, University of Maryland, College Park, MD; James Schauer, University of Wisconsin, Madison, WI; Rodney Weber, Georgia Institute of Technology, Atlanta, GA; Warren White, University of California, Davis, CA

The Saint Louis - Midwest Supersite (East St. Louis, IL) commenced operation in April 2001 and has conducted sustained measurements at varying levels of sophistication for more than 3.5 years. In particular, the first two years (April 2001 through May 2003) featured daily 24-hour integrated PM-2.5 speciation and a battery of semicontinuous measurements for aerosol chemical and physical properties. The presentation will summarize the aerosol climatology for PM-2.5 mass and its major chemical components (sulfate, nitrate, organic carbon, elemental carbon) as well as particle size distributions. Summary results will be presented for reconstructed mass, parameter-specific diurnal profiles, and seasonal trends. The Supersite data will be placed in a historical context by drawing upon measurements conducted in St. Louis over the past three decades. A contemporary spatial context will also be provided by comparing the Supersite results to FRM and STN measurements in the St. Louis metropolitan area.

1A-5

ATOFMS MEASUREMENTS AT URBAN AND RURAL LOCATIONS: COMPARISON OF SINGLE PARTICLE SIZE AND COMPOSITION, XUEYING QIN, Kimberly A. Prather, University of California, San Diego, La Jolla, CA; Prakash V. Bhave, U.S. EPA, Research Triangle Park, NC

The San Joaquin Valley (SJV) is located in central California and surrounded by mountains on three sides. Pollutants are trapped inside the valley deteriorating the air quality due to the secluded geographic features. PM2.5 and PM10 concentrations reach their highest levels in urban areas during winter when multiple sources simultaneously contribute to the PM concentrations, with secondary ammonium nitrate dominating and carbonaceous species being the second largest PM constituents. In order to address the particulate matter pollution and perform source apportionment on pollutants in the San Joaquin Valley, it is important to obtain information on the particle size, chemical composition, transformation, and spatial and temporal distributions. Two aerosol time-of-flight mass spectrometers (ATOFMS) were deployed for the California Regional Particulate Air Quality Study (CRPAQS) in Fresno and Angiola, respectively, between December 2000 and January 2001. During two months of continuous ambient measurements, data on the size and chemical composition of more than 1,700,000 particles were acquired at each site, making it the most extensive ambient ATOFMS dataset to date. Results from the ATOFMS ambient measurements in Fresno and Angiola are presented and compared. Major particle types in Fresno (urban area) and Angiola (rural area) are compared and the temporal evolutions of these major types are illustrated. A semivolatile organic compound (SVOC) particle type unique to the CRPAQS studies is identified with characteristic mass spectral fingerprint and distinct diurnal temporal variations. The source of Fresno SVOC particles is mainly attributed to biomass burning emission, and the diurnal variation is the result of rapidly increased biomass burning activities in the evenings and nights in urban area. Due to the lack of local emission sources, particles detected in Angiola were transported from urban areas and therefore are highly transformed. They do not display the same diurnal temporal variation as those observed in Fresno. Quantitative results on size resolved particle composition obtained from ATOFMS measurements during CRPAQS study are also presented. These results are obtained by scaling the ATOFMS measurements using data from a micro-orifice uniform deposit impactor (MOUDI). Detailed scaling procedures will be presented in addition to the concentrations and temporal variations of major scaled particulate components, such as ammonium nitrate and carbonaceous type particles. In addition, the sensitivities of field-based ATOFMS to particles with different chemical compositions in the San Joaquin Valley are also determined. These parameters can be directly applied to ambient measurements and will help to elucidate the relative importance of varying ambient factors. All of the above information obtained from ATOFMS measurements will aid in furthering our understanding of the sources and formation mechanisms of particulate air pollution in the San Joaquin Valley.

1B-1

AMBIENT ELEMENTAL SIGNATURES OF DIESEL AND AUTOMOTIVE PARTICULATE MATTER BY SIZE, TIME, AND CONCENTRATION, THOMAS A. CAHILL, , Steven S. Cliff, Michael Jimenez-Cruz, Lee Portnoff, DELTA Group, UC Davis, CA, Kevin D. Perry, Meteorology Department, U. Utah, Earl Withycombe, Health Effects Task Force, American Lung Association Sacramento Emigrant Trails, CA

The impact of roadway pollution on downwind residential areas was a major motivator in efforts to remove lead from gasoline in the 1970s and 1980s. Recent data on the toxicity of diesel and automobile particulate matter once again requires examination of near roadway impacts. The California Air Resources Board estimates that 70% of all California airborne toxic impact comes from diesel exhaust alone. However, present studies of diesels and smoking cars lack the unique automotive fine lead signature of the 1970s, making such estimates difficult. Smoking cars are becoming a more serious problem as diesel emission continue to drop, as now diesels are only about 20 times that of the average car on the roadway. Thus, a highway with 5% diesels and 95% cars emits roughly equal amounts of diesel and automotive particles. Further, several recent studies have shown a higher fraction of PAHs in auto particulates versus diesel particulates, with potential impacts on the toxicity of automotive particulates. In order to improve estimates of roadway impact, we have performed a series of studies of freeways and heavily travel secondary highways in Sacramento, California, and developed a series of criteria for diesel and smoking car particulate matter. Two components are required for isolation of vehicular impact analysis: 1) separation of roadway aerosols from regional aerosols, and 2) separation of diesel and car impacts. In the first case, simultaneous upwind-downwind sampling across the roadway is the 'gold standard'. For roadway aerosols, we find that the most reliable tracers of vehicular impact are the ash of lubricating oils stabilized with zinc thiophosphate, and often with anti-acids such as calcium carbonate, giving aerosols in the $0.26 > Dp > 0.09$ µm very fine (vf) size mode (ideally with a correction for the particles between 0.05 and 0.09 µm.). The aerosol components zinc and phosphorus are usually correlated, and often with vf potassium. For the second problem, the amount of correlated sulfur present is a rough estimate of the diesel fraction, since little sulfur comes from the low sulfur California gasoline. With traffic and meteorological data and these emission factors in mg/km, we both measured and modeled transmission of aerosols form roadways into nearby neighborhoods, including schools. We show additional examples from Fresno and South Lake Tahoe. In the latter case, we also used the NO/CO ratio, which is greater than 90 for diesels versus cars.

We gratefully acknowledge funding and support from the Health Effects Task Force of the Sacramento-Emigrant Trails section of the American Lung Association (ALASET), including Jananne Sharpless, Chair, Betty Turner, consultant, and numerous volunteers, and the DOE sponsored Advanced Light Source, Beam Line 10.3.1, LBNL.

1B-2

SEARCHING FOR SECONDARY CARBON IN SEMI-CONTINUOUS OBSERVATIONS: PART II,

GEORGE HIDY, Aerochem, Placitas NM, C. Blanchard, Envair, CA

Semi-continuous observations of particulate organic carbon (OC) and black carbon (BC) from the SEARCH network in the southeastern U.S. provide a rich data set for investigating the origins of the carbon. Diurnal and seasonal patterns indicate that OC is enriched in the summer months, and that OC levels vary with O3 concentrations. Using the ratio of OC/CO, estimates of the fraction of secondary organic carbon (SOC) produced locally compared with regional carryover of SOC were developed. Variations of the ratio of primary OC (POC) to carbon were examined, and their effects on estimates of SOC formation were determined. Additional analyses showed that variations of OC were correlated with sulfate, nitrate, and VOC variations. The VOC observations used include certain aromatics that are believed to represent anthropogenic emissions, and isoprene or terpenes representing biogenic VOC emissions. Principal component analysis (PCA) indicated that the larger portion of the OC concentrations covaried with primary pollutant levels, including CO and BC, while smaller covariances with ozone, sulfate, and nitric acid were also observed. Using the PCA method and other inferences, the potential importance of different mechanisms producing SOC was explored. Indicators for a photochemical component were identified, supporting an organic vapor oxidation process associated with O3 and OH. Interpretation of this component could not rule out the possibility that acid catalysis could be involved in SOC formation as well. Other major factors of interest derived from the data include association of OC with an apparent primary aerosol component, and weather related components. The estimate of the fraction of SOC found in the urban and rural aerosols was refined and compared with results from other complementary methods. The results of this analysis are useful in interpreting marked differences in diurnal OC characteristics at three different rural sites, and for evaluating differences between rural and urban locations.

1B-3

SOURCES OF VOLATILE ORGANIC COMPOUNDS IN BALTIMORE, MD,

Joseph Patrick Pancras, GREGORY BEACHLEY, Melissa Rury, John M Ondov, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742; Walter Cooney, Maryland Department of Environment, Baltimore, MD 21224

Hourly VOCs, criteria gases, and particulate EC and OC, were measured for 9.5 months in 2002 at the Baltimore Supersite at Ponca St., in East Baltimore, where air quality is affected by a large number of primary anthropogenic VOC sources, including automotive emissions from the I895 and I95 freeways to the east, and city traffic to the west of the site, petroleum storage facilities, a sugar beet plant, an asphalt plant, automobile painting plant, the world’s largest Yeast Plant, and various chemical processing industries. Herein, we compare results from receptor models such as Principle Components Analysis-Multi Linear Regression and Positive Matrix Factorization. Time series and wind directional analyses are also used to determine sources and their locations and to develop an optimum set of tracers for use in advanced models, including our Pseudo-Deterministic Receptor Model (PDRM). Of special interest will be traffic related sources.

1B-4

RESOLUTION OF DISTANT AND AGED PM SOURCES USING HIGHLY-TIME RESOLVED PM CONSTITUENT AND SIZE-SPECTRAL DATA,

MELISSA RURY, Joseph Patrick Pancras, Gregory Beachley, Narayanan Nair, and John M. Ondov, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742

Particle-size spectra containing 104 intervals between 9 nm to 19 µm were collected at 5-minute intervals at the Baltimore Supersite at Ponca St., for 9.5 months in 2002. Herein, number and derived surface and volume distributions are binned as indicated above and used along with simultaneous highly time-resolved measurements of PM2.5, EC, OC, sulfate, 12 elemental constituents, and selected VOC and criteria gases in multivariate models to apportion sources by age and source category. Because the different modes have different characteristics (e.g. ultrafine particles dominate number concentration, but have small mass concentrations) different distribution moments will be applied to each of the different ranges. This is, number and surface area concentrations will be used to represent ultrafine and fresh accumulation aerosol, respectively; and volume concentrations will be used to represent the aged and dust particle ranges. Application of the data into a grand model as well as modeling of periods selected on the basis of meteorological transport regime will be discussed.

1B-5

EVALUATIONS OF SOURCES TO NANOPARTICLES IN THE AMBIENT ATMOSPHERE,

YEE-LIN WU, Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan

Measurements of particle size distributions for 10 to 875 nm were conducted by using SMPS in urban area. The temporal resolution was 6 minutes and there were 44 channels from 9.8 nm to 874 nm. In addition to particle size distribution, the airborne concentrations for NO, CO, particulate sulfate and nitrate, and micrometeorological conditions were also monitored simultaneously. The measured particle size distributions were decomposed into combinations of log-normal distributions. Generally, two or three log-normal distributions were able to account for more than 95% of measured results. Most of the time, the major mode was with mode diameter around 90 nm and the average contribution was 81%. The minor mode was generally with mode diameter around 30 nm and the average contribution was 19%. The particle size distributions and concentrations changed significantly along with the change of wind directions. Therefore, the changes of wind directions, implying different air parcels, will change the characteristics of the airborne particles. For example, the major mode diameters were from 75 to 85 nm and 100 to 100 nm, respectively, for winds from north and west. During persistent wind direction, significant increments in the concentrations for minor mode were observed near noon and those for major mode were about the same. The contributions from mobile sources were identified by comparing the temporal variations for particle, NO, and CO concentrations. The residual peak concentrations were from the secondary aerosol formation. For particles from mobile sources, the mode diameters were the same at about 35 nm while concentrations increased significantly. Both the mode diameter and concentrations increased for secondary aerosol formation near noon; the mode diameter increased from 11 nm to 30 nm in 90 minutes and the mode concentration increased from 15 to 95 #/cm3 during the same time period. Therefore, the temporal variation patterns for the mode diameter and concentrations were different for mobile sources and secondary aerosol and the temporal patterns can be used to differentiate the contribution sources.

1C-1

REFERENCE MATERIALS AND QUALITY ASSURANCE FOR THE CHARACTERIZATION OF ORGANIC COMPOUNDS IN PARTICULATE MATTER, MICHELE M. SCHANTZ and Stephen A. Wise, NIST, Analytical Chemistry Division, Gaithersburg, MD 20899; Stephen McDow, US EPA, Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, Research Triangle Park, NC, 27709; Joellen Lewtas, University of Washington, Dept. of Environmental and Occupational Health, Seattle, WA 98105

One of the first environmental matrix Standard Reference Materials (SRMs) developed by the National Institute of Standards and Technology (NIST) for determination of organic species was SRM 1649 Urban Dust, ambient total suspended particulate matter (PM) collected in Washington DC in the late 1970's. Since SRM 1649 was issued in 1981, it has found widespread use in the PM measurement community, and NIST has assigned values for over 100 organic species in this material. However, there is a growing need for additional SRMs to support organic speciation in PM, particularly for the fine PM fraction and representative of contemporary combustion sources. NIST is collaborating with the U.S. Environmental Protection Agency (EPA) to develop SRMs and to provide interlaboratory comparison exercises to improve the accuracy and comparability of organic speciation measurements in PM. As part of the NIST/EPA collaboration, the Organic Speciation Working Group was formed in 2000 to assist in this effort by participating in interlaboratory comparison studies and to provide input for the development of SRMs to support these measurements. This group has participated in three interlaboratory comparison studies for the determination of polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs, alkanes (including hopanes and cholestanes), sterols, carbonyl compounds (ketones and aldehydes), acids (alkanoic and resin), phenols, and sugars in PM-related samples. Because these interlaboratory comparison studies are performance-based, participating laboratories are encouraged to use the analytical methods that they routinely use in their laboratories to analyze PM samples. The results from the participating laboratories, following outlier testing, are used to assign a consensus concentration for each analyte in the unknown PM samples. Results are used in the consensus value assignment for the unknown PM sample only if the laboratory's results for analysis of SRM 1649a Urban Dust, which is provided as a control material, are within 30% of the uncertainty limits of the certified values. The consensus values, accuracy and precision assessments, and the methods used by each laboratory are summarized in a report provided to the participants. The third NIST/EPA interlaboratory study was recently completed, and the results will be presented. Based on the results of these studies, the list of target analytes has been refined and priorities for the development of SRMs have been identified. Calibration solution SRMs are currently under development for: polycyclic aromatic hydrocarbons (PAHs) (two redesigned solutions with an expanded list of 53 PAHs and alkyl-substituted PAHs), aliphatic hydrocarbons, nitro-substituted PAHs (redesigned with an expanded list of 27 compounds), hopanes/steranes, and 13C-labeled and deuterium-labeled levoglucosan (for use as internal standards). The status of the development of these organic solution SRMs and the priorities for future SRM development will be discussed. Although this work was reviewed by EPA and approved for publication, it may not reflect official Agency policy.

1C-2

ORGANIC PM2.5 AT THE BALTIMORE PM SUPERSITE: DIURNAL VARIATIONS DURING SUMMER AND WINTER WITH A TIME-RESOLUTION OF THREE HOURS, WOLFGANG F. ROGGE, Anna Bernardo-Bricker, Orhan Sevimoglu, Florida International University, Miami, FL; Yu Chen Chang, John Ondov, University of Maryland, College Park, MD.

Within Baltimore, the composition and concentration of organic aerosol is only known to a limited extend. Consequently, the lack of suitable organic PM2.5 data has so far precluded refined source/receptor reconciliation. Here, for the very first time, ambient concentrations of organic compounds associated with PM2.5 are determined on a three hour interval for a total of 29 days during summer 2002 and winter of 2002-2003. PM2.5 is collected using a specially designed sampling system that allows the collection of organic matter on filter and PUF substrates. The sampling system has five separate sampling channels connected to one PM2.5 inlet and is operated in a sequential mode. Individual sampling time is three hours and the nominal flow rate is 600 l/min. Filter and PUF samples separately, are solvent extracted and analyzed by GC/MS for more than 100 organic compounds, including: normal and branched-alkanes, alkylcyclohexanes, n-alkanoic acids, n-alkenoic acids, dicarboxylic acids, aromatic acids, resin acids, phenolic type compounds, sterols, hopanes, steranes, PAHs, oxy-PAHs, sugars, thiazoles, secondary oxidation products and others. Here, diurnal variations of selected organic compounds during summer and winter will be discussed and the seasonal variability of the ambient organic compound concentrations will be highlighted. Next, an overview will be provided for key organic compounds that are potential source markers for primary sources and secondary atmospheric reaction products originating from natural or man-made organic precursor compounds.

1C-3

SEMI-VOLATILE ORGANIC COMPOUND CHARACTERIZATION AT THE FRESNO SUPERSITE DURING WINTERTIME STAGNATION EPISODES,

BARBARA ZIELINSKA and Lynn Rinehart. Desert Research Institute, Reno, NV.

Semi-volatile organic compounds (SVOC) measurements were conducted in Fresno during the winter of 2000/2001 to characterize the significance of the inversion formation and breakup and its effects upon the Fresno Supersite particulate matter air quality. The four daily sampling periods were selected (0000-0500, 0500-1000, 1000-1600, and 1600-2400 PST) to bracket diurnal patterns in emissions and meteorology. Organic measurements were also collected on corresponding days and times at three additional anchor sites in the San Joaquin Valley as part of the California Regional PM10/PM2.5 Particulate Air Quality Study (CRPAQS). One of the major objectives of CRPAQS was to determine the contributions of various sources categories to episodic levels of fine particles. Emission source sampling and source profile development for receptor-oriented source apportionment was also conducted. The emission sources include on-road gasoline and diesel vehicles, off-road construction equipment, meat cooking, residential wood combustion, agricultural and prescribed burning, brake and tire wear, and petroleum refinement. Analyzed compounds include polycyclic aromatic hydrocarbons (PAH), hopanes, steranes, aliphatic alkanes, and after derivatization with bis(trimethylsilyl)trifluoroacetamide (BSTFA), polar organic compounds such as: aromatic and alkanoic organic acids, methoxylated phenol derivatives, cholesterol, and levoglucosan. Results indicate a high contribution of residential wood combustion to overall PM2.5 wintertime concentrations. Biomass combustion molecular markers, levoglucosan and methoxylated phenol derivatives have been evaluated and in general their maximum concentrations correspond to time segments reflecting home heating and inversion formation. This presentation will discuss the diurnal changes in the SVOC concentrations.

1C-4

MOLECULAR COMPOSITION OF ORGANICS IN PM-2.5 AT THE NEW YORK CITY SUPERSITE DURING WINTER 2004,

Min Li, MONICA A. MAZUREK, Department of Civil & Environmental Engineering, Center for Advanced Infrastructure and Transportation, Rutgers, The State University of New Jersey, Piscataway, NJ (CAIT); Stephen R. McDow, Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, U.S. EPA, Research Triangle Park, NC; James Schwab, Kenneth Demerjian, Atmospheric Sciences Research Center and Department of Earth and Atmospheric Science, University of New York at Albany; Dirk Felton, New York State Department of Environmental Conservation

Organic compounds in PM-2.5 were studied at the New York City Supersite at Queens College, NYC as part of the NYC Supersite Winter 2004 Intensive from January 15 to February 5, 2004. The Queens fine particle samples were collected on a daily basis. Eight composites containing 3 to 4 filters were generated to provide sufficient organic carbon (OC) mass for the determination of individual organic molecular tracers within the OC fraction. A field blank composite (extracted exactly as the ambient PM-2.5 filters) and a trip blank composite were analyzed to monitor sampling and analytical background levels of the OC molecular constituents. The filter composites were extracted with organic solvent (1:1 methylene chloride:acetone) and analyzed for 52 molecular marker compounds by gas chromatography/ion trap mass spectrometry (GC/IT MS). Normal alkanes (C25 to C32), n-alkanoic acids (C10 to C30), dicarboxylic acids (C3 to C9) and hopanes (C27 to C32) were identified in most sample composites. Ambient mass concentrations for these molecular marker groups were determined. Ratios of the ambient mass concentrations of the molecular markers to the EC and the OC fractions were established to study wintertime variation of urban emission sources in the metropolitan New York City area. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

1C-5

SIZE-SEGREGATED CHARACTERIZATION OF PARTICULATE MATTER - OC/EC AND SEMIVOLATILE NONPOLAR ORGANICS IN SAXONY,

KONRAD MUELLER, Erika Brueggemann, Thomas Gnauk, Antje Plewka, Gerald Spindler, Hartmut Herrmann, Leibniz-Institut fuer Troposphaerenforschung, Leipzig, Germany, Holger Gerwig, Landesamt fuer Umwelt und Geologie, Dresden, Germany

Berner impactor and MOUDI samples were collected in Dresden, Leipzig and the rural site Melpitz to identify contributions of nonpolar organic compounds from natural and anthropogenic sources to PM. A comparison of samples from different sites and seasons allows us to identify these sources. With a minimum of sample treatment alkanes and PAH were quantified by Curie-Point pyrolysis GC-MS from impactor samples. From Berner samples 5 to 10 % of the stage mass was analyzed using four deuterated internal standards. From the MOUDI samples 27.5 % were used for the organic speciation analysis. Other parts of the samples were used for analysis of water soluble ions and for OC/EC analysis. The OC/EC group analyses were added to get some information about the total volume of carbonaceous material in PM fractions. The distribution of alkanes between size classes is dependent on the season and the sampling site. Alkanes have typical pattern from biogenic and anthropogenic sources as well. Alkanes from the traffic found in smallest particles (up to 140 nm) near a traffic rich street but in suburban and rural sites their concentration maximum was found in medium-sized particles (up to 560 nm). During the winter time a conglomerate of alkanes from traffic and from domestic heating was found. The biogenic hydrocarbons were found between spring and fall in coarse mode particles typically. During the summer and fall the amount of biogenic hydrocarbons in the coarse mode PM is much higher than from anthropogenic sources. The CPIodd/even reaches in Leipzig during summer values up to 6 whereas in the winter this value was not higher than 1.5 in the coarse mode PM. In the region of investigations a decreasing amount of brown-coal briquette stoves still exist which emit high amounts of PAH. The PAH concentrations in PM were measured during different campaigns in the last 12 years. The concentration of PAH in winters decreased in this period by one order of magnitude depending on the rapid modernization of domestic heating. The distribution of PAH between PM and gas phase is highly temperature dependent but not for benzo(g,h.i)perylene or benzo(e)pyrene which were found in winter samples at a more than tenfold level from summer data. The back trajectory analyses compared to the PAH concentration measured have shown that long range transports from Eastern Europe were higher loaded by PAH than air masses from Western Europe. The content of EC and sulphate is higher in PM from eastern origin whereas form SW nitrate is higher. The OC data are changing between days of investigation. OC and EC in smallest particles (<140 nm) are the main components up to 80 % but in medium size and coarse mode particles the content of organic matter and EC is typically below 50 % because ionic components and ground dust were found herein.

2A-1

DECONVOLUTING HIGH TIME RESOLUTION DATA TO OBTAIN INSIGHTS INTO SPATIAL SCALES OF REPRESENTATION,

JASON HILL, Jay Turner, Washington University, St. Louis, MO

Following the methodology of Watson and Chow (J. Air & Waste Manage. Assoc., 51, 1522-1528 (2001)), we have deconvoluted high time resolution (5-minute) black carbon (BC) from a single Aethalometer into high temporal frequency and low temporal frequency components. The components are presumably indicative of different spatial scales of emissions relative to the monitoring site. This approach has been applied to more than two years of sustained data collected at the St. Louis – Midwest Supersite core monitoring location in East St. Louis, IL. Diurnal profiles of the low frequency component reveal a pattern influenced by atmospheric ventilation. Concentrations are relatively high in the nighttime and early morning when the effects of atmospheric ventilation are minimal. Following a local maximum concentration coincident with morning rush hour, a broad local minimum is observed during midday which corresponds to the period of maximum atmospheric ventilation (as expressed by the ventilation index). The high frequency component is consistent with local emission sources. Concentrations are relatively low during the nighttime and early morning, exhibit a local maximum coincident with morning rush hour, and are relatively constant from the late morning through the evening. This profile is consistent with local, ground-level emissions being insensitive to diurnal patterns in atmospheric ventilation. High frequency diurnal profiles are distinctly different between weekdays and weekends, with the weekends exhibiting a damped morning rush hour peak and lower concentrations throughout the day. On average, the high frequency BC contribution was about 15% of the total BC for the East St. Louis site. The high frequency BC concentration exceeded 100 ng/m3 for 50% of the hours over a two-year period, and exceeded 500 ng/m3 for 5% of the hours. Temporal patterns in the high frequency component were further investigated using 10-minute resolution meteorological data and 5-minute resolution particle size distribution data. Results are also presented for two rural sites – Park Hills, MO and Reserve, KS.

2A-2

CHARACTERIZATION AND SOURCE APPORTIONMENT OF ATMOSPHERIC ORGANIC AND ELEMENTAL CARBON IN 2003 AUTUMN AND WINTER OVER XI'AN, CHINA,

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Continuous observation of atmospheric organic and elemental carbon has been conducted at Xi'an supersite station from September 2003 to October 2004. Time series of PM2.5, OC and EC of 2003 autumn and winter have been presented in this paper. PM2.5 samples were collected on pre-fired quartz filters with mini-volume samplers every day and analyzed using thermal optical reflectance (TOR) method. Three major emission source samples, i.e., coal-combustion, motor exhaust and biomass burning, have also been collected for OC and EC analyses. The average PM2.5 OC concentrations in autumn and winter were 34.1± 18.0 µg m-3, 61.9 ± 33.2 µg m-3, respectively, while EC were 11.3 ± 6.9 µg m-3, 12.3 ±5.3 µg m-3, respectively. The OC and EC at Xi'an are higher than most urban cities in the world. The OC and EC in the autumn were found to be strongly correlated (R2 >0.9), while they were found to be moderate correlated in the winter (R2 = 0.66). The carbonaceous aerosol accounted for 48.8 ± 10.1% of the PM2.5 in the autumn and 45.9 ± 7.5% of the PM10. All the OC/EC ratios were larger than 2.0. The average OC/EC ratio was 3.3 in the autumn and 5.1 in the winter. This may be related to the primary emission sources. The contribution of secondary organic carbon was not significant in the winter. Total carbon was appointed by absolute principal component analysis (APCA) of the 8 carbon fraction data (OC1, OC2, OC3, OC4, EC1, EC2, and EC3, and OP). The contribution of gasoline-fueled vehicular exhaust accounts for 73% of TC, diesel-fueled vehicular exhaust accounts for 23%, and biomass burning for 4% in the autumn. However, the contribution of coal-combustion to TC reached 44%, the contributions of gasoline-fueled, diesel-fueled vehicular exhaust and biomass burning were 44%, 9%, and 3%, respectively.

2A-3

THE RELATIONSHIP BETWEEN REAL-TIME AND TIME-INTEGRATED COARSE, INTERMODAL, AND FINE PARTICULATE MATTER IN THE LOS ANGELES BASIN,

MICHAEL D. GELLER, Philip M. Fine, Constantinos Sioutas, Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA 90089-2531, USA

A periodic review of the National Ambient Air Quality Standards for Particulate Matter by the U.S. Environmental Protection Agency (EPA) will assess the standards with respect to levels, particle size, and averaging times. Some members of the scientific community in the United States and Europe have suggested the use of PM1 instead of PM2.5 as the fine particle measurement standard. This proposed standard is intended to reduce the influence of coarse particle sources on PM2.5, because some evidence suggests that PM1–2.5 is dominated by coarse particulate matter (PM) sources. In this study, coarse (PM2.5–10), intermodal (PM1–2.5), and fine (PM2.5) mass concentrations at four different sites are measured with continuous and time-integrated sampling devices. The main objective is to compare variations in these three size ranges while considering the effects of location, sources, weather, wind speed, and wind direction. Results show strong correlations between PM1 and intermodal PM in receptor sites. The contribution of PM1–2.5 to PM2.5 is highest in the summer months, most likely due to enhanced long-range transport. Coarse PM is poorly correlated with intermodal PM. Continuous data suggest that PM1 is growing into PM1–2.5 via complex processes involving stagnation of the aerosol during high relative humidity conditions, followed by advection during daytime hours.

2A-4

COMPARISON OF CONTINUOUS AND FILTER-BASED MEASUREMENTS OF SPECIATED PM2.5 IN THE SOUTHEASTERN US, PATRICIA BREWER, VISTAS, NC; Scott Reynolds, South Carolina Department of Health and Environmental Control, SC; Ben Hartsell, Atmospheric Research and Analysis, TX; Roger Tanner, Tennessee Valley Authority, AL; Joe Adlhoch, Air Resources Specialists

VISTAS is the regional planning organization for visibility for 10 states in the southeastern US and is responsible for the technical analyses and planning activities to support state implementation plans for regional haze. VISTAS is evaluating components of PM2.5 in urban, rural, and Class I areas in southeastern US, using filter-based measurements from the Interagency Monitoring of Protected Visual Environments (IMPROVE), Speciated Trends Network (STN), and Southeastern Aerosol Research and Characterization Study (SEARCH) monitoring networks. Data as available from 2000 to 2003 were analyzed. The IMPROVE, STN, and SEARCH measurement methods are comparable for gravimetric PM2.5 mass, sulfate, nitrate, and soils. SEARCH and STN measure ammonium while IMPROVE infers ammonium from the combined mass of sulfate and nitrate assuming that all sulfate is fully neutralized. All 3 networks collect carbon on quartz filters. IMPROVE and SEARCH use Thermal Optical Reflectance (TOR) to separate organic carbon (OC) from elemental carbon (EC). STN uses Thermal Optical Transmittance (TOT). IMPROVE and SEARCH report OC that has been corrected for carbon on blank filters. STN reports OC that has not been corrected for carbon on the filters, although methods are being developed to do so. Across the southeastern US, on the days with high fine PM mass and poor visibility, ammonium sulfate is the largest contributor to PM2.5 mass and haze. Sulfate values at Class I areas are very similar to those at nearby urban areas with average summer quarter values near 10 µg/m3 for interior and Southern Appalachian sites and near 5 µg/m3 for Gulf and Atlantic coastal sites. Organic carbon is the second largest contributor, with somewhat higher values in the urban areas than in nearby Class I areas. Differences in methods may account for some of the differences in OC mass between urban and Class I areas. Ammonium nitrate has small contributions to PM2.5 mass and visibility, with higher values in winter than in summer and slightly higher values in urban areas than in Class I areas. Soils and elemental carbon has small contributions except during episodes of African or Asian dust and fire. VISTAS is also funding continuous speciated PM2.5 measurments at three Focus sites that were chosen to represent a Southern Appalachian, a southern coastal, and an urban environment: Look Rock in Great Smoky Mountains National Park, TN (IMPROVE); Cape Romain National Wildlife Area, SC (IMPROVE), and Millbrook, NC (north of Raleigh, STN). These data will improve our understanding of diurnal trends in PM2.5 and will improve the data base available for evaluating atmospheric models performance. The Focus sites have a full suite of surface meteorological measurements plus 1-in -3 day speciated PM2.5 mass (IMPROVE or R&P monitor), continuous fine particle mass (TEOM monitor), and filter-based PM10 mass. Light extinction is directly measured using a nephalometer at Great Smoky Mountains and Cape Romain. The Rupprecht and Patashnick continuous sulfate (R&P 8400S), nitrate (R&P 8400N), and carbon (R&P5400) monitors, and an aethalometer (black carbon) are operated at all three sites. The Thermo Environmental sulfate monitor is used at Millbrook, NC, and intermittently at Look Rock, TN. Air Research and Analysis (ARA) is also continuously measuring nitrate and ammonium (ARA monitor) at Millbrook, NC. Continuous monitors are being operated from April 1, 2003 through December 31, 2004 at all sites; SC and NC will extend operation at their sites. Hourly sulfate, nitrate, total carbon, and black carbon were evaluated to determine diurnal trends. For example, at Great Smoky Mtns there is little diurnal variation in suflate, nitrate, or black carbon, at least compared to the diurnal variation in ozone. Seasonally, sulfate and black carbon are highest in the summer and lowest in the winter; nitrate is highest in the winter and spring and lowest in the summer. These seasonal trends in the continuous monitoring data are similar to those in the filter-based data. The values of 24-hr composite data for sulfate, nitrate, total carbon, and black carbon from the continuous monitors are lower than those for the filter-based data. Continuous sulfate values are well correlated with filter sulfate values. Continuous nitrate, total carbon, and black carbon are less well correlated to the filter data for these species. Comparison of the continuous data to filter-based IMPROVE and STN data for the 2003-2004 period is underway and will be discussed in detail in the paper.

2A-5

MEASUREMENT AND ANALYSIS OF FINE PARTICULATE MATTER (PM2.5) IN NORTH CAROLINA, Viney Aneja, STEPHEN GOETZ, North Carolina State University, Raleigh, NC; Hoke Kimball, Joette Steger, North Carolina Division of Air Quality, Raleigh, NC

Daily PM2.5 samples and metereology have been monitored and analyzed at seven sites (Fayetteville, Goldsboro, Jacksonville, Kenansville, Kinston, Raleigh & Wilmington) located in North Carolina(NC) during 2001-2003. Chemical analysis showed that the major component in NC is organic matter(OM); and the major soluble component is sulfate (SO4 2-) and then ammonium (NH4 +) and nitrate. (NO3 -) The coastal sites typically had lower concentrations (ranging from ~0 to 20 µg/m3), when compared with the inland sites. (ranging from ~0 to 30 µg/m3) The mass concentration trends related to wind speed and relative humidity were observed. The wind direction was analyzed to examine the prevalant sources of fine particulate and/or their precursors. The impact of increased ammonia emissions on PM2.5 composition in Eastern North Carolina is examined.

2B-1

ESTIMATING OF THE IMPACT OF PRIMARY COAL FIRED BOILER EMISSIONS TO PM2.5 AND PM10 USING COMPUTER CONTROLLED SCANNING ELECTRON MICROSCOPY DATA, GARY CASUCCIO, Traci Lersch, RJ Lee Group, Inc., Monroeville, PA; Alan Robinson, Emily Weitkamp, Carnegie Mellon University, Pittsburgh, PA; Donald Martello, U.S. Department of Energy, National Energy Technology Laboratory, Pittsburgh, PA

Quantifying the impact of primary emissions from coal fired power plants continues to be of interest to the environmental and health effects communities as numerous uncertainties remain regarding the linkage between coal-fired boiler emissions and health-related concerns. Methods based on individual particle analysis offer the potential to provide additional insight on this issue because spherical alumino-silicate (SAS) particles can be used as a tracer of primary emissions from high temperature, pulverized coal combustion. Electron microscopes are capable of providing both morphological and compositional information on fine particulate matter and thus are well suited to identify SAS particles in ambient samples. In an effort to develop a method for estimating the contribution of primary emissions from coal-fired boilers to ambient PM2.5 concentrations, a study was performed using computer controlled scanning electron microscopy (CCSEM) techniques. Ambient samples were collected on polycarbonate filters for CCSEM analysis. Information on particle size and elemental composition was acquired during the CCSEM analysis along with a digital image of each particle. Images of particles composed of silicon-aluminum were distinguished based on morphological characteristics to identify SAS. Following this approach, SAS concentrations in ambient PM2.5 and PM10 samples were determined for the Summer (July 2001) and Winter (January 2002) Intensives of the Pittsburgh Supersite. SAS particle emission factors were determined through the CCSEM analysis of source samples collected from a pilot-scale pulverized coal combustion system at the DOE National Energy Technology Laboratory using dilution sampling techniques. Measurements were made while firing a variety of bituminous and sub-bituminous coals. The source samples were analyzed following procedures established for the ambient samples to determine the ratio of SAS emission to PM2.5 mass emissions for each fuel. The SAS emission ratios were combined with the ambient SAS concentrations to estimate the contribution of primary coal boiler emissions to ambient fine particulate levels. Using this approach, primary coal emissions are estimated to contribute 0.3 +/- 0.2 ug/m3 (average and standard deviation based on 25 daily measurements) to the PM2.5 mass at the Pittsburgh Supersite. An overview of the analysis methodology along with results obtained is provided. The relationships of ambient SAS concentrations to atmospheric sulfur and trace element concentrations are also illustrated.

2B-2

SOURCE SAMPLING AND CHARACTERIZATION USING A SINGLE PARTICLE MASS SPECTROMETER DURING THE PITTSBURGH SUPERSITE EXPERIMENT, KEITH J. BEIN, Department of Land, Air and Water Resources, Yongjing Zhao, Department of Mechanical and Aeronautical Engineering, Anthony S. Wexler, Departments of Mechanical and Aeronautical Engineering, Civil and Environmental Engineering, and Land, Air and Water Resources, University of California, Davis, CA; Eric Lipsky, Allen L. Robinson, Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, PA; Murray V. Johnston, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE

Emissions from several point and area air pollution sources in Pittsburgh, Pennsylvania, were characterized using a single particle mass spectrometer (RSMS). The procedure involved collecting emissions from the source in a large Teflon bag and transporting the Teflon bag to a laboratory where the samples were analyzed using RSMS, an SMPS and a MOUDI. The measurements were performed to create source profiles of single particle size and composition, which can be used to determine the extent to which sources contribute to local and regional air pollution. Results from four different sources will be considered here: a coke processing plant, road dust, a roadway tunnel and wood smoke emissions. Source signatures were developed for each source type by clustering single particle positive ion mass spectra into distinct particle classes. These signatures have also been identified and isolated within a twelve month ambient data set collected as part of the Pittsburgh Supersite experiment, allowing for quantitative estimates of the contribution of each of these sources on a particle number basis. Particle size data from RSMS, in conjunction with the SMPS data, has been used to construct size distributions for each particle class detected in the source samples and the corresponding groups of spectra observed during the ambient sampling to further validate the connection between the source signatures and ambient concentrations. In addition, classification of the negative ion mass spectra from the ambient data set has been used in combination with the size distributions to elicit information about particle aging during the transport from source to receptor.

2B-3

EMISSIONS OF TRACE GASES AND PARTICLES FROM MARINE VESSELS, ERIC WILLIAMS and Brian Lerner, CIRES, University of Colorado, Boulder, CO 80309 and Aeronomy Laboratory/NOAA, Boulder, CO 80305; Ann Middlebrook, Aeronomy Laboratory/NOAA, Boulder, CO 80305; and Patricia Quinn and Tim Bates, Pacific Marine Environmental Laboratory/NOAA, Seattle, WA 98115

Emissions from marine vessels are a significant source of gas-phase and particulate pollution. For example, it is estimated that nitrogen oxides emissions from world-wide shipping may represent more than 25% of the global total (Corbett et al., 1999; Corbett and Koehler, 2003). Further, it is likely that these emissions are even more significant regionally in coastal areas and locally in ports. The source strengths of emissions from marine vessels are estimated from fuel consumption data, engine operation characteristics, and pollutant emission factors which have been derived from both laboratory (test-bench) and field (underway) measurements of exhaust effluent. In general, sulfur emissions are related to the sulfur content of fuel, nitrogen emissions are related to the engine type (slow-speed diesel, medium-speed diesel, steam-turbine) and operating parameters, and particulate emissions depend on fuel type, engine type, and engine operating conditions. Emission factors for gaseous pollutants are reasonably well-known while those for particulate emissions are less certain. In the summers of 2002 and 2004, as part of the New England Air Quality Studies (NEAQS), the NOAA research vessel Ronald H. Brown was equipped with trace gas and aerosol monitoring instrumentation for the purpose of investigating the factors that affect air quality in coastal New England. During these missions, numerous opportunities arose to measure gaseous and particulate emissions from marine vessels, and from these data emission factors were calculated. This talk will present measurements from the NEAQS field campaigns and relate those data to current estimates of marine vessel emission factors.

Corbett, J.J., P.S. Fishbeck, and S.N. Pandis, Global nitrogen and sulfur inventories for oceangoing ships, J. Geophy. Res., 104, 3457-3470, 1999. Corbett, J.J., and H.W. Koehler, Updated emissions from ocean shipping, J. Geophy. Res., 108 (D20), 4650, doi:10.1029/2003JD003751, 2003.

2B-4

ALTERNATIVE SOURCE TESTING METHOD FOR FILTERABLE AND CONDENSABLE PARTICULATE, MARK DISTLER, O'Brien & Gere, East Syracuse, NY

Distler Method 2 is an air pollution measurement method (source emission test method) that measures the amount of filterable and condensable particulate being emitted by an industrial process. The current USEPA method for condensable particulate (Reference Method 202) cools the sample gas by bubbling it through cold water. Whatever particulate condenses and solubilizes in the water is considered condensable particulate. Distler Method 2 cools the sample gas in a water-jacketed probe where condensable particulate is allowed to condense in air (rather than water), thereby more realistically simulating the condensation that occurs when source emissions exit a stack and condense in the atmosphere. Whatever is condensed in the probe and caught by a downstream filter is considered both filterable and condensable particulate. This method solves a significant problem currently being realized by many industrial facilities that have PM10 emissions (particulate less than 10 microns in diameter). It also solves a pending problem that will occur when EPA promulgates emissions standards for PM2.5 (particulate less than 2.5 microns in diameters). The USEPA method overstates the amount of these pollutants above the amounts estimated by mass balance calculations. It also mis-classifies certain volatile organic compound emissions as particulate emissions. Both the overestimation and mis-classification are causing many facilities to unknowingly exceed their allowable emission limits specified in their air permits. Distler Method 2 modifies USEPA Method 5 by adding a water-jacketed probe, source of cold water, water pump, and thermocouples placed ahead and behind the Method 5 filter. The temperature to which the sample gas is cooled is achieved by the water circulating system and monitored by the thermocouples. This cooling and monitoring operation is unique to USEPA Methods. However, jacketed probes are sometimes used for cooling sample gas in extremely hot emission sources and are commercially available, but they are not specified for use to cool and condense sample gas in the probe and before the filter. Distler Method 2 has been used and approved for compliance testing in some states and is patent pending.

2B-5

MODELING THE IMPACTS OF LAND-USE CHANGE ON REGIONAL EMISSIONS OF AIR POLLUTANTS,

YUN WANG

Air pollution is one of the most important human impacts resulted from urbanization. It not only causes harm to human health but also has other negative effects such as reducing crop production, disturbing or ruining ecosystem, and damaging material. In addition, some air pollutants also contribute to climate change. Therefore, changes in regional air quality accompanying with urban sprawl has been a major concern to urban planners since the 90s, particularly to those who are interested in smart growth or "new urbanism". Emission inputs are one of the critical inputs into air quality model. Estimating, allocating and locating emissions across space and time provide answers to the following questions: • Where will be emission hotspots in the future • How sensitive is the spatial and temporal distribution of emissions to the driving forces such as land-use change, technology, and planning policies? • How do emission patterns vary among different pollutants? The ability to answer such questions is particularly important for areas that are near the border of compliance with the National Ambient Air Quality Standards. Based on the answers, effective approaches may be developed to mitigate or assess and prevent future emissions problems within the region. Unfortunately, the current state-of-the-art for predicting future emissions simply increases emissions from existing locations. Although the approach calculates future total emissions in the region, it does not take into account a common phenomenon accompanying urbanization: the changing amount and location of emission sources as new areas develop. In addition, because primary pollutant concentrations govern chemical reaction rates and hence subsequent human exposure, models that assume increased future emissions without capturing their spatial distribution over time would tend to overestimate the resulting consequences at some locations and underestimate them at others. A “bottom-up” approach based on Geographic Information System (GIS) was proposed, evaluated, and applied to a case study at St. Louis Metropolitan Area (SLMA). The methodology started from the 1992 land-use map of SLMA and used technology-based emission factors developed for 1999 to spatially estimate the regional stationary emissions of PM2.5. The total regional emissions were compared to the 1999 National Emission Inventory (1999 NEI). Next step will involve predictions of future emissions using simulated land-use maps of SLMA between 2005 and 2050. Various land development scenarios and emission control scenarios will also be assessed to support regional decision-making.

2C-1

CONTRIBUTION OF ATMOSPHERIC POLYMERS TO OC AT A RURAL AND AN URBAN SITE IN THE AREA OF VIENNA,

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In the AUPHEP project of the Austrian Academy of Sciences a dual site approach was chosen to investigate the regional background level of the PM2.5 and PM10 aerosol compared to the urban levels. It turned out that the background levels of organic carbon were already 75% of the urban level and coarse OC was around 1/3 of total OC. In the preparations for implementing an advanced apportionnement model for OC we found, that five major sources of OC, namely traffic exhaust, water and alkaline soluble atmospheric polymers, plant debris as well as bacteria and spores can be attributed by the use of corresponding macro-tracers. The macro-tracers applied are "ECTraffic", levoglucosan, cellulose. Soluble humic like substances and fungal spores are determined and the result directly converted to OC(1). The investigation was perfomed in a differential way using winter and summer data from the rural upwind site and the city site in Vienna. In summer up to 50%, in winter up to 80% of the OC at the two sites could be apportionned by five the major sources. Seasonal differences were found for the sources, with traffic exhaust, wood smoke and water soluble humic like substances relatively enriched during winter, spores and plant debris with higher contributions to total OC during summer. Although the sources for soluble humic like substances are still unclear yet, the amount of OC from this group needs further consideration. (1) Bauer H., Kasper-Giebl A., Zibuschka F., Kraus G.F., Hitzenberger R., Puxbaum H. (2002) Determination of the carbon content of airborne fungal spores. Anal. Chem. 74, 91 -95.

2C-2

PRIMARY BIOPOLYMER ASSOCIATIONS WITH FINE PARTICULATE MATTER, MARK HERNANDEZ and Lisa Clarke. University of Colorado at Boulder; Lars Angenent, Washington University in St. Louis; Allen Robinson, Carnegie Mellon University

Between July 2001 to August 2002, fine airborne particulate matter (PM2.5) samples were collected on polycarbonate filters at a site in Pittsburgh, Pennsylvannia. These samples were analyzed for carbohydrate, protein and endotoxin content on a daily basis. The following methods were used to quantify common biopolymers: (i) a dextrose-standard colorimetric acid digestion for carbohydrate measurement; (ii) an albumen-standard fluorometric intercalating assay for water-soluble protein measurement; and (iii) a commercially standardized enzyme assay for endotoxin measurement. Carbohydrates were detected in most of the samples, and seasonal trends emerged where the carbohydrate levels in the spring and fall months were markedly higher than those in the winter and summer. Over the entire study period, daily carbohydrate levels varied from below detection limit (0.25 µg/m3) to over 2.9 µg/m3, and comprised an average of 11% of the total organic carbon on an annual basis. Water-soluble proteins were also detected in many samples, although with significantly less frequency and magnitude than carbohydrates. Seasonal trends emerged where the protein levels measured during the fall and winter months were markedly higher than those during the spring and summer months. Over the entire study, daily protein levels varied from below detection limit (0.04 µg/m3) to 1.3 µg/m3 and comprised an average of less than 2% of the total organic carbon on an annual mass basis. Endotoxin analyses were executed during four mid-season months – July 2001, October 2001, January 2002, and April 2002. Endotoxin levels were significantly different than detection limit (1.3 EU/m3) only during the summer and spring months, and on most days were less than indoor levels reported from a large literature database. However, several excursions (10 days) of Endotoxin levels were observed during spring and summer months that were in excess 4 EU/m3. The seasonal pattern in the carbohydrate data are consistent with variations in higher odd n-alkanes (29 and 33 carbon atoms) that are commonly used as markers for plant wax. However, the measured contribution of carbohydrate to ambient OC is a factor of 5 to 10 higher than the estimated contribution of plant waxes. These results suggest that microscopic primary biological materials may have a significant contribution to fine particle organic carbon levels.

2C-3

LEVOGLUCOSAN IN URBAN PARTICULATE MATTER STANDARD REFERENCE MATERIALS 1649A, 1648, AND PM 2.5 INTERIM REFERENCE MATERIALS, RANDOLPH LARSEN, St. Mary's College of Maryland, St. Mary's City, MD, Michele Schantz, National Institute of Standards and Technology, Gaithersburg, MD

Source identification is critical for the effective management of air pollution. The ratio of levoglucosan to organic carbon has not only been used to identify biomass combustion but to assign the fraction of organic carbon in aerosols resulting from biomass combustion. Therefore, accurate levoglucosan measurements in particulate matter are important. This study determined levoglucosan concentrations in urban dust reference materials to facility the validation of experimental methods and techniques. Levoglucosan from SRMs 1649a, 1648, and NIST/EPA interim PM2.5 reference material and control material, was extracted using both pressurized fluid and Soxhlet techniques. Quantification was performed with a GC/MS using deuterated levoglucosan internal standards and two different GC columns (DB-5MS and DB-17MS). Levoglucosan concentrations were 81.1 ± 9.4 µg g-1 for SRM 1649a, 107 ± 18 µg g-1 for SRM 1648, 225 ± 41 µg g-1 for the PM2.5 interim reference material and 138 ± 39 µg g-1 for the fine particulate control material.

2C-4

ESTIMATES OF SECONDARY ORGANIC AEROSOL FROM THE SOUTHEASTERN AEROSOL RESEARCH AND CHARACTERIZATION STUDY (SEARCH),

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Carbonaceous matter (organic matter + black carbon) comprises 30-45% of PM 2.5 mass in the southeastern U. S. Black carbon is formed during the incomplete combustion of organic compounds, primarily from fossil-fuel-powered vehicles. The organic material in PM 2.5 is a mixture of a myriad of organic compounds, a portion of which is emitted directly into the atmosphere (primary organic aerosol), and a portion of which that is formed from chemical reactions of reactive organic compounds in the atmosphere (secondary organic aerosol). In order to formulate effective control strategies for atmospheric particulate matter, it is important to gain a better understanding of the relative contributions and sources of primary and secondary organic aerosol. Continuous measurements of PM 2.5 mass and chemical composition have been performed since 1998 as part of the Southeastern Aerosol Research and Characterization study (SEARCH). The SEARCH measurement network consists of eight monitoring sites, organized as three urban-rural pairs in Georgia, Alabama, and Mississippi, and one urban-suburban pair in Florida. At each of these sites a variety of gaseous, particulate, and meteorological measurements are obtained on a routine basis, including continuous particulate black carbon via aethalometry and total particulate carbon via a Rupprecht & Patashnick Model 5400 carbon analyzer. In this work, we analyze hourly measurements of particulate black carbon and total carbon from the SEARCH network over 1999-2003 to estimate the contribution of secondary organic aerosol in the southeastern U.S. By using various tracers of primary combustion-generated carbon emissions in conjunction with ratios of other continuously-measured gaseous species, we derive estimates of secondary organic aerosol mass as a fraction of total measured organic particulate mass. Urban-rural, diurnal, and seasonal differences in secondary organic aerosol formation are examined.

2C-5

MEASUREMENT AND SPECIATION OF CARBONACEOUS PARTICLES USING ELECTRON MICROSCOPY TECHNIQUES,

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Ambient PMcoarse measurements from the Southeastern Aerosol Research Characterization (SEARCH) study show a large unexplained component for both rural and urban locations. Over a 5-year period from 1999-2003, the unexplained PMcoarse mass, varied from 54-66%. Given the likelihood of a PMcoarse standard in the near future, there is a clear need to understand the nature of this unknown component. To this end, an investigation using electron microscopy techniques was initiated in an effort to identify and measure the contribution of potential sources of PMcoarse with emphasis on carbonaceous material. To facilitate the microscopy analysis, samples were collected on 37 mm diameter polycarbonate filters using dichotomous samplers. A total of 38 samples were collected at two SEARCH sites (1 rural, 1 urban) in Alabama during November-December 2000 and May 2001. Computer-controlled scanning electron microscopy (CCSEM) analyses were performed on 19 of the samples. CCSEM was used to provide information on size and elemental composition of individual particles. A digital image was also obtained of each individual particle detected during the analysis. Images of particles having a carbon composition were examined and classified into categories including vegetative material, carbon chain agglomerates (soot) and other. Identification of the carbonaceous component was based on distinctive morphological features and elemental properties of individual particles. The CCSEM analysis indicated that carbonaceous material contributes significantly to PMcoarse in the southeastern U.S. A high percentage of the carbon material was attributed to pollen, spores and other vegetative material for both the spring and winter samples accounting for anywhere from 40% to nearly 100% of the carbonaceous mass. In general, the weight percent of carbon material with respect to the total PMcoarse concentrations remained consistent between the two sites. However, higher concentrations of vegetative material were typically observed at the urban site during both seasons. This could be due to proximity of the sampler to vegetation, type of vegetation and/or effects of local traffic and other human activities. As expected, the highest concentrations of vegetative material were measured in the spring. The urban site also frequently contained higher concentrations of carbon chain agglomerates, which are typically associated with anthropogenic sources such as vehicular emissions. In summary, the microscopic analyses confirm the presence of significant amounts of pollen, spores, vegetative detritus and other carbonaceous particles on samples collected in urban and rural locations. The CCSEM results indicate that this carbonaceous material accounted for the majority of the unexplained PMcoarse mass.

3A-1

THE IMPORTANCE OF COARSE MODE AEROSOL NITRATE AT SEVERAL IMPROVE MONITORING SITES,

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Nitrate comprises an important part of aerosol mass at many non-urban locations during some times of the year. Little is known, however, about the chemical form and size distribution of particulate nitrate in these environments. While submicron ammonium nitrate is often assumed to be the dominant species, this assumption is often not tested. Properties of aerosol nitrate were characterized at several IMPROVE monitoring sites during a series of field studies. Study sites included Big Bend National Park, Texas (July-Oct, 1999), Yosemite National Park, California (July-Sept 2002), Bondville, Illinois (February 2003), San Gorgonio Wilderness Area, California (April and July 2003), Grand Canyon N.P., Arizona (May 2003), Brigantine National Wildlife Refuge, New Jersey (November 2003), and Great Smoky Mountains N.P., Tennessee (July/August 2004). 24 hour average PM2.5 nitrate concentrations and gaseous nitric acid concentrations were determined by annular denuder/filter-pack measurements. Nitrate size distributions were measured using a Micro-Orifice Uniform Deposit Impactor (MOUDI). Concentrations of PM2.5 nitrate and other ions were also measured at 15 minute intervals using a Particle Into Liquid Sampler (PILS) coupled to two Dionex ion chromatographs. Nitrate was found predominantly in submicron ammonium nitrate particles during the Bondville and San Gorgonio (April) campaigns. Coarse mode nitrate particles, resulting from reactions of nitric acid or its precursors with sea salt or soil dust, were more important at Big Bend, Yosemite, Grand Canyon, San Gorgonio (July), and Great Smoky Mountains. Both fine and coarse mode nitrate were important during the Brigantine study. These results suggest a need to more closely examine common assumptions regarding the importance of ammonium nitrate at non-urban sites and to include pathways for coarse mode nitrate formation in regional models.

3A-2

CONTINUOUS OBSERVATIONS OF PM2.5 AND GAS SPECIATION AT A RURAL ILLINOIS SITE,

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Continuous measurements of PM2.5 and gas composition taken with a gas-particle ion chromatographic sampling system are reported for a one-year period at an established background aerosol monitoring site in central Illinois. Particulate compositions are reported for ammonium, sulfate, and nitrate and gaseous species are reported for nitric acid, sulfur dioxide, and ammonia. Seasonal diurnal averages are computed to determine the average daily behavior and to investigate how the daily compositions vary with season. Generally, during the daylight hours the PM2.5 ammonium nitrate decreases, leaving ammonium sulfate as the primary inorganic constituent. The ammonium/sulfate/nitrate ionic charge balance in the aerosol is also analyzed from the standpoint of wind direction. The diurnal average inorganic aerosol mass loading is approximately twice as large when the winds at this central Illinois site are from a general southerly direction compared with a general northerly direction. The aerosol has higher proportions of sulfate for southerly winds, and higher proportions of nitrate for northerly winds.

3A-3

GLOBAL BACKGROUND AEROSOL CONCENTRATION LEVELS OF WATER-SOLUBLE DICARBOXYLIC ACIDS, HAOBO WANG, Kimitaka Kawamura, Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan

Marine aerosols were collected over the Antarctic Sea and western Pacific Ocean in a cruise conducted in late November 1994 to mid February 1995. Water-soluble dicarboxylic acids (DCAs) in the samples were measured using gas chromatography. It was found that the aerosol concentrations of DCAs over the Antarctic Sea were significantly lower than those over the western Pacific and those in the summer sample in Antarctica continent. The DCA concentration levels over the Antarctic Sea were also lower than those observed in other marine environments and continental background sites. It is therefore suggested that the aerosol concentrations of water-soluble DCAs over the Antarctic Sea in this work may represent their global background concentration levels. Oxalic acid was found to be the most abundant species, followed by malonic acid and then succinic acid. Over the Antarctic Sea, the total concentrations of DCAs in the marine aerosols ranged from 2.9 to 7.2 ng m-3 with a mean of 4.5 ng m-3. The average aerosol concentrations of oxalic, malonic and succinic acids were 2.4, 0.75, and 0.44 ng m-3, respectively.□The average ratio of DCAs-C/TC (carbon in DCAs/total carbon) was 1.8%. On the other hand, DCAs have constituted a significantly larger fraction in the aerosol organics over the western Pacific with a mean of 7% for DCAs-C/TC.□ Studies on the relative abundance of individual DCAs revealed that oxalic acid was significantly depleted over the Antarctic Sea as a function of latitude, most of other DCAs, in contrast, showed a reverse pattern. It is proposed that over the Antarctic Sea DCAs may have been derived mainly by in situ photochemical reactions, with their precursors being predominately from sea-to-air emissions. However, long-range transported continental air masses were found to have strong impact on the occurrence of DCAs over the western Pacific. It is also suggested that photochemical transformation of longer-chain DCAs to oxalic may have been significant in the marine atmosphere. This work may provide useful data for the modelling of global distribution/cycling of organic substances.

3A-4

COMPARISON OF THE PM2, 5 MAIN COMPONENT CONCENTRATIONS, DIETRICH VON BAER. Universidad de Concepción; Departamento de Análisis Instrumental; Casilla 160-C; Concepción; VIII th Region 3; Chile

During several episodes of high air pollution over the last winters in Santiago de Chile, the Pudahuel station of the MACAM monitoring network, located in the western periphery of the city, has shown levels of particulate matter, PM10 as well as PM2,5, being significantly higher than in other areas of the city. Therefore, during the last years the main effort towards the chemical characterization of PM2,5 in Pudahuel, in comparison to other areas of the city. Sampling was done during winter, between June and September, at Pudahuel (2000, 2002 and 2003) and at Parque O´Higgins, which is located in the south-central area of Santiago, using Partisol Speciation Samplers (model 2300, Rupprecht & Pataschnick, East Greenbush, NY, USA) with PM2,5 impactor. In each case, samples were collected during a 12 hour period (diurnal sampling: 6 am to 6 pm; overnight sampling: 6pm to 6am:) passing the air succesively through a teflon filter, followed by two glassy fiber filters impregnated with sodium carbonate and citric acid. Whereas in the western area (Pudahel) a marked difference between day and night concentrations of PM2,5 was observed, the latter being in average significantly higher (42.0 and 78,3 micrograms/m3, respectively, between 25.06.03 and 11.08.03), differences in the south-center area were smaller (60.5 and 76,8 micrograms/m3). The increase of PM2,5 during critical episodes in Pudahuel was largely due to higher levels of organic carbon, which represented approx. 35 - 42% of total PM2,5 , followed by elemental carbon (15 - 20%). In the inorganic fraction of PM2,5, nitrate predominated (19% in Pudahuel, 18% in Parque O¨Higgins), followed by ammonia (9% in Pudahuel, 8% in Parque O´Higgins), sulphate (7% in Pudahuel, 8% in Parque O´Higgins), potassium (4% in Pudahuel, 1% in Parque O´Higgins) and minor proportions of chloride and calcium. The incidence of various factors that can have an influence on the differences observed between the western periphery and the south-central area of the city is discussed. Possible reasons are the sporadic burning of biomass in the periphery, for which potassium is used as a marker, in combination with the atmospheric transport of pollutants from the center of Santiago to the periphery during the night, a decreased height of the inversion layer over night and meteorologic factors, like wind speed and direction, temperature and relative moisture. The authors thank to CONAMA for financial support and to Rupprecht & Pataschnick, East Greenbush, NY, USA for providing the Partisol Speciation Samplers, Model 2300.

3A-5

SPATIAL AND TEMPORAL VARIABILITY OF PARTICULATE MATTER IN TWO NEIGHBORHOODS NEAR A MAJOR INTERNATIONAL TRADE BRIDGE AT BUFFALO, N. Y. AND FORT ERIE CANADA,

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Exposure related non-carcinogenic effects from diesel exhaust and diesel particulate matter (DPM) have been on the increase (HEI, 2000). These health effects include exacerbation of asthma, respiratory inflammation, and allergic responses, especially in children. The Peace Bridge Plaza Complex (PBC), located in Buffalo, New York, is the busiest U.S. - Canada border crossing in northeastern U.S.A. A previous study found that in a community directly to the northeast of the PBC two times the number of households had at least one asthmatic compared to an upwind community (Lwebuga-Mukasa, 2002). Heavy-diesel trucks tend to dominate the traffic backup on the bridge and along both entrances leading to it, including local perpendicular roads in Buffalo, and along the Queen Elizabeth Way (QEW) to the west in Fort Erie. A prevailing southwesterly wind exists in the summer, effecting local PM transport to the northeast. To evaluate the spatial variability of particulate emission exposures in the communities on both sides of the border of the PBC during the summer of 2004, a mobile lab (recreational cargo van) was outfitted with several semi-continuous air particulate monitors to measure particle size and number, PM2.5 mass, Black Carbon, and particle bound PAH's. Measurements between 2 minutes and several hours were made at an array of sites away from the PBC within about 1 kilometer to the east of the bridge and several kilometers to the west. The high time resolution mobile measurements resulted in repeated spatial and temporal particulate measurements at each site for a given period of consistent weather and traffic conditions. In general, upwind particlulate measurements were relatively consistent by particle number (~10,000 p/cc), size (40 – 150 nm), and PM2.5 mass (15 – 20 ug/m3). Depending on the location of the mobile lab and time of day, local sources tended to contribute to the overall temporal and spatial patterns, but clear separation of nearby and distant sources are observed. Results from a typical day in Buffalo with consistent southwesterly winds and with the bridge continuously backed up shows expected trends in particle size and number at increasing distances away from the PBC, with some local source contributions. For example, at 200 meters, modes of 20 nm (with Canadian bound traffic at about 70-100 meters) or 35 nm (with U.S. bound traffic at about 200 meters) were measured, respectively ranging between 6 to 180 nm or 15 to 180 nm with the total overall number between 80,000 - 150,000 p/cc. At 800 meters downwind, the number and size concentrations were similar to the upwind site, but variably effected by local mobile sources passing by or idling near the mobile lab (mode of 6nm, between 6 and 20 nm). In contrast PM2.5 mass remained relatively consistent between the upwind site and 200 to 800 meters downwind, where PM2.5 was not correlated with distance from the bridge (ranging between about 21 and 28 ug/m3). Additional comparisons between the spatial and temporal distributions of all measured components on both sides of the bridge will be presented and discussed.

3B-1

CHARACTERISTICS OF DIESEL- AND GASOLINE ENGINE EMISSIONS FROM VEHICLE CLUSTERS,

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Diesel exhaust particles are receiving attention due to their adverse health effects. To characterize the emissions from diesel-engine vehicles, there are several sampling methods, such as the EPA FTP using chassis dynamometer; tunnel sampling, on-board sampling and near road sampling. All of the methods have both advantages and disadvantages. The association of the properties of the diesel particles, such as mass concentration, number concentration or shape with the health effect is still not clear. In this study, samplings were performed near clusters of trucks (training school, weigh stations) and school buses (school bus depot). In addition, individual diesel trucks and gasoline vehicles were recruited for either direct tailpipe or chassis dynamometer measurements. The particle phase vehicular exhausts were collected on Teflon and Quartz filters using Harvard-type PM2.5 impactors. Time series mass concentrations were measured by Tapered-Element Oscillating Microbalance (TEOM) 1400a. Number concentrations were measured using Portable CPC and OPC. Particle size distributions were measured using Scanning Mobility Particle Sizer (SMPS). Diesel particle deposited on the SEM-grid were used for further morphology analysis. The chemical elements and carbon compounds including elemental carbon (EC) and organic carbon (OC) were determined by X-ray fluorescence (XRF) and thermal-optical transmittance (TOT) techniques, respectively. As expected, EC and OC are the dominant compounds in all the samples. The ratio of EC/OC varies from 0.05 (1992 gasoline vehicle) to 0.70 (truck station in Cincinnati). This ratio is lower than the value measured in other published studies. The chemical species measured in all the samples including: S, Si, K, Ca, Fe and Zn. In addition, Al, Cl and Br were detected in either the cluster of diesel trucks or in individual truck emissions. The number concentration showed that large fractions of the diesel exhaust particles are in the size range less than 1 micron in diameter. The results will be used to establish the chemical source profiles for future receptor modeling applications.

3B-2

ON-ROAD MEASUREMENTS OF PARTICLE NUMBER AND MASS CONCENTRATIONS AND SIZE DISTRIBUTIONS IN FREEWAY AND TUNNEL ENVIRONMENTS,

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Few studies have attempted to determine emission factors in terms of particle number per mass of fuel burned in tunnel environments, and none have compared these to freeway environments. Particulate matter emissions were measured in two bores of the Caldecott Tunnel in northern California during August/September 2004. One bore (Bore 1) is open to both heavy- and light-duty vehicles while heavy-duty vehicles are prohibited from entering the second bore (Bore 2). Micro-orifice impactors, high-volume impactor samplers, and Scanning Mobility Particle Sizers (SMPS) were deployed simultaneously at the entrance and inside the tunnel. Particulate matter number and mass size distributions, chemical composition, and gaseous co-pollutants were recorded for four consecutive days in each bore. Emission factors will be presented for particle number, particle mass, EC, OC, sulfate, and nitrate. These will be compared to those submitted by similar studies conducted in the same tunnel in 1997. Since size-distribution and PM mass data is available for both all-gasoline and mixed-fuel freeways in Los Angeles, the feasibility of using tunnel emission factors to predict pollutant concentrations immediately surrounding freeways will be determined. Results indicate that average Bore 1 concentrations of coarse, accumulation and ultrafine PM were 17, 29 and 29 mg/m3, respectively, while those of Bore 2 were 6, 17 and 9 mg/m3, respectively. Similarly, Bore 1 particle number concentrations were higher than Bore 2, with the former being 7 e5-1.7 e6 p/cc and the latter measured at 6 -8 e5 p/cc.

3B-3

ON-ROAD SIZE-RESOLVED PARTICULATE EMISSION FACTORS,

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The elevated number concentration of ultrafine particles raises concerns since it may pose increased health threats to people living and traveling near freeways. On-road size-resolved particulate emission factors were acquired by a) using carbon monoxide (CO) measurements as a dilution indicator and b) correlating roadside particle measurements to CO measurements. The total number emission factors derived from this study agree well with previous on-road investigations. The distance-dependent, size-resolved, grid-level emission factor distributions derived from this study are unique. Results from freeways with distinctly different percentages of Heavy-Duty Diesel Truck traffic are compared. Both mileage-based and fuel-based emission factors are presented.

3B-4

PARAMETRIC EVALUATION OF SECONDARY PM10 EMISSION BY PRECURSORS INVENTORY DATA: POTENTIAL AND LIMITATIONS OF THE APPROACH,

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The assessment of the role of the emissions sources is a basic element for the design of long-term intervention strategies and for the definition of the priority of effective actions to be undertaken for air quality control. For fine particulate matter (PM10), this assessment is rather difficult since fine PM emissions consist of a primary fraction (PM10p), directly emitted into the atmosphere, and a secondary fraction (PM10s), formed in the atmosphere from gaseous precursors (SO2, NOx, NH3 and VOC). In order to assess the total PM emissions from different sources, a parametric approach accounting for both emissions of primary and secondary PM10 has been recently proposed and applied for the analysis of time trend of total fine PM emissions at European scale. PM10s is calculated by a weighted summation of the emissions of inorganic precursors (NOx, SO2 and NH3), according to the following formulation: PM10s = 0.88 • NOX + 0.54 • SO2 + 0.64 • NH3 Providing an estimate of the overall PM10 emissions, inclusive of secondary PM10, this approach allows for the direct comparison of the role of different sources: in fact, whilst some sources are characterised by large primary particulate emissions, for some others the secondary emissions are largely prevailing, due to substantial emission of precursors. This work discusses the application of this approach at local scale: case study is the Milan Province, one of Italy's most industrialised area. Based on the PM10p and secondary PM precursors emission inventories data, total PM10 emissions are evaluated for different activity sectors, pointing out the total strength of their particulate emissions. Special focus is on the role of fuels used for household heating and on the contribution of vehicles categories to total PM10 emission. In order to assess the effective potential application of the parametric approach at the local scale, results obtained for the expected presence and composition of total emitted PM, are compared to experimental data of chemical speciation of fine atmospheric particulate, collected during sampling campaigns carried out in the city of Milan. From this comparison, the following key-points come out: - estimated aggregated emissions of secondary inorganic PM10 largely exceed measured relative contribution of the total secondary component of fine PM, up to 50% for PM10 and 75% for the PM2.5, inclusive of secondary organic aerosol (SOA); - estimated nitrates/sulphates mass ratio (equal to 11) is in sharp contrast to the average measured value of about 1 resulting by chemical speciation of PM10 samples. Therefore, even though the parametric approach is a pragmatic tool for the assessment of total fine PM emissions and is suitable for the definition of effective actions for air quality improvement, its proper application at the local scale has to be carefully verified, also based on the following considerations: - validation of the weight factors might be required, according to the local availability of gaseous precursors; - Local meteorological conditions may affect the transport and the budget of precursors for secondary formation processes; - SOA, not considered by this approach, may increase the share of secondary PM10 fraction.

3B-5

ASSESSMENT OF CO2, SO2, AND NOX EMISSIONS FROM ELECTRIC UTILITY POWER PLANTS USING AIRBORNE MEASUREMENTS,

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SO2 is an important precursor for secondary aerosol formation in the atmosphere. Furthermore, SO2 and NOx are the primary sources of acid deposition, while NOx is known to play a catalytic role in photochemical ozone formation. In the US, approximately 2/3 of all SO2 and 1/4 of all NOx come from electric power generation. As a result, under the Acid Rain Program, each utility must measure and record its emissions of SO2, NOx, and CO2 via a continuous monitoring system (CEMS). The emissions inventories derived from these data are integral to air-quality modeling, which in turn guides control strategies. Thus it is imperative that the inventories are regularly validated against ambient data. Intensive field campaigns conducted in 1999, 2000, 2002, and 2004 provided an excellent opportunity for such an exercise. Data from near-field transects downwind of more than thirty CEMS-equipped power plant sources are used to determine both emissions ratios and absolute emissions rates. In general, both of these quantities are found to agree, within uncertainties, with reported CEMS data. However, occasional significant discrepancies are observed. Potential implications of these findings are discussed.

3C-1

GAS/PARTICLE PARTITIONING OF PAH IN THE VICINITY OF A BUS DEPOT AND THE IDENTIFICATION OF SUBSTANTIAL PAH MASS IN NANO-PARTICLES,

DOUGLAS LANE, Cristian Mihele, Margaret Baroi, Environment Canada, Toronto, ON, Canada; Antonio Miguel, Arantza Eiguren-Fernandez, University of California at Los Angeles, CA, USA; Lara Gundel, Lawrence Berkeley National Laboratory, CA

As part of the Pacific 2001 air sampling program in Vancouver, BC, we measured the gas/particle partitioning of polycyclic aromatic hydrocarbons (PAH) using a conventional (filter-sorbent) sampler, an IOGAPS (Integrated Organic Gas And Particle Sampler) and a high capacity IOGAPS (HiCAPS). The denuder samplers utilize an 8-channel annular diffusion denuder followed by a particle filter and two or three XAD-impregnated filters. The samplers were located in Slocan Park, in the heart of residential Vancouver but within approximately 50 m of a bus depot. Samples were collected from 8:00 am to 7:30 pm and from 8:00 pm until 7:30 am, thus corresponding roughly to daytime and nighttime sampling respectively. The lighter PAH, those that would be expected to be primarily in the gas phase, showed a marked difference between day and night concentrations. The nighttime loadings were about 5 times greater than those during the day. Since there was much less difference for the higher PAH we feel that the difference is primarily the result of daytime photochemical degradation of the PAH. Increased nighttime concentrations could also result from a lower boundary layer that keeps the emitted PAH closer to the ground. The results revealed an apparent artifact. High molecular weight PAH were found in the denuder (where only gas phase material should be collected) for both the IOGAPS (16.7 L/min) and the HiCAPS (85 L/min). In most cases, more high molecular weight PAC mass was found in the IOGAPS than was found in the HiCAPS. This can only be explained by small particle diffusion to the walls of the denuder. We hypothesize that this was the result of sampling close to the Diesel bus depot. Diesel buses are well known to emit huge quantities of nano-particles. By modeling the diffusion of particles as a function of particle size, at each flow rate, the difference between the amounts of PAH found in the two denuder samplers can be interpreted as an indication of the PAH mass that occurred in the 20 to 50 nm particle size range. This very closely correlates with the results using nano MOUDI samplers in which two of the authors (Miguel and Eiguren-Fernandez) found substantial PAH mass in the Aitken particle size range (10-32 nm) when sampling in vehicular traffic. This presentation will contrast the daytime and nighttime PAH results and will show how, by comparing the particle diffusion in normal flow and high flow denuder samplers, we were able to identify a fourth mode of PAH mass in the air in the nano-particle size range. The denuder and nano-MOUDI results will be compared.

3C-2

PARTICULATE CARBON AND GAS/PARTICLE PARTITIONING OF AROMATIC HYDROCARBONS IN SEATTLE,

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This presentation focuses on clarifying the influence of semi-volatile organic species on PM mass closure while presenting winter and summer data for OC, EC and aromatic hydrocarbons. For this purpose we deployed conventional and diffusion-based sampling technology at a central monitoring site and both indoors and outdoors at several residential sites, during part of the extensive exposure assessment efforts of the Northwest Center for the Study of the Health Effects of Particulate Matter (Seattle, 1999-2001). Organic and elemental carbon and polycylic aromatic hydrocarbons (PAH) concentrations were compared for particles collected with several types of samplers. The role of semi-volatile species both indoors and outdoors can be clarified by comparing gas/particle partitioning data for PAH to particulate carbon and particulate mass concentrations. Semi-volatile species were collected with Integrated Organic Gas and Particle Samplers that incorporate XAD-4 coated annular diffusion denuders upstream of a filter and back-up sorbent substrate. This diffusion-based measurement technology minimizes artifacts that are associated with sampling semi-volatile organic species (SVOC). During sampling the gas phase SVOC were trapped on the XAD-4 coated denuders. Particles were collected on the filter. The post-filter sorbents (XAD-4 impregnated filters) trapped any SVOC that volatilized from the collected particles. Extracts of the denuder, filter and sorbent were analyzed separately for PAH. Particulate organic (OC) and elemental carbon (EC) were determined from sections of quartz filters by thermal optical transmission. Questions to be addressed include: 1. How do denuded and non-denuded OC concentrations correlate with concentrations and phase distributions of individual PAH? 2. Are denuders necessary for improving PM mass closure? 3. How does the observed gas/particle partitioning of retene influence its usefulness as a tracer for woodsmoke?

3C-3

BUDGET OF GAS AND PARTICLE-PHASE ORGANIC CARBON IN A POLLUTED ATMOSPHERE: RESULTS FROM THE NEW ENGLAND AIR QUALITY STUDY IN 2002,

JOOST DE GOUW, Ann Middlebrook, Carsten Warneke, Paul Goldan, William Kuster, James Roberts, Fred Fehsenfeld, NOAA Aeronomy Laboratory, Boulder, CO; Douglas Worsnop, Manjula Canagaratna, Aerodyne Research, Billerica, MA; Alex Pszenny, University of New Hampshire, Durham, NH; William Keene, University of Virginia, Charlottesville, VA; Matt Marchewka, Stephen Bertman, Western Michigan University, Kalamazoo, MI; Timothy Bates, NOAA Pacific Marine Environment Laboratory, Seattle, WA

An extensive set of volatile organic compounds (VOCs) and particulate organic matter (POM) measurements was performed in polluted air during the New England Air Quality Study in 2002. Using VOC ratios the photochemical age of the sampled air masses was estimated. This approach was validated (1) by comparing the observed rates at which VOCs were removed from the atmosphere with the rates expected from OH oxidation, (2) by comparing the VOC emission ratios inferred from the data with the average composition of urban air, and (3) by the ability to describe the increase of an alkyl nitrate with time in terms of the chemical kinetics. A large part of the variability observed for oxygenated VOCs (OVOCs) and POM could be explained by a description that includes the removal of the primary anthropogenic emissions, the formation and removal of secondary anthropogenic species, and a biogenic contribution parameterized by the emissions of isoprene. The OVOC sources determined from the data are compared with the available literature and a satisfactory agreement is obtained. The sub-µm POM was highly correlated with secondary anthropogenic species in the gas phase, and was consequently attributed by the method to secondary anthropogenic sources. Examples are given that demonstrate the limited contribution from primary anthropogenic and biogenic sources of sub-µm POM. The results of the analysis are used to describe the speciation and total mass of organic carbon in the gas and particle phase in an urban air mass as a function of photochemical age. Shortly after emission the organic carbon mass is dominated by primary VOCs; after two days there is a dominant contribution from OVOCs and sub-µm POM. The total measured organic carbon mass decreased by about 40% over the course of two days. The increase in sub-µm POM could not be explained by the removal of aromatic precursors alone, suggesting that other species must have contributed and that the mechanism for POM formation is more efficient than previously assumed.

3C-4

EVALUATION AND MINIMIZATION OF ORGANIC AEROSOL SAMPLING ARTIFACTS USING IMPACTORS AND QUARTZ FIBER FILTER DENUDERS,

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Many constituents of particulate organic carbon (POC) are found in significant fractions in both gas and particulate phases depending on factors such as volatility, polarity, and the nature of other particulate components. When PM is collected on fiber filters, POC may volatilize once collected, or gaseous components may adsorb to either the filtration medium or previously collected particulate matter. These processes, known as collection artifacts, may be positive or negative compared with the actual concentration in the air at the time of collection. These collection artifacts have been studied for some time by a number of researchers; quantitatively measuring the particulate content free from gas-phase artifact processes has been proven to be difficult. Our objective was to better characterize the magnitude of these processes to assess the contribution and source of POC to PM2.5. The most appropriate method for this quantification uses a denuder to remove gas phase interfering species and then samples with a filtration medium capable of quantitatively capturing the particulate phase. We evaluated the POC collection artifact under ambient conditions using the best approaches developed to date. Our basic approach was to simultaneously collect POC using nine sampling configurations and compare the results with the US EPA PM2.5 Federal Reference Method to estimate sampling uncertainty due to collection artifacts. Sample trains used quartz fiber filter and carbon-impregnated cellulose filter denuders to minimize the positive collection artifact. Particulate material was collected using impaction onto aluminum substrates and filtration by both quartz fiber and carbon-impregnated glass fiber filters. The sampling approach is shown below: 1. A federal reference sampler to collect PM2.5 on a quartz fiber filter. This is the standard to which the uncertainty due to OC collection artifacts will be evaluated. 2. A federal reference sampler with a Teflon front filter followed by a quartz back filter. The Teflon filter measured PM2.5. The OC on such a back filter has previously been used to estimate the positive adsorption artifact due to adsoption of organic gases. 3. Sampling with a pair of quartz fiber filters below a denuder consisting of strips of quartz fiber filtration media. This denuder has been shown to remove most gaseous carbon that would tend to be collected by the second quartz filter. The front filter provided a measure of POC collection without VOC that would cause a positive artifact. 4. Sampling with an impactor/after filter combination and analyze for POC. A low pressure impactor with a final cut-point of 0.05 µm was used. It was expected that impaction methods largely eliminate volatilization and that the after filter contains an excessive amount of OC due to an adsorption artifact from VOC. Aluminum, unlike quartz, has a very low affinity for adsorbing VOC. 5. Collected as (4) above but using a quartz fiber filter parallel plate denuder (QFD) at the impactor inlet to minimize the hypothesized VOC adsorption artifact. 6. Collected as in (5) above but using a QFD at the impactor outlet to remove VOC and volatilized POC. The QFD will remove any volatilized POC that would adsorb onto the after filter. 7. Collected as (5) above but using a Teflon filter at the impactor inlet to collect dynamic blanks. 8. Collected POC and volatilized POC on quartz and carbon-impregnated filters using activated carbon denuders to remove VOCs. 9. Collected as (8) above but using a quartz inlet filter as a correction for denuder breakthrough. Samples were collected in southern California. Particulate organic and elemental carbon was measured using a thermal volatilization-oxidation approach. A practical approach for minimizing artifacts for routine PM2.5 sampling using denuders followed by particle impaction is recommended.

3C-5

CHARACTERIZATION OF TOBACCO TAR VAPOR PRESSURE USING A NON-ISOTHERMAL KNUDSEN EFFUSION TECHNIQUE, XU CHEN, Philip Morris USA Postgraduate Research Program, Richmond, VA; W. Geoffrey Chan and Mohammad R. Hajaligol, Philip Morris USA Research Center, Richmond, VA

Tar generated during the smoking process of burning tobacco contains more than 3,000 chemical compounds, many of them are condensable at room temperature. The knowledge of vapor pressure of tar generated from burning tobacco is scarce in the literature, due to difficulties in analyzing the vaporization and condensation behavior of tar from aerosol particles in tobacco smoke. Tobacco tar not only has low volatility at room temperature but it is a temperature labile mixture of compounds. These limitations prohibit the measurement of vapor pressure using conventional techniques. A molecular effusion/thermogravimetric technique has been developed as a reliable method to characterize the vapor pressure of coal and biomass tars. In the present study this method was applied to determine the vapor pressure of tobacco tar. The Knudsen effusion device used in the present study was a modified thermogravimetric analyzer (TGA) working under high vacuum. Tar collected from heating tobacco to 500 C was first loaded inside a hermetic cell with a small orifice on top and the cell was placed in a thermogravimetric analyzer (TGA). A non-isothermal Knudsen effusion method was applied for tar vapor pressure measurement. The tobacco tar continuously sustained heating and cooling cycles under vacuum using a slow heating rate. The vapor pressure inside of the cell was obtained by monitoring the sample weight loss through the orifice and the cell temperature during the heating/cooling cycles. The number average molecular weight of tobacco tars at various extents of evaporation was separately determined by a vapor pressure osmometer. The volatility of tobacco tar, as any other mixtures, is strongly correlated to its chemical composition and the structure of its chemical components. Based on an assumption that each evaporation fraction can be treated as single pseudo compound, a modified Clausius-Clapeyron equation was applied to describe the relationship between vapor pressure and temperature for different tobacco tar fractions. The sublimation enthalpies of tar fractions were also calculated from the same equation. The knowledge of tobacco tar vapor pressure is expected to improve the understanding of formation and evolution of aerosol particles in tobacco smoke.

4A-1

A HYBRID RECEPTOR MODEL INTEGRATING AIR QUALITY DATA AND EULERIAN MODELING RESULTS TO APPORTION BIG BEND TEXAS' SULFATE TO UNITED STATES AND MEXICAN SOURCE REGIONS, Bret Schichtel, Kristi Gebhart, Michael Barna, William Malm, National Park Service, Fort Collins, CO

The Big Bend Regional Aerosol and Visibility Observational Study (BRAVO) was an intensive air quality monitoring project that measured speciated fine aerosols from July through October 1999 at 36 sites throughout Texas. A primary goal of BRAVO was to identify the major emission sources that contribute to haze in Big Bend National Park (BBNP), which is located in southwestern Texas. In support of this, the Regional Modeling System for Aerosols and Deposition (REMSAD) and the Community Multiscale Air Quality (CMAQ) models were used to predict the sulfate concentrations in most of North America, and to estimate the contributions from U.S. and Mexican source regions to sulfate measured at Big Bend and the other BRAVO monitoring sites. Several biases were identified in the original model source apportionment results. For example, during October the REMSAD predicted contribution of the eastern U.S. sources to eastern Texas were up to two times larger than the measured sulfate. In addition, on days with transport predominately from Mexico to southwest Texas, including Big Bend, the predicted sulfate concentrations systematically underestimated the measured sulfate. Thus, indicating an underestimation of Mexico's contributions. In order to remove these biases, the REMSAD and CMAQ source apportionment results were merged with the measured sulfate data using a synthesis conservation of mass inversion technique to derive daily source apportionment scaling factors. This technique essentially regresses the source apportionment estimates against the data from multiple monitoring sites. Similar techniques have been used with success to estimate global CO2 emission rates. Due to the inherent ill-posed nature of this inversion problem, a Bayesian least square regression was used. This method incorporates a-priori estimates of the parameters and variance. The synthesis inversion reduced the REMSAD predicted average eastern U.S. contribution to sulfate at Big Bend from 42 to 30%, while Mexico's contribution increased from 23 to 40%. Texas' contribution remained about 15%. In addition to the large source areas, REMSAD was used to estimate the contribution from the Carbón power plant facilities located 210 km southeast of Big Bend in Mexico. The synthesis inversion resulted in Carbón's contribution increasing from 14% to 22%.

4A-2

CHEMICAL CHARACTERIZATIONS OF MOBILE SOURCE EMISSIONS – RELATION TO AMBIENT MEASUREMENTS IN VEHICLE DOMINATED AND URBAN BACKGROUND LOCATIONS, ERIC FUJITA, Barbara Zielinska, William P. Arnott and David E. Campbell; Desert Research Institute, Reno, NV

DOE's Gasoline/Diesel PM Split Study was conducted to quantify the relative contributions of tailpipe emissions from gasoline-powered motor vehicles and diesel-powered motor vehicles to the ambient concentrations of fine particulate matter (PM2.5) in the urbanized region of Southern California using an organic compound-based chemical mass balance model (CMB). Source testing included 59 light-duty vehicles and 34 heavy-duty diesel trucks. Ambient samples were collected at two fixed monitoring stations and from a mobile sampling van at several urban background sites and at locations with expected higher proportions of PM emissions from diesel trucks and gasoline vehicles. Photoacoustic and DustTrak instruments monitored black carbon and total particulate matter continuously. A description will be given of the variations in relative abundances of the organic and elemental carbon fractions (IMPROVE protocol) and key organic marker compounds in the dynamometer samples relative to the source-dominated ambient samples and samples from regional air quality monitoring sites. In addition, the CMB source attributions based on carbon fractions alone are compared to corresponding apportionments with addition of organic compounds.

4A-3

AN APPROACH TO ESTIMATING TRAFFIC SOURCE CONTRIBUTIONS (TSCE) FOR AN EPIDEMIOLOGICAL STUDY: SPATIAL DISTRIBUTION OF TSCE IN THE GREATER CINCINNATI REGION, Shaohua Hu, Stefan Falke, Pratim Biswas,* Environmental Engineering Science, Washington University in St. Louis, St. Louis, MO; Dainius Martuzevicius, Sergey A. Grinshpun, Patrick Ryan, Grace LeMasters, Department of Environmental Health, University of Cincinnati, Cincinnati, OH

In urban arrears, traffic sources, such as gasoline- or diesel-powered vehicles are considered as one of the dominant contributors to the fine fraction of the ambient particular matter. In this study, a monitoring network was established in the Greater Cincinnati region to investigate the exposure of population to highway traffic related aerosols. Elemental carbon was chosen as the indicator of traffic source. Traffic source contribution estimates (TSCE) to element carbon (EC) were determined by receptor models applied to data from 24 monitored sites. Normalized TSCEs are characterized into 3 regions: low (0.12-0.3), medium (0.3-0.6) and high (above 0.6) and generally indicate that sites located in the urban city or close to highways are most influenced by traffic sources. Epidemiological studies require TSCE estimates over the entire study region, not just at specific monitoring sites. To map the TSCE over the region of interest, a spatial estimation method is developed. Conventional spatial interpolation methods, such as kriging, are not suitable for mapping traffic source contributions because TSCE does not exhibit spatial autocorrelation. Two methods are examined to account for the spatial heterogeneity in TSCE, traditional regression analysis and a modified spatial interpolation method. Both methods use multiple parameters to characterize TSCE, including distance from the highway to the monitoring sites, average daily traffic counts for cars and trucks, and wind direction. In the regression analysis, the relationship between these parameters and the TSCE are investigated using a curve fitting method that showed a sharp drop in TSCE within a short distance of highways but with a positive correlation with truck counts. The spatial interpolation based approach uses both distance to the highway and truck density in allocating spatial interpolation weights for the nearby sites. The two methods are compared using a cross validation analysis.

4A-4

COMBINING SIZE DISTRIBUTION AND CHEMICAL SPECIES MEASUREMENTS INTO A MULTIVARIATE RECEPTOR MODEL OF PM2.5,

TIMOTHY LARSON, David Covert, Astrid Schreuder, Thomas Lumley, University of Washington, Seattle, WA

Here we examine the use of accompanying particle size distributions to provide constraints on source contribution estimates and also the use of “missing mass” to provide constraints on the derived source profiles. We used the ME2 algorithm in order to apply hard constraints on selected elements of the source profiles, F. In order to apply these constraints in a straightforward manner, we not only used the measured chemical species in the mass balance equation, but also included the unmeasured mass as an additional ‘specie’. Inclusion of the missing mass as an additional specie provides a useful additional model constraint, specifically the mass fraction of all species for a given source must sum to one. This constraint must be true for all sources, within measurement error. We must also require that for all sources and species that the mass fraction of any given specie is less than one. We can also add additional constraints on the source contributions using simultaneously measured size distributions by solving a simultaneous set of mass and volume balance equations involving the aerosol density of particles emitted by a given source (as opposed to the bulk density). While the assumption of constant aerosol density for a given source is not exact, it does provide a useful set of constraints on the source contributions. We applied this model to a data set consisted of 24-hour filter measurements reported by the EPA Speciation Trends Network at Beacon Hill from 2000 to 2002. The Beacon Hill site is centrally located within the Seattle urban area on a hilltop, 325 feet above sea level. During this same period, we measured the particle size distribution at this site using a differential particle sizer and an aerodynamic particle sizer. We were able to resolve eight sources. Estimated specie abundances and associated size distributions for each source were found to be consistent with previous apportionments at this site and with size distribution emissions literature.

4B-1

SEMI-CONTINUOUS PM2.5 SULFATE AND NITRATE MEASUREMENTS IN NEW YORK: ROUTINE FIELD MEASUREMENTS AND INTENSIVE FIELD CAMPAIGNS,

OLGA HOGREFE, James Schwab, Silke Weimer, Kenneth Demerjian, Atmospheric Sciences Research Center, U-Albany, Albany, NY; Oliver Rattigan, Division of Air Resources, New York State Department of Environmental Conservation, Albany, NY; Frank Drewnick, Cloud Physics and Chemistry Department, Max-Planck-Institute for Chemistry, Mainz, Germany; Kevin Rhoads, Chemistry Department, Siena College, Loudonville, NY

Over the past few years several R&P Ambient Particulate Sulfate (8400S) and Nitrate (8400N) Monitors have been evaluated as part of the PM2.5 Technology Assessment and Characterization Study in New York (PMTACS-NY). These PM2.5 monitors were deployed during three intensive field campaigns, where they were operated side-by-side with other semi-continuous PM2.5 speciation instruments. Two of these campaigns were in Queens, New York City; July-August 2001 and January-February 2004. The third campaign was carried out during July-August 2002 at Whiteface Mountain, a rural location in upstate New York. During these campaigns the instruments were exposed to several pollutant episodes covering a range of PM2.5 concentrations and compositions. In addition to the intensive campaigns, the R&P Sulfate and Nitrate monitors have been used for routine semi-continuous measurements since May 2002 in the Bronx, New York City and since July 2002 at Whiteface Mountain. This has provided over two years of data, which is used to examine the diurnal, seasonal and yearly variability of PM2.5 sulfate and nitrate at both locations. Integrated 24-hr filter measurements of speciated PM2.5 carried out every 3rd day as part of the STN program at these sites were used to compare with 24 hr averaged measurements of the semi-continuous sulfate and nitrate instruments. In general both R&P particulate sulfate and nitrate instruments responded well to changing concentrations and tracked other collocated instruments. The results show that for these sites the R&P sulfate monitor agrees reasonably well (within 85 %) with other collocated instruments - both semi-continuous and filter based methods. In contrast the R&P nitrate monitor at these locations was found to be consistently lower (30-40%) than other semi-continuous and filter based nitrate measurements. Based on the above results, as well as the operational experiences during their deployment, the potential use of the R&P sulfate and nitrate particulate monitors for routine monitoring is evaluated.

4B-2

SEMI-CONTINUOUS PM2.5 NITRATE AND SULFATE MEASUREMENTS AT THE PITTSBURGH AIR QUALITY STUDY SUPERSITE, ANN WITTIG, CUNY at City College of New York, New York NY; Andrey Khlystov, Duke University, Durham NC; Satoshi Takahama, Spyros Pandis, Cliff Davidson, Carnegie Mellon University, Pittsburgh PA; Susanne Hering, Aerosol Dynamics Inc., Berkeley CA

A method for semi-continuous (10 minute time resolution) PM2.5 nitrate and sulfate measurements, based on the humidified impaction with flash volatilization (Hering and Stolzenburg, 1998), was evaluated during the Pittsburgh Air Quality Study from July 2001 to August 2002 (Wittig et al., 2004). Quality control data were acquired on a regular basis and were used to evaluate and correct the semi-continuous measurements for several operating parameters (Wittig et al., 2004b). The overall corrections were less than 10% on average, but could be quite large for individual 10 minute measurements. These corrections resulted in an improvement in the agreement of the measurements with the filter-based measurements, with a major axis regression relationship of y=0.83x+0.20 ug m-3 and R2 of 0.84 for nitrate and y=0.71x +0.42 ug m-3 and R2 of 0.83 for sulfate. The corrected semi-continuous measurements were calibrated over the entire year using collocated denuder/filter-pack based measurements. These calibrated semi-continuous measurements were used in conjunction with temporally resolved gas phase measurements of total (gas and aerosol phase) nitrate and meteorological measurements to investigate short-term phenomena at the Pittsburgh Supersite. The gas-to-particle partitioning of nitrate varied daily and seasonally, with a majority of the nitrate in the particle phase at night and during the winter months. Hering SV, Stolzenburg MR, 1998. Automated, high time resolution measurement of fine particle nitrate. Journal of Aerosol Science 29:S1189-S1190. Wittig AE, Anderson N, Khlystov AK, Pandis SN, Davidson C, Robinson AL, 2004a. Pittsburgh Air Quality Study Supersite Program Overview. Atmospheric Environment 38:3107–3125. Wittig AE, Pandis SN, Hering SV, Kirby BW, Khlystov AK, Takahama S, Davidson C, 2004b. Semi-continuous PM2.5 Inorganic Composition Measurements during the Pittsburgh Air Quality Study. Atmospheric Environment 38:3201-3213.

4B-3

CONTINUOUS MEASUREMENT OF AMMONIA AND ACID GASES, PARTICULATE AMMONIUM AND ANIONS, PURNENDU DASGUPTA, Masaki Takeuchi, SM. Rahmat Ullah, Department of Chemistry, Texas Tech University, Lubbock, TX

Efforts to make semi continuous (10-15 min time resolution) acid-gas/ammonia and similar particle constituent (anions, ammonium) measurement started in our laboratory in 1992 and a first paper on ammonia – ammonium N deposition in agricultural fields using steam condensation to increase aerosol size prior to continuous collection by impaction was first published with Swiss collaborators in 1994. Since that time, the basic instrument has undergone many changes. Several applications of several versions of the steam condensation based particle collection instrument were published. With the recognition that NO2 is not removed by upstream denuders and a small fraction of the NO2 is converted into HONO (primarily) and HNO3 by the steam, we sought alternatives. The strategy for collecting and removing potentially interfering gases by a continuously operating wetted parallel plate denuder, operating upstream of the particle collector remained the same. An alternating filter based instrument was first deployed in the Atlanta 1999 Supersite. While the general scheme is meritorious, fiber bleed from the filters and the resulting problems on the downstream analytical system caused problems. A hydrophobic mist refluxing collector was developed then and was used in Houston (2000), Philadelphia (2001) and Tampa (2002, 2003). During the last effort, initial studies were also made towards using a smaller miniature system that uses a smaller membrane based denuder and a novel filter based collector. This system runs with a multi-port selector valve syringe pump, providing a high degree of system reliability. Instrumentation and field data will be discussed.

4B-4

FINE PARTICULATE MATTER ION MEASUREMENTS AT THE ST. LOUIS – MIDWEST SUPERSITE BY THE PARTICLE-INTO-LIQUID SAMPLER (PILS),

Megan Yu, JAY TURNER, Washington University, St. Louis, MO; Andrea Clements, California Institute of Technology, Pasadena, CA; Rodney Weber, Georgia Institute of Technology, Atlanta, GA

A Georgia Tech / Brookhaven National Laboratory Particle-Into-Liquid Sampler (PILS) was deployed in June 2001 at the St. Louis – Midwest Supersite core monitoring location in East St. Louis, IL. PILS was coupled to anion and cation chromatographs to measure selected PM-2.5 water-soluble ions at fifteen minute time resolution during the first two years of operation. The data was validated at hourly resolution. Two key issues were identified during data validation: 1) sulfur dioxide plumes from a nearby point source could break through the denuder upstream of PILS and cause positive artifacts in the reported sulfate concentrations; and 2) there were periods of duration (hours-to-days) where the reported nitrate concentration was anomalously low (likely due to problems with the ion detector or nitrate losses in the sample lines). For the first year of operation (June 2001 – June 2002), after screening the data for such incidences, the daily-average PILS sulfate and nitrate showed excellent agreement with daily-integrated filter ion concentrations obtained using the Harvard-EPA Annular Denuder System (HEADS). PILS ion recoveries with respect to filter measurements were 88% and 86% for sulfate and nitrate, respectively, and the data were well-correlated over the entire period which featured a range of aerosol and environmental conditions. In addition to sulfate and nitrate, a suite of other inorganic and organic ions were measured during the first two years of the deployment and quantified for selected periods of interest. For example, November 2002 featured several successive days with hourly fine particulate matter oxalate concentrations reaching 0.5 micrograms per cubic meter. Oxalic acid exhibited diurnal profiles with a distinct daily midday maximum which lagged a few hours after the maximum solar radiation, consistent with oxalate arising from secondary formation. The midday maximum was positively correlated with solar radiation and negatively correlated with temperature. Such distinct profiles generally were not observed during other times of year and arise from a relatively narrow set of environmental conditions which are conducive to photochemical production of oxalate yet with sufficiently low temperature to yield significant partitioning of the oxalate to the particle phase. This presentation will summarize PILS operation at the St. Louis – Midwest Supersite, demonstrate its performance compared to both integrated filter ion measurements and other semicontinuous ion instruments, and demonstrate selected insights gained into the behavior of ambient particulate matter ion species through a series of examples.

4C-1

HIGH VOLUME INJECTION FOR GCMS ANALYSIS OF PARTICULATE ORGANIC SPECIES IN AMBIENT AIR,

John Turlington, ManTech Environmental Technology, Inc., Research Triangle Park, NC; David Olson, John Volckens, Leonard Stockburger, and STEPHEN R. MCDOW, Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, U.S. EPA, Research Triangle Park, NC

Detection of organic species in ambient particulate matter typically requires large air sample volumes, frequently achieved by grouping samples into monthly composites. Decreasing the volume of air sample required would allow shorter collection times and more convenient sample collection, potentially resulting in more distinctive source mixtures and expansion of source apportionment capabilities to micro-environmental applications. Most previous efforts for GCMS analysis of airborne particulate matter used splitless injection, which limits sensitivity by permitting injection of only a small fraction of the total extract. The Human Exposure and Atmospheric Sciences Division's recently developed Organic Aerosol Laboratory has completed characterization of a high volume injection method that increases analytical sensitivity by allowing injection of a considerably larger fraction of the extract. Samples are extracted under pressure using a Dionex Accelerated Solvent Extractor in 1:1:1 pentane:dichloromethane:methanol for measurement of both polar and non-polar compounds. Extracts are concentrated and introduced into an Agilent 6890 GC with a 5973 MS Detector by injection of 100 microliters with a Gerstel Programmable Temperature Vaporization Injector. Reproducibility of five point calibration curves run in triplicate has been demonstrated for eleven n-alkanes, three hopanes, and seven polycyclic aromatic hydrocarbons. Linear correlation coefficients for individual calibration curves for hopanes and polycyclic aromatic hydrocarbons in all cases were $r2 > 0.999$ and for n-alkanes in all cases were $r2 > 0.999$. Relative standard deviations were less than 3% for concentrations greater than or equal to 50 picograms per microliter and less than 20% for concentrations of 5 and 15 picograms per microliter. Agreement between the average determined concentration and its predicted value was within 10% for concentrations greater than or equal to 50 picograms per microliter. Although high signal-to-noise ratios were observed at concentrations as low as 1.5 picograms per microliter, precision between calibration curves was poor. These results indicate a capability for determining concentrations with good precision for all compounds at concentrations as low as 100 picograms per cubic meter even for a 24-hour 10 liter per minute sample (14.4 m3 air). Although this work was reviewed by EPA and approved for publication, it may not reflect official Agency policy.

4C-2

TRENDS IN REGIONAL ORGANIC ACIDS AND ALCOHOLS AS MEASURED BY THERMAL DESORPTION-GAS CHROMATOGRAPHY MASS SPECTROMETRY,

REBECCA J. SHEESLEY, James J. Schauer, University of Wisconsin-Madison, Environmental Chemistry and Technology Program, Madison, WI; Mark Meiritz, Jeff DeMinter, University of Wisconsin-Madison, State Lab of Hygiene, Madison, WI

In order to respond to the increasing need for detailed organic analysis of ambient atmospheric particulate matter (PM), in-situ derivatization combined with thermal desorption-gas chromatography mass spectrometry is being developed as a quicker, more cost-effective alternative to solvent extraction methods. Derivatization is a necessary step for the analysis of more polar organic species such as simple carbohydrates, steroids and organic acids. These polar species, including levoglucosan, cholesterol and aromatic acids are vital for source apportionment modeling and comprehensive characterization of ambient PM. A multi-step derivatization procedure has been developed for the analysis of these polar species. To demonstrate the viability of the method, a set of Midwestern samples has been analyzed. The trends in ambient concentrations of organic acids including alkanoic and aromatic acids, levoglucosan, glucose, sucrose, cholesterol and other species will be compared throughout the region. The combination of the simple carbohydrate species and the pattern of alkanoic acids will be used to describe the contribution of soil and biological material to fine PM.

4C-3

ANALYTICAL METHOD FOR SEMI-VOLATILE POLAR ORGANIC COMPOUND CHARACTERIZATION,

LYNN R. RINEHART, Barbara Zielinska, Desert Research Institute, Reno, NV

The speciation of polar organic compounds provides an important contribution to our understanding of carbonaceous aerosol. Oxygenated organic compounds are present in all emission sources including vehicles, wood combustion, cooking, etc., and may be formed during atmospheric transformation processes of primary emissions. Therefore quantitation of these compounds is important for characterization of both rural and urban environments. However, these compounds do not chromatograph well due to their high boiling point, thermal instability and molecular interactions with chromatographic columns. To address these analytical challenges, a silylation method has been developed to analyze 100 semi-volatile polar organic compounds many of which are unique for specific emission sources. Rather than two derivatization steps for carboxylic acids and hydroxylated compounds, we report a single derivatization which can be done for both of these functional groups using bis (trimethylsilyl)trifluoroacetamide (BSTFA) and 1% trimethylchlorosilane (TMCS). This derivatization performs well on hydroxyl groups, phenolic compounds, and carboxylic acid groups in the complex sample matrix of ambient and source samples. The range of compounds analyzed by this method includes: levoglucosan, methoxylated phenol derivatives, methoxylated carboxylic acid derivatives, resin acids, and alkanoic and aromatic carboxylic acids. This analytical method was compared to derivatization of carboxylic acids by diazomethane using separate fractions of samples. Results from the analysis of trimethylsilyl (TMS) derivatives have been compared to the results of methyl ester derivative analysis for separate fractions of 30 winter ambient samples with a biomass combustion influence. Wood smoke samples were used in this comparison due to the high prevalence of polar organic species emitted in the combustion of biomass. In addition, these samples provide a realistic sample matrix for derivatization. We have found good agreement for most compounds between the two derivatization methods, however some compounds have been found to be different. These differences are due to hydroxyl group derivatization by BSTFA +1% TMCS, which is not possible with diazomethane. The derivatization greatly enhances the thermal stability and volatility, thus providing an improvement in calibration response linearity and detection limits. Results of this experiment provide data for evaluation of the two polar organic speciation derivatization methods.

4C-4

THRESHOLDS OF STIMULATED RAMAN SCATTERING IN POLYMER AEROSOL PARTICLES AND RESONATORS WITH INCLUSIONS,

MIKHAIL JOURAVLEV and Gershon Kurizki; Department of Chemical Physics, Weizmann Institute of Science

THRESHOLDS OF STIMULATED RAMAN SCATTERING IN POLYMER AEROSOL PARTICLES AND RESONATORS WITH INCLUSIONS. M.V. Jouravlev and G. Kurizki. Department of Chemical Physics, Weizmann Institute of Science, 76100, Rehovot, Israel. Stimulated Raman scattering of low-intensity laser radiation on microparticles is a novel tool for spectroscopic detection of chemical impurities in aerosol particles. Problems related to cavity enhanced Raman gain and morphology dependent resonances are now extensively discussed in the literature [1]. The threshold intensity of stimulated Raman scattering observed in experiments with liquid droplets were quite low (1-10 kW/cm^2) [1,2]. Our present work is aimed at calculating the thresholds, the concentration of Raman active chemical molecules and the cavity enhanced gain for polymer aerosol particles and the fused silica resonators. A quantum mechanical approach was used to study the problem of stimulated Raman scattering in a transparent dielectric spherical and spheroid particles as well resonators. Our theory yields the analytical expressions for the Raman scattering threshold intensity, the concentration of the Raman active molecules and cavity enhanced Raman gain on the whispering gallery modes. The integral coefficients describing the nonlinear interaction between the whispering gallery TE and TM modes are introduced and the second and third-order nonlinear susceptibility of the substance are considered. In what follows we assume that the incident laser beam has a Gaussian intensity profile. We present that the thresholds at the resonant condition at the wavelength of 840 nm consists of 0.1 kW and less for whispering gallery modes of TE(6,21-30)-TE(3,21-30) in two modes regime interaction. Normalized gain is 500 and more. The particles size is 4.3 mkm, the refractive index is 1.47. The reduction of the threshold is attributed to increase of the overlap between the whispering gallery modes. The threshold is low and thus advantageous for measurements of the concentration of the chemical impurities. 1. G. Schweiger, (1990) Raman scattering on single aerosol particles and on flowing aerosols: A review. J. Aerosol Sci. Vol.21, 483-509. 2. H.-B. Lin, A.J. Campillo, (1997) Microcavity enhanced Raman gain. Opt.Comm. 133, p.287 -292.

5A-1

THE DEVELOPMENT OF A MULTIVARIATE RECEPTOR MODEL FOR VERTICAL PROFILE DATA BASED ON NONPARAMETRIC REGRESSION TECHNIQUES,

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Multivariate receptor modeling is a challenging problem. The current state of the art statistical tools, such as PMF and UNMIX, accurately apportion the number, composition, and contribution of variable sources as well as uncertainty estimates from ground-based PM speciation data. However, both models were designed solely for speciation data and are, therefore, constrained by measurements of the total particulate mass. Not to mention, both models assume receptors that are spatially invariant. Analyzing surface-based speciation and trace gas data is an effective means of apportioning sources, especially considering the extent of current PM networks. Still, because the receptors are fixed at the surface, these data only provide a portion of the overall picture. Vertical profile data on the other hand, collected by aircraft, lidar, and sondes, can provide greater insight into the transport processes, dynamics, and underlying mechanisms that drive pollution events. Except for the occasional speciation data collected aboard large aircraft, none of these platforms is capable of providing meaningful particulate mass and speciation data. When the model inputs are not constrained by total particulate mass and the receptor varies in space, the problem of multivariate receptor modeling becomes considerably more challenging. To address these additional challenges, we are currently designing a source apportionment tool based on a nonparametric regression statistical technique to be used on vertical profile measurements collected by aircraft and sondes of meteorological variables, trace gases, and aerosol microphysical and optical data. Regression analyses are used to estimate the value of a response, or dependent, variable (y) as a function of one or multiple predictors or independent variables (xs). Parametric regression techniques assume that the functional relationship between the response variable and the predictors is known, typically relying on a linear least-squares approach. Nonparametric regression techniques, however, assume no a priori knowledge of the functional relationship between the response variable and the predictors. Relaxing any assumptions of functional dependence is important when dealing with a complex set of variables such as those measured in the vertical profiles. The statistical tool we are developing will employ multiple nonparametric regression techniques that can be simultaneously run to determine the most efficacious approach in untangling the complex data sets. This will be an important tool in deriving meaningful statistical relationships, apportioning sources, and determining mechanistic forces from the multi-year climatologies of aircraft and sondes data currently at our disposal.

5A-2

SOURCE APPORTIONMENT OF PM 2.5 USING A THREE-DIMENSIONAL AIR QUALITY MODEL AND A RECEPTOR MODEL,

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Sources of PM2.5 are apportioned using a three-dimensional air quality model and a receptor model. Objectives of this paper are to compare source contributions calculated from the two modeling approaches, and to identify origins of discrepancies. In addition, this paper investigates ways by which methods of source apportionment can be improved. Air quality modeling is done with CMAQ applied over the United States, with a detailed grid over the southeastern US, and receptor modeling is conducted using the chemical mass balance model with organic molecular markers (CMB-MM) applied to observations from eight SEARCH stations in July 2001, and in January 2002 (ESP01/02). Sources of primary PM2.5 in the JST station are apportioned as detailed in Table1. Results from the two different methods match reasonably well, but discrepancies exist. Discrepancies can come from the direct comparison between point measurement (CMB-MM) and the volume-averaged prediction(CMAQ), but more importantly differences come from the uncertainty of each model. Sources of uncertainty in CMB-MM include source profiles and ambient data, which have been studied by Yan et al., (2004). When different source profiles of wood burning are used, contributed masses change from 1.7 to 14.4ug/m3 on January 27, 2002. When different levels of uncertainty are applied to the ambient data, contributed masses from gasoline emissions change as much as 35%. Sources of uncertainty in CMAQ include the size of the grid emission inventory, and meteorological field uncertainties. As can be seen in Table 1, contributed masses are different up to 43% when different sizes of the grids are applied. Emission inventory uncertainties include not only the total mass of emissions, but the temporal and compositional profiles and spatial surrogate as well. At this point, it is difficult to assess which approach is "better", and indeed, they both have their strengths and limitations, which are further explored.

Table 1. Source apportionments of primary PM2.5 in the JST station using CMB-MM and CMAQ. Unit:[ug/m3]

	July 2001		January 2002	
	CMB-MM	CMAQ(12/36km)	CMB-MM	CMAQ(12/36km)
Diesel exhaust	1.35	2.28/1.48	1.84	2.17/1.44
Gasoline exhaust	0.07	0.61/0.48	0.60	0.65/0.50
Road dust	0.44	2.29/1.97	0.00	2.86/2.45
Wood burning	0.33	1.96/2.34	3.09	2.24/2.67
Sec. Sulfate	7.85	10.76/11.37	2.21	3.56/3.19
Sec. Nitrate	0.44	1.77/1.38	1.65	8.05/8.23
Sec. Ammonium	3.26	4.36/4.18	1.34	3.68/3.60
Other organic matter	3.35	2.76/3.23	1.47	2.55/2.25
Unclassified mass	5.44	3.52/2.99	1.08	4.53/3.74

Reference: Bo Yan, Mei Zheng, Armistead Russell, 2004, Uncertainty and sensitivity analysis of chemical mass balance modeling using organic tracers for PM2.5 source apportionments, AAAR 2004, Atlanta GA

5A-3

APPLICATION OF THE UM MULTIVARIATE PSEUDO-DETERMINISTIC RECEPTOR MODEL TO RESOLVE POWER PLANT INFLUENCES ON AIR QUALITY AT THE CMU SUPERSITE,

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A Multivariate Pseudo-Deterministic Receptor Model (PDRM), combining mass balance and Gaussian plume dispersion equations, was designed to exploit highly time-resolved ambient measurements to determine emission rates of SO2 and elemental constituents of particles from known stationary sources and to predict their contributions to ambient levels. Highly time resolved data facilitates source resolution by i) reducing the number of sources influencing the measurements, ii) preserving directionality (i.e., source angle relative to wind angle) and plume width information, iii) and by better preserving the signal-to-background ratios of data from their plumes. The model was previously applied with excellent results to ambient data influenced by 6 sources in the topographically flat Tampa Bay area. Herein, we apply the model to measurements of SO2 and 11 elements determined in particles collected with the University of Maryland Semicontinuous Elements in Aerosol Sampler (SEAS) at the Carnegie-Mellon Supersite in Pittsburgh, an area characterized by rough terrain. Ambient SO2 and particle measurements, the latter made every 30 minutes for Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn, during a 12.5 hr period on April 1st, when winds blew from 290 to 3300, i.e., wherein lie four small coal-fired power plants. During the study period, temporal SO2 concentration profiles were similar to those of As, Cr, Cu, Ni, Pb, Se, Zn, and to a lesser extent, Al, and Fe. Agreement between predicted and observed SO2 concentrations was excellent (R2 of 0.84; their ratio of 1.09±0.22) when 4 emission sources were used in the model. Average ratios of predicted and observed concentrations for As, Cr, Cu, Ni, Pb, Se, and Zn varied from 0.97±0.20 for Cr to 1.07±0.44 for As. These results suggest that the PDRM approach is feasible in a city encompassing complex topography.

5A-4

PM2.5 SOURCE APPORTIONMENT USING RECEPTOR AND SOURCE-ORIENTED MODELS: CONCEPTUAL DIFFERENCES AND IMPLICATIONS FOR HEALTH STUDIES,

AMIT MARMUR, Sun-Kyoung Park, James A. Mulholland and Armistead G. Russell, Georgia Institute of Technology, Atlanta, GA

Several ongoing epidemiologic studies now explore possible associations of health outcomes with specific sources contributing to fine particulate matter (PM2.5), in addition to health outcomes with measured concentrations of PM constituents. This will potentially allow for the identification and regulation of sources more associated with health outcomes. In addition, this may allow for the assessment of associations of an outcome and unmeasured species. Several techniques can be used to derive these source contributions to a specific site or region. Here we compare two conceptually different approaches: observational based (receptor) models and source-oriented air quality models. Using receptor models measured PM2.5 is apportioned into impacting source categories based on knowledge of the typical compositions of emissions at these sources and speciated ambient PM2.5 data. Source-oriented air quality models simulate the source impacts based on an emissions inventory and meteorological transport mechanisms. The Atlanta Jefferson Street SEARCH site was used as a case study. Daily source impacts for July 2001 and January 2002 were calculated using a recently developed, extended, chemical mass balance approach incorporating gas-phase data, and using EPA's Models-3 suite of air-quality models (MM5, SMOKE, CMAQ). Results show that the variability in source impacts from the receptor-based analysis is greater than those obtained from the air quality model. This resulted in low correlations between the corresponding daily source impacts found using the source-oriented and receptor-based models, though on average the results look in reasonable agreement for some of the sources. Daily contributions from various categories based on the source-oriented model are highly correlated, indicating a meteorological trend as the factor driving the various source impacts. Source impacts based on receptor modeling show a different pattern, indicating to local effects, sensitivity to changing wind patterns and variances in source activity. When applied to a rural site (Yorkville, GA), higher correlations between the corresponding source impacts from the two techniques are observed. This suggests that the monitor is being more affected by regionally transported emissions, rather than local sources (as in the case of the Atlanta site). Hence, in the rural site, the air quality model was able to better characterize the source impacts compared to the urban site. This analysis has many implications for health studies. Receptor-based models are affected by local sources (as is the monitor). Thus, the source impacts at one site might not be representative of a study region. In addition, uncertainties due to measurement error and detection limits of tracer species might cause source impacts to fluctuate more than the true case. Source-oriented models, on the other hand, are less subject to local effects, but might not be characterizing the temporal trends in emissions to a level reflecting true variance. Hence, source-oriented models might be produce less variance in source impacts than the true case, diminishing the power of the health study to detect an association. Resolving these differences presents a major challenge for the air quality modeling community.

5B-1

EVALUATION AND QUALITY ASSURANCE OF CONTINUOUS AND SEMI-CONTINUOUS PM INSTRUMENTATION,

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Continuous and semi-continuous instruments for the measurement of PM-fine and PM-coarse are increasingly available and will become even more important as the technology improves. Continuous and semi-continuous methods and instruments measure PM mass and/or selected chemical or physical parameters of the aerosol. High time resolution data (1 hour or less) are very useful or even necessary for modeling studies, exposure studies, and process studies. Measurement methods and instrumentation are evolving rapidly to fill the need for more detailed information to address scientific and regulatory issues related to airborne particulate matter. Before new methods can rightfully take their places as fully accepted methods, they should undergo a rigorous evaluation, and be linked with a traceable quality assurance protocol. Three primary methods of evaluating continuous and semi-continuous PM instruments exist at the present time. First is comparison with filter measurements. For mass, the continuous data are compared to the FRM; for chemical components, the data may be compared to the data from the STN. Second is laboratory evaluations and comparisons. This exercise requires a substantial commitment into aerosol generation and characterization equipment and training. It does provide useful insight into instrument operation in a highly controlled setting. Third is field intercomparisons of methods and instruments. If two identical instruments are operated side-by-side, the result is a measure of the operational precision of the instruments. If different instruments that measure the same parameter are operated side-by-side, one obtains a measure of the "comparibility" of the instruments. If one of the methods is traceable to a reference standard, a measure of instrument accuracy can also result. The presentation will present applications of these three methods of instrument evaluation; and the strengths and weaknesses of each method. Examples will be given for a number of new and evolving classes of instruments.

5B-2

A NEW COMPACT AEROSOL CONCENTRATOR FOR USE IN CONJUNCTION WITH LOW FLOW-RATE CONTINUOUS AEROSOL INSTRUMENTATION,

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Currently available versatile aerosol concentration enrichment systems (VACES) have proven useful for providing elevated levels of ambient particulate matter to human and animal exposures, as well as for the collection of particles in aqueous solutions for in vitro studies. Previous studies have demonstrated that such systems do not significantly alter the physical or chemical properties of the particles. The current VACES configuration consumes significant electrical power for pumping and cooling, and requires attended operation by expert operators. A recent application of the VACES has been to provide a concentrated aerosol stream to continuous particle mass spectrometers in order to increase the spectrometer's hit-rate or sensitivity. These instruments usually require low intake flow rates (< 1 l/min) and often sample unattended, 24-hours per day. In order to better meet the requirements of these instruments, a new "mini VACES" (m-VACES) system with a lower intake flow rate (30 l/min), a lower minor flow rate (1 – 1.5 l/min) and allowing for more automated operation was designed, built, and tested. The system is a scaled down version of the current VACES design, with many important design improvements. Humidification of the air stream is achieved with a re-designed saturator consisting of a heated, moist absorbent material surrounding the intake flow. Cooling to achieve super-saturation, and thus particle growth, is accomplished using a commercially available, solid-state, thermo-electric chiller. Once grown, the aerosol is concentrated using a new, smaller virtual impactor. Particles are then dried to their original size using a diffusion dryer filled with silica gel. Results of the laboratory evaluation include near ideal enrichment factors for laboratory-generated particles of different composition (ammonium nitrate, ammonium sulfate, adipic acid) as well as ambient aerosols. Particle size distributions measured by an SMPS before and after enrichment show that particle size distributions are not altered. An APS provided data on the size distribution of particles after growth and concentration, but before drying. Filter-based and continuous field experiments in which concentrated aerosol was compared to ambient outdoor levels also showed near ideal enrichment factors for PM2.5 mass and black carbon, with no significant alteration of the particle size distribution.

5B-3

FIELD VALIDATION OF THE THERMO MODEL 5020 CONTINUOUS SULFATE ANALYZER,

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Measurement of ambient sulfate aerosol in real time is an important component of many programs, including studies of regional haze, assessment of PM source contributions, model development and evaluation, and health effects. Several methods have been used over the last 30 years, but their reliability and complexity have limited deployment to intensive research projects. With the current U.S. EPA focus on wider deployment of real-time aerosol speciation methods into state and local air monitoring programs, robust instruments from the data quality and field operations perspectives are essential. This presentation evaluates the field performance of a new commercial method for continuous sulfate measurement. The Thermo Electron model 5020 sulfate analyzer is based on technology developed at the Harvard School of Public Health; sulfate is quantitatively converted to SO2 at 1000 C in a quartz tube furnace using stainless steel to promote the reduction chemistry. The method is a true continuous measurement, has high conversion efficiency of both laboratory generated and ambient sulfate, and requires no support gases or liquids for operation. The model 5020 was evaluated during 2004 at the St. Louis Supersite, where it was compared to hourly sulfate data from the Georgia Tech / BNL Particle-into-Liquid Sampler (PILS), as well as sub-daily and 24-hour integrated Nylon filter IC sulfate data. A second 5020 was collocated to assess method precision. Good numerical agreement and correlation was observed between the model 5020, PILS, and filter sulfate measurements. The model 5020 detection limit is 0.3 ug/m3 for 1-hour means, sufficient to provide good precision at ambient sulfate levels observed in the eastern U.S. As an example of technology transfer from the supersite program to state monitoring agencies, the model 5020 was deployed in a network of several rural, high elevation sites in the Northeast U.S. in 2004. RAIN (Rural Aerosol Intensive Network) is designed to provide detailed characterization of transported pollution with both a visibility and PM-fine focus as part of the MANE-VU regional haze planning organization effort. RAIN is the first use of the 5020 at routine ongoing state-run sites. Data quality and operational issues from this deployment are discussed, as are data examples from regional sulfate events.

5B-4

INTERPRETING AEROSOL BLACK CARBON MEASUREMENTS FROM A MAGEE SCIENTIFIC AETHALOMETER, BRADLEY GOODWIN, Neil Deardorff, Jason Hill, Jay Turner, Washington University, St. Louis, MO; James Schauer, Min-Suk Bae, University of Wisconsin, Madison, WI

Under the St. Louis – Midwest Supersite program, aerosol black carbon (BC) measurements were conducted at three sites using the Magee Scientific Aethalometer □. These sustained measurements resulted in a forty-three month time series (to date) for the East St. Louis, IL, urban site (April 2001 – October 2004), a three-month time series for the Park Hills, MO, rural site (mid-August 2001 – mid-November 2001), and a four-month time series for the Reserve, KS, rural site (September 2002 – December 2002). All sites included contemporaneous daily-integrated elemental carbon measurements using offline thermal-optical analysis (ACE-ASIA protocol which conforms to NIOSH 5040); the East St. Louis site also featured semi-continuous elemental carbon measurements using Sunset Laboratory OCEC field analyzers. BC concentrations were consistently higher in the summer and lower in the winter; in contrast, EC showed much less systematic seasonal variation. For example, at East St. Louis the geometric mean BC concentrations were 1.10 and 1.13 micrograms per cubic meter for the summers of 2001 and 2002, respectively and 0.67 and 0.69 micrograms per cubic meter for the winters of 2001 and 2002, respectively; the corresponding daily-integrated filter EC concentrations were 0.70 and 0.63 micrograms per cubic meter for the summers, and 0.49 and 0.66 micrograms per cubic meter for the winters. Sulfate was found to be a good correlating parameter for the BC to EC differences, with high sulfate-to-soot ratios corresponding to enhanced BC relative to EC. This trend was observed for daily-average data at all three sites and also hourly-average data at the East St. Louis site. One possible explanation is the enhanced absorption by soot for an internal mixture with sulfate. Another possible explanation is that sulfate is a surrogate for different carbon emission fields with varying physical and/or chemical properties for the carbon-containing component. We are currently investigating these hypotheses by mining other data streams collected at East St. Louis site.

5C-1

OC/EC ANALYSIS WITH THERMAL-OPTICAL METHODS: EFFECTS OF TEMPERATURE PROTOCOL AND NON-CARBONACEOUS COMPOUNDS, R SUBRAMANIAN, Allen Robinson, Carnegie Mellon University, Pittsburgh, PA; Andrey Khlystov, Duke University, Durham, NC

Particulate carbon is classified as organic and elemental carbon (OC/EC) by analyzing an aerosol sample collected on a quartz filter with a thermal-optical method such as IMPROVE or NIOSH. The OC/EC split is difficult to determine because some of the organic carbon pyrolyzes during the analysis. This pyrolyzed carbon (PC) needs an oxidizing atmosphere to evolve off the filter similar to EC, resulting in an over-estimate for EC if no correction is made for the pyrolysis. The thermal-optical methods correct for pyrolysis by measuring either the transmittance or reflectance of the sample, defining EC as the mass of carbon that evolves after the transmittance (or reflectance) returns to its original, pre-analysis value. The underlying assumption of the optical pyrolysis correction is that either (a) PC and EC have similar optical properties (transmittance or reflectance), or (b) PC volatilizes or combusts off the filter completely before EC. These two assumptions were examined by washing ambient samples with organic solvents (to reduce OC and minimize pyrolysis) before the OC/EC analysis. A comparison of the washed and unwashed filters shows that PC evolves at the same time as EC, and that the optical transmittance of PC and EC are different. Thus, neither of the assumptions behind the optical correction is valid, and the OC/EC split is dependent on the relative rate at which PC and EC evolve off the filter. The relative rate at which EC and PC evolve is sensitive to both the maximum temperature used in the Helium mode and non-carbonaceous material in the sample. Too high of a peak Helium temperature can lead to premature loss of EC that will bias the OC/EC split. A peak Helium temperature of 870 ºC leads to loss of EC in the Helium mode (i.e. EC evolves faster than the PC). A lower peak Helium temperature of 700 °C reduces the premature loss of EC, increasing the measured EC by about 25% compared to the 870 °C protocol for ambient samples collected in Pittsburgh. Analysis of refractory doped ambient samples and refractory doped standards suggest that metal oxides are the probable cause of premature evolution of EC in the inert mode. Too low of a peak Helium mode temperature can also effect the OC/EC split. Ambient and source samples were doped with levoglucosan and certain humic/fulvic acids and analyzed using both the 700 °C peak Helium temperature and a peak Helium temperature of 550 °C. The lower temperature protocol results in a positive bias in EC for some samples, e.g. leonardite (a humic acid standard), due to unpyrolyzed OC evolving in the Helium/Oxygen mode when EC is expected to come off the filter.

5C-2

FUNCTION AND PERFORMANCE OF A NEW REAL-TIME BLACK CARBON MONITOR DURING THE 2003-2004 WINTER IN FRESNO, CA,

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A new instrument is presented which measures the atmospheric black carbon loading by the application of a radiative transfer scheme to a particle-loaded glass fiber filter tape. The MAAP (Multi-Angle Absorption Photometer) is a method that includes multiple-scattering effects into the analysis of the aerosol-filter layer and therefore reduces the uncertainties of the measured aerosol absorption coefficient and the black carbon mass loading of the filter sample. During the 2003-2004 wintertime black carbon study at the Fresno Supersite, two (2) MAAP monitors were collocated and compared against elemental carbon results measured by onsite PM2.5 Speciation samplers. Additional data comparisons are compared with other available continuous carbon analyzers and monitors. The principle of operation and performance of the instrument are presented, and potential applications in the field and research studies are discussed here within.

5C-3

OPTICAL TRANSITIONS OF CARBONACEOUS PARTICLES UNDER HEATING,

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Carbonaceous particulate matter resulting from combustion of carbon-based fuels is one of the major components of submicron aerosol particles. It is well known that measurements of carbonaceous particles by different thermal-optical analyzers (TOA) disagree, particularly with regard to the differentiation between organic carbon (OC) and the light-absorbing elemental carbon (EC). Various studies have examined temperature programs, artifacts, charring behavior, and catalytic behavior as reasons for these differences. The present study seeks to reconcile the results of these varying methods as far as possible. In particular, data generated by TOA include both the release of carbon and optical transitions as the sample is heated in different environments. We report on a “bottom-up” approach to interpreting these combined transitions. We apply our approach to a reference “black carbon” (hexane soot), a complex organic mixture (wood combustion products), and diesel-generated particles. We first investigate whether thermally-driven changes in particle optics result in interpretation artifacts, independent of whether the particles’ chemistry changes under heating. We present our first estimates of quantitative corrections for some of these artifacts. We use both an optical model of the changing, heated filter-particle system, and controlled experiments designed to isolate the specific effects of interest. These potential effects include temperature-dependent changes in material properties, and changes in particle size or coating state. The particle optics are measured as the particles are deposited on the TOA filter, and these properties are used to initialize the theoretical model. Elemental carbon is often treated as a conserved tracer in source apportionment studies, and its ratio with organic carbon is used to identify whether secondary organic aerosol has contributed to a particular sample of fine PM. In addition, carbon “fractions”—those evolving under specific, narrow sets of conditions—are presently being investigated for use in source apportionment. These investigations are obviously sensitive to the assumption that TOA results do not change with atmospheric processing. We examine this assumption by collecting identical particle samples and comparing their TOA responses after simulated atmospheric aging. We report on treatment-dependent changes in the times and nature of carbon evolution, and again present quantitative corrections. Finally, the use of real-time optical methods to determine “black carbon” concentrations has promise for monitoring in urban areas. However, the relationship between these optical results and TOA analysis is prone to large uncertainties. We report preliminary results from a small experiment (COSMIC-2004 or COlored SMoke InterComparison) that compared both filter-based absorption measurements and TOA analysis with a reference absorption measurement.

5C-4

SPATIAL VARIABILITY OF PM2.5 SPECIES IN THE CALIFORNIA CENTRAL VALLEY,

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The San Joaquin Valley (SJV) in central California is one of the largest PM10 non-attainment areas in the United States. In winter, highly elevated fine particulate matter (PM2.5) concentrations are frequently observed throughout the valley, covering urban and rural areas. The Fresno supersite, located at the center of SJV, recorded a persistent 24-hr PM2.5 concentration of >100 µg/m3 during a winter episode (1999–2000). One of the objectives of the California Regional Particulate Air Quality Study (CRPAQS) was to determine the spatial variations of PM2.5 mass and its important components at different temporal scales. Twenty-four-hour speciated measurements —including mass, ions, elements, organic carbon (OC), and elemental carbon (EC)—were made at 36 sites in SJV every sixth day from December 1999 to February 2001. Four intensive operating periods (IOPs), in which more detailed measurements were performed within longer pollution buildup periods (IOP_1: 12/15/00–12/18/00; IOP_2: 12/26/00–12/28/00; IOP_3: 1/4/01–1/7/01; and IOP_4: 1/31/01–2/3/01), were also carried out at the five anchor sites. The site-specific annual PM2.5 mass concentration was between 3.7 ug/m3 (Olancha) and 29.9 ug/m3 (Fresno Feedlot). The valley-wide average was ~17 ug/m3, slightly higher than the U.S. Environmental Protection Agency (EPA) national ambient air quality standard (NAAQS) for annual PM2.5. At 30 of the 36 sites, the highest 24-hr PM2.5 concentration occurred on either 1/1/2001 or 1/7/2001. In winter, nitrate appears to accumulate in the southern part of the valley over an area of ~200 km in diameter centered at Angiola; outside this zone, nitrate concentration dropped to less than half of that level. Carbonaceous material is more influenced by immediate urban (especially Fresno) emissions, consistent with the property of primary aerosols. The major contrast between winter and summer in the SJV is the ammonium nitrate concentration. The highest summer PM2.5 mass concentration occurred in Fresno and was relatively confined within its urban area. This mass consisted of ~50% organic matter (OM) and 25% crustal material (CM). Elevated CM concentrations were also observed at Bakersfield and Bethel Island, likely related to road dust. The IOP_3 captured the highest PM2.5 level during January 2001. Nitrate concentration peaked initially at Bakersfield but later moved northward to Angiola. The northern valley sites, including Bethel Island, measured maximum concentrations less than one-third of those at Bakersfield or Angiola, which reached the episode peak 1–2 days after Bakersfield. This is consistent with the pollution plume dispersed northward at a speed of ~100 km/day. For OC and EC, the highest concentrations were observed at urban centers and showed limited day-to-day variations during the episode. Speciation of OC included alkanes, PAHs, hopanes, steranes, and polar organic compounds, which were quantified for 20 annual average satellite sites and also at 4 anchor sites during IOPs. Marker compounds may be used to indicate relative contributions of diesel, gasoline, wood combustion, and secondary aerosol to the ambient OC concentration in the SJV. The most abundant individual organic pollutant was levoglucosan, a unique molecular marker for combustion of cellulose, especially abundant in wood smoke. Considering most species, a strong linear relationship was found for 4 of 11 mass normalized sites. Auberry in the Sierra Nevada Foothills, Bethel Island, and Modesto—when compared to Sacramento—had slopes near 1 with correlation coefficient values of 0.97 and higher. CRPAQS reveals detailed characteristics of PM2.5 distribution and variations (both inorganic and organic species) in California's central valley. These data form a basis for source and receptor modeling and provide insights for the formulation of pollution regulations.

6A-1

SOURCE APPORTIONMENT OF MIDWEST PM2.5 USING ADVANCED RECEPTOR MODEL,

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Daily PM2.5 (particulate matter with aerodynamic diameter less than 2.5 µm) speciation data were collected at two Speciation Trends Network (STN) sites located in metropolitan St. Louis, Missouri. Expanded multilinear engine (ME) model was applied to daily PM2.5 speciation data to apportion sources to the Midwest fine particles. An advanced expanded model consists of both the basic bilinear equations (source contribution and source profile factors) and a set of multilinear model equations (factors of wind direction/wind speed, weekend/weekday, and time-of-year). Eight to nine sources were identified at the two sites. Regional transport of particulate sulfate and nitrate contributed 50 - 60% to total PM2.5 mass concentration. Potential source regions of sulfate are distributed in eastern U.S. and source regions of nitrate are located in upper Midwest. Influence of African dust to the Midwest was also observed. Local industries, located in Illinois and Missouri, such as zinc/lead smelters, steel processing, copper production, and cement were identified to be contributing sources to metropolitan St. Louis PM2.5. In addition, motor vehicle emissions and biomass burning sources were found. Expanded ME modeling was able to both apportion the sources and identify the directionality of source locations with combined wind direction and wind speed data.

6A-2

ENHANCED SOURCE IDENTIFICATION OF SOUTHEAST AEROSOLS USING TEMPERATURE RESOLVED CARBON FRACTIONS AND GAS PHASE COMPONENTS,

Wei Liu, Yuhang Wang, Armistead Russell and Eric S. Edgerton

Five gas components (CO, SO_2, NO, HNO_3(gas) and NOy) and PM2.5 (particulate matter ≤ 2.5 µm in aerodynamic diameter) composition data including eight individual carbon fractions collected at four sites in Atlanta, Birmingham, Centreville, and Yorkville were analyzed with Positive Matrix Factorization (PMF). Multiple linear regression (MLR) was applied to regress the total PM mass against the estimated source contributions. The regression coefficients were used to scale the source profiles. Nine factors were resolved at two urban sites (Atlanta, GA (JST) and Birmingham, AL (BHM)) and one rural site (Centerville, AL (CTR)). Eight factors were resolved at another rural site (Yorkville, GA (YRK)). Soil, Coal combustion /other, Diesel emission, Secondary sulfate, Secondary nitrate, and Wood smoke are six common factors among the four sites. Two similar industry factors are found at the two sites in each of the same state. Comparing to the previous studies using only particle data with traditional EC, OC data, diesel and gasoline emission factors were found at two urban sites instead of only one single motor vehicle factor; diesel and gasoline emission factors were found at CTR site and a diesel emission factor were found at YRK instead of no motor vehicle factor at the two rural sites. The inclusion of gas components also improved the identification of coal combustion /other factor among the four sites. This study shows that the inclusion of gas phase data and temperature resolved fractional carbon data in factor analysis enhances source identification and apportionment, especially for the motor vehicle and coal combustion/other factors.

6A-3

USE OF ADVANCED RECEPTOR MODELLING FOR ANALYSIS OF AN INTENSIVE FIVE-WEEK AEROSOL SAMPLING CAMPAIGN,

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Advanced receptor modelling is an increasingly important technique for use in characterization of sources and source apportionment of urban aerosols. The application of advanced receptor modelling techniques to highly time-resolved, on-line sampled aerosol compositions and size data has, to date, not been extensively investigated. The objective of this study was to assess if a highly time-resolved, diverse data-set, collected over a short period of time, would allow for adequate characterization of aerosol sources using an advanced receptor model. The data utilised in this study were collected during a 5-week long intensive aerosol sampling campaign that took place in Toronto, Ontario, in fall of 2003. The data set consists of a total of 2637, 15-minute averaged aerosol concentrations, measured using an Aerosol Mass Spectrometer (AMS) and a Particles in Liquid Solution (PILS) system. The AMS was used for on-line analysis of ammonium (NH_4), nitrate (NO_3), sulphate (SO_4), mixed organics, chlorine, polyaromatic hydrocarbons (PAHs), and particulates with mass-to-charge ratios of 43, 44 and 57. The PILS was used for continuous analysis of sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}). In addition, particulate size distributions and meteorological data were also collected during the sampling campaign. This study utilised Positive Matrix Factorization (PMF), through the applications of PMF-2 and the Multilinear Engine (ME-2) to characterize and apportion sources using the high time-resolution aerosol concentration and meteorological data. PMF-2 was initially applied for source identification and apportionment using the AMS and PILS data. Recently, ME-2 has been developed as a more flexible and general model which by the inclusion of parametric variables, such as wind speed and direction, allows for generation of not only source profiles but also interesting parametric factors providing additional information about potential sources. ME-2 was used for analysis of the AMS and PILS aerosol concentration data, aerosol size distributions, and included the parametric variables of wind speed, wind direction and time of day. A comparison of the source composition profiles generated using the ME-2 and those identified using PMF-2 was completed. Using the Multilinear Engine it was possible to demonstrate that an aerosol sampling campaign of short duration, but involving diverse and highly time-resolved data allows for identification and characterization of aerosol sources.

6A-4

POSITIVE MATRIX FACTORIZATION (PMF) AND CHEMICAL MASS BALANCE (CMB) RECEPTOR MODELING APPLIED TO IMPROVE DATA SETS FROM THE NORTHEASTERN USA,

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This paper presents Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB) results from the four IMPROVE sites, Boundary Waters Canoe Area, Lye Brook Wilderness Area, Shenandoah National Park and Washington DC, all in the northeastern USA. The samples were collected over a more than 10 year period, from 1988 (1991) to 2002. The species included in the receptor modeling are 16 elements, eight carbon fractions and the nitrate and sulfate ions. PMF receptor modeling was applied to the total data sets as well as to the seasonal data subsets. This is a factor analysis procedure where two matrices corresponding to the scores and loadings are calculated to have non-negative values. The model provides a weighted least squares fit with the weights taken from the uncertainties in the input ambient data set. Source types were assigned to the modeled factors by comparing their compositions to those of measured chemical source profiles. Criteria used to identify sources include the major and trace species contents, as well as the relative abundances of the carbon fractions contained in the factors. In most instances factors could be interpreted as individual or combinations of aged or reacted source profiles. A set of 20 “modeled source factors” was calculated from the PMF factors by subtracting the sulfate and nitrate and correcting for the oxygen and hydrogen, not chemically analyzed for. The averaged seasonal ambient data from each of the four sites together with the “modeled source factors” were used as input to the CMB receptor model. The source attributions for the mean and seasonal data subsets from the four sites are presented. The modeled source types include secondary sulfate, secondary nitrate, vegetative burning, geological dust, vehicle emissions, coal fired power plants, residual oil combustion, iron ore handling, marine salt and smelters. In the absence of appropriate measured source profiles, the combination of PMF and CMB modeling provided reasonable source attribution results. However, the organic and elemental carbon contained in the secondary organics remain difficult to resolve.

6B-1

A SMALL FOOTPRINT GAS PARTICLE ION CHROMATOGRAPHY SYSTEM,

S.M. Rahmat Ullah, Masaki Takeuchi, PURNENDU K DASGUPTA

A new compact Gas Particle Ion Chromatography (GPIC) instrument has been developed for the measurement of soluble ionogenic gases and ionic constituents in PM2.5. This instrument has two independent sampling channels for gases and particles. A closed liquid flow path membrane denuder collects soluble gases. In the second channel, a cyclone removes larger particles and an identical membrane denuder removes the soluble gases. Then a continuously wetted hydrophilic filter-based particle collector collects the particles. A single multiport syringe pump handles both channels, following principles of Sequential Injection Analysis and Zone Fluidics. A single conductivity detector is used to measure not only gaseous acid derived anions but also ammonia and ammonium. Relative to previous systems, no peristaltic pump is used and the system operates with lower gas and liquid flow rates. Robustness is greatly improved and the system is compact at the cost of time resolution. Using electrodialytically generated gradient hydroxide eluents and 3 mm bore high efficiency columns, providing every 40 min data for both gases and particles, each collected for 40 min but staggered 20 min apart. The liquid samples from the gas denuder and particle collector are drawn by the syringe pump and preconcentrated on a sequential cation and anion concentrator housed in a 10-port valve, staggered 20 min in time. The Ion Chromatograph (Dionex ICS-2000) and associated software controls all valves and the syringe pump. The preconcentrated samples (cations and anions) are injected to ammonia transfer device and anion separation column using respective eluents. The flow configuration and valve timing results in the ammonia peak appearing in front of the anion peaks, thus constituting a single chromatogram that separates and detects ammonia, organic acid like acetic and formic acids, HCl, HONO, SO2, C2H2O4, HNO3 and ammonium, acetate, formate, chloride, nitrite, sulfate, oxalate and nitrate in particle phase in a single chromatogram. Detection limits of low to subnanogram per cubic meter concentrations of most common gases and particulate constituents are readily attained.

6B-2

CONTINUOUS AMMONIA MEASUREMENTS AT 2 SEARCH SITES, ERIC S. EDGERTON, Atmospheric Research & Analysis, Inc., 410 Midenhall Way, Cary, NC 27513. Benjamin E. Hartsell Atmospheric Research & Analysis, Inc., 720 Ave. F, Ste. 220, Plano, TX 75074. John J. Jansen Southern Co., 600 18th Street N, Birmingham, AL 35291. Callie J. Waid Atmospheric Research & Analysis, Inc., 720 Ave. F, Ste. 220, Plano, TX

Ammonia (NH3) is the predominant basic gas in the troposphere. As such, it plays an important role in gas-particle partitioning, chemical composition and physical properties of atmospheric aerosols. Under thermodynamically favorable conditions, reaction between NH3 and nitric acid (HNO3) produces ammonium nitrate, which is a major component of PM2.5, especially during winter, in many areas of the U.S. Reaction between NH3 and sulfuric acid aerosol produces a variety of ammonium sulfates and modifies light scattering characteristics of the bulk aerosol. Despite the above, little is known about atmospheric NH3 concentrations in rural or urban environments. This presentation will describe continuous measurements of NH3 for 2 SEARCH sites: Yorkville, GA and Jefferson Street, Atlanta, GA. NH3 is measured with a double difference technique developed for SEARCH. In this approach, fine particulate NH4+ and NHy (NH3 plus NH4+) are measured continuously and NH3 is calculated by difference. The particulate-NH4+ analyzer is described in a companion presentation. The NHy analyzer is a 2-channel system. Sample air is drawn directly into a 350C Mo catalytic converter (Channel 1) or a 750C Pt/350C Mo converter (Channel2). NOy is reduced to NO in channel 1 and NOy plus NHy are converted to NO in Channel 2. NO is measured sequentially using a Thermo-Environmental Model 43 ctl NO/NOy analyzer and the difference between channels is interpreted as NHy. Output data from each instrument are acquired with 1-minute time resolution. Automated method of additions calibrations with NO and n-propyl nitrate are performed daily and gas replacement zeros are performed every 6 hours. Comparison of continuous and 24-hour integrated measurements generally show reasonable agreement (slope = 1.12 +/0.06; intercept = -0.24 +/- 0.13 ppb). Results for Yorkville (a rural-agricultural site) show that NH4+ concentrations exhibit a relatively narrow range over the period of record (0.1-7.8 ppb) and vary smoothly over time. The NH3 time series, in contrast, exhibits a much broader range of concentrations (0.2-47.8 ppb) punctuated by a large number of sharp spikes lasting from several minutes to several hours. Between NH3 spikes, concentrations of NH4+ and NH3 are generally quite similar. Average and median NH3 concentrations were 3.3 ppb and 1.9 ppb, respectively, while average and median NH4+ were 1.4 ppb and 1.4 ppb, respectively. Concentrations above 5 ppb accounted for more than 55% of the NH3 “dose” observed at Yorkville. Data will be used to investigate sources, diurnal patterns and relationships between NH3 and meteorology at both sites.

6B-3

AMBIENT NITROGEN DIOXIDE DETECTION BY CAVITY ATTENUATED PHASE SHIFT SPECTROSCOPY (CAPS), Paul L. Kebabian, Scott C. Herndon, ANDREW FREEDMAN, Center for Sensor Systems and Technology, Aerodyne Research, Inc., Billerica, MA

We present initial results obtained from an optical absorption sensor for the monitoring of ambient atmospheric nitrogen dioxide concentrations (0-200 ppb). This sensor utilizes cavity attenuated phase shift spectroscopy, a technology related to cavity ringdown spectroscopy. A modulated broadband incoherent light source is coupled to an optically resonant cavity formed by two high reflectivity mirrors. The presence of NO2 in the cell causes a phase shift in the signal received by a photodetector which is proportional to the NO2 concentration. The sensor, which employed a 0.5 m cell, was shown to have a sensitivity of 0.3 ppb in the photon (shot) noise limit. Improvements in the optical coupling of the LED to the resonant cavity would allow the sensor to reach this limit with integration times of 10 seconds or less (corresponding to a noise equivalent absorption coefficient of < 1 x 10-8 cm-1 Hz-1/2). Over a two day long period of ambient atmospheric monitoring, a comparison of the sensor with an extremely accurate and precise tunable diode laser-based absorption spectrometer showed that the CAPS-based instrument was able to reliably and quantitatively measure both large and small fluctuations in the ambient nitrogen dioxide concentration.

6B-4

MEASUREMENT OF NITRIC ACID AND AMMONIA WITH FABRIC DENUDERS,

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Nitric acid and ammonia are in a temperature-dependent equilibrium with ammonium nitrate and serious sampling errors are likely when either gas is collected on an adsorbent after particles are removed with a filter. For accurate sampling, diffusion denuders have been developed to remove the gases while allowing the particles to pass. While these diffusion denuders have been shown to be the method of choice for collecting nitric acid and ammonia in the atmosphere, they are generally expensive and require coating by a skilled technician. A simple fabric material used as a diffusion denuder has been shown to be an effective and inexpensive method to collect these species. Cotton fabric with size of 100 µm spaced on centers of 250 µm has been shown to efficiently remove gaseous species when coated with a suitable adsorbent. With a 47mm diameter denuder the collection efficiency at 10 l/min is over 90%. Two such denuders are therefore used in series for high collection efficiency. Ammonia was collected on a fabric coated with a solution of phosphoric acid while nitric acid was collected on sodium chloride coated fabric denuders. The coated substrates can be loaded directly into a standard filter holder and can be extracted after sampling using standard filter extraction techniques. This approach allows direct denuder sampling with no additional capital costs over filter sampling and simplifies the coating and extraction process. The ammonia and nitric acid measurements were in good agreement when compared to the results from a collocated long pathlength, folded optics FTIR system. The low cost of this approach compared with other types of denuders may encourage more measurements of these air pollutants. With a larger database available, the environmental and health affects of these species may be better assessed.

6C-1

NATURAL AND TRANSBOUNDARY POLLUTION INFLUENCES ON VISIBILITY DEGRADATION IN THE UNITED STATES,

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We use a global 3-D coupled oxidant-aerosol model (GEOS-CHEM) to quantify natural and transboundary pollution influences on visibility degradation in the United States, and to assess the implications for the EPA Regional Haze Rule (RHR). The model is evaluated extensively with frequency distributions of aerosol concentrations and visibility degradation measured at the IMPROVE network of sites. We examine in particular the ability of the model to simulate the spread in the frequency distributions, which is a critical metric for application of the RHR. Model results show that transboundary transport of pollution, including transpacific transport of sulfate from Asia, makes the RHR aspiration of natural visibility in federal class I areas unachievable through domestic controls only. Transboundary pollution also affects significantly the schedule of emission reductions under Phase I implementation of the RHR (2004-2018). Satellite (MODIS) and ground-based (AERONET) measurements of aerosol optical depth confirm the model simulation of transpacific transport of sulfate pollution. In particular, we show that Asian dust events over the western U.S. are accompanied with a substantial Asian pollution enhancement. Sulfur is exported from Asia in the model mostly as SO2, which escapes precipitation scavenging. The resulting sulfate is acidic and highly hygroscopic, magnifying its contribution to visibility degradation.

6C-2

IMPLICATION OF THE BRAVO SOURCE ATTRIBUTION RESULTS FOR REGIONAL HAZE CONTROL STRATEGIES, BRET SCHICHTEL, William Malm, Michael Barna, Kristi Gebhart, National Park Service, Fort Collins, CO

The Regional Haze Rule is a national air quality program designed to reduce haze in our national parks and wilderness areas (class I areas) to natural conditions by 2064. Haze is primarily the result of fine particles which can exist in the atmosphere for multiple days and transported thousands of kilometers. Therefore, sources over a broad region can contribute to haze. This is recognized in the Regional Haze Rule which encourages multiple States, through Regional Planning Organizations (RPO), to work with each other on control strategies to resolve visibility impairment in a given class I area. Due to errors in modeling and source apportionment analyses, it is not possible to examine the contribution of all individual sources. Instead, a small number of source regions are used, with their size generally increasing with distance from the class I areas. This arrangement can lead to misleading results. A large distant source region could have equal contribution to haze as a smaller nearby source region. However, the total emissions of the large source region may also be larger and the contribution per emission rate, or haze contribution efficiency, would not be equal. For example, the recent BRAVO study apportioned the particulate sulfate to Big Bend NP in Texas during July - October, 1999 from 5 source regions: Texas (17%), eastern U.S. (30%), western U.S. (7%), Carbón power plants, in Mexico (20%) and other Mexican sources (18%). The parenthetical values are the source regions' contributions to Big Bend's sulfate. Texas and Carbón have similar average contributions, but Carbón is located only 225 km from Big Bend and its SO2 emissions are 20% of those in Texas. Therefore, Carbón emissions are ~4 times more efficient at contributing sulfate to Big Bend than Texas'. Similarly, Texas' SO2 emissions are 8 times more efficient than those in the eastern U.S. Consequently, less absolute SO2 reductions are likely needed in Texas than in the eastern U.S. for commensurate reductions in Big Bend's sulfate concentrations. In the presentation, the BRAVO source attribution results will be used to further explore the question of the efficiency of a source's contribution to Big Bend's sulfate on low, average and high haze days. In addition, the potential contributions from near and more distant sources on class I areas in the Colorado Plateau will be explored though a plume particle dispersion model.

6C-3

CARBON-14 ANALYSIS OF PM 2.5 AEROSOLS AT 5 IMPROVE SITES, Graham Bench, Stewart Fallon, Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, CA; WILLIAM MALM, National Park Service, Atmospheric Science (CIRA), Colorado State University, Fort Collins CO; Charles McDade, Crocker Nuclear Laboratory, University of California, One Shields Avenue, Davis, CA

The impact of aerosol particulate matter of mean mass aerodynamic diameter <= 2.5 um (PM 2.5 aerosols), on health, visibility, and compliance with EPA's regional haze regulations is a growing concern. Techniques that can better characterize particulate matter are required to better understand the constituents, causes and sources of PM 2.5 aerosols. Measurement of the 14C/C ratio of the PM 2.5 aerosols, the absence of 14C in fossil carbon materials and the known 14C/C levels in contemporary carbon materials allows use of a two-component model to derive contemporary and fossil carbon contents of the particulate matter. Such data can be used to estimate the relative contributions of fossil fuels and biogenic aerosols to the total aerosol loading. Here, we report measurements carried out on the radiocarbon-to-total carbon ratio of aerosols of mean mass aerodynamic diameter <= 2.5 um collected using total suspended particulate Hi-vol aerosol samplers on quartz fiber filters from June 1 to Aug 30 2004. Aerosols were sampled at the following IMPROVE (Interagency Monitoring for Protection Of Visual Environments) sites: Brigantine National Wildlife Refuge, New Jersey; Mount Rainier National Park, Washington; Puget Sound, Washington; Great Smoky Mountains National Park, Tennessee; Proctor Maple Research Facility, Vermont. Individual filters were exposed to aerosols for six consecutive days. Each week, the sampling began at midnight Tuesday night/Wednesday morning and ended at midnight the following Monday night/Tuesday morning. When possible the aerosol carbon loading (ug/m3) as well as the 14C/C ratio of the PM 2.5 aerosols sampled by each filter was determined. Using a two-component model the fraction of the carbon on each filter that was derived from contemporary carbon and fossil carbon was determined from the 14C/C ratio using Accelerator Mass Spectrometry. The contemporary and fossil aerosol loading varied across the five sites and suggests different percentages of carbon source inputs for the 5 sites. The most "urban" site, Puget Sound typically had the highest fossil carbon aerosol-loading component. This is not completely unexpected considering its distance from an urban center. The more remote sites (Mount Rainier National Park, Washington; Great Smoky Mountains National Park, Tennessee; Proctor Maple Research Facility, Vermont) had lower fossil carbon aerosol-loading components that implied a higher fraction of contemporary carbon in the PM2.5 aerosols. Data from the Great Smoky Mountains National Park, Tennessee and the Proctor Maple Research Facility, Vermont indicated that variation in the total carbon loading almost completely arose from variation in the contemporary carbon loading. This is not unexpected considering their distance from urban centers. Finally, although, the carbon aerosols at Brigantine may be influenced by nearby Atlantic City the total carbon loading at Brigantine appeared to be primarily dominated by variation in the contemporary carbon loading with the fossil carbon loading relatively unchanged. The data from the more remote sites suggest contemporary carbon aerosols tend to dominate those from fossil carbon. This suggests that control of anthroprogenic sources of fossil carbon aerosols may result in little reduction in carbonaceous aerosol loading at the more remote sites.

6C-4

CHARACTERISTICS OF FINE PARTICULATE MATTER AND ITS IMPACT ON VISIBILITY IMPAIRMENT AT TWO URBAN SITES IN SEOUL AND INCHEON, KOREA,

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In order to investigate the causes of fine particulate pollution and visibility degradation in the Seoul area, extensive aerosol chemical and optical monitoring had been conducted at two urban sites, Junnong, Seoul and Yonghyun, Incheon during several intensive monitoring periods from August 2002 to August 2004. Light extinction, scattering, and absorption coefficients were measured simultaneously with a transmissometer, a nephelometer, and an aethalometer, respectively. Continuous measurements of aerosol chemistry and size distribution were also made with an EC/OC carbon analyzer and an on-line ion monitor and an ambient aerosol particulate profiler. Mean light extinction budget for five major aerosol components: ammonium sulfate, ammonium nitrate, fine carbonaceous particles (EC+OC), fine soil, and coarse particle was estimated based on the aerosol chemistry data and compared with the results of aerosol optical measurement. Impact of air mass characteristics on the fine particulate matter and visibility degradation in the Seoul metropolitan area was also analyzed.

7PA-1

FIELD EVALUATION OF A HIGH-VOLUME DICHOTOMOUS SAMPLER,

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This study presents the field evaluation of a high-volume dichotomous sampler that collects coarse (PM10-2.5) and fine (PM2.5) particulate matter. The key feature of this device is the utilization of a round nozzle virtual impactor with a 50% cutpoint at 2.5 mm to split PM10 into its coarse and fine fractions at a very high flow rate. The high-volume dichotomous sampler operates at a total flow rate of 1100 lpm with major and minor flows of 1000 and 100 lpm, respectively. The virtual impactor was characterized in the Particle Instrumentation Unit of the Southern California Particle Center and Supersite (SCPCS), with ambient aerosols before it was put into its current configuration. Furthermore, to evaluate its performance, the virtual impactor was connected to a 100 lpm virtual impactor (2.5 mm cut point) in series, and ambient aerosols were measured using an aerodynamic particle sizer (APS, Model 3320, TSI Inc). By connecting the two virtual impactors in series, concentration enrichment of 150 times ambient was achieved. The high-volume dichotomous sampler was then collocated with a MOUDI (Micro Orifice Uniform Deposit Impactor, Model 110, MSP Corporation, Minneapolis, MN) and a dichotomous PM10 Partisol sampler (Model 2025, R & P) at University of Southern California in Los Angeles. The MOUDI and the high-volume sampler agreed well, with an average ratio (N = 19) of high-volume to MOUDI measured coarse PM concentration being 0.84 ± 0.08. Similarly, good agreement was also observed between the high volume dichotomous sampler and the Partisol (Ratio of the high-volume to Partisol is found to be 0.86 ± 0.1). In addition to time integrated coarse PM mass measurements, filter and impaction substrate samples were analyzed for inorganic ions (nitrate and sulfate), elemental carbon (EC) and organic carbon (OC) and will also be compared as part of further investigation in this study. The ultimate goal of this study was to demonstrate the feasibility of using this high-volume dichotomous sampler as an effective system to collect simultaneously sufficient coarse and fine mass samples for improving the sensitivity for organic aerosol speciation and the measurement of potentially toxic compounds and to allow for comprehensive standard chemical analysis over short time intervals as may be desired from one filter set for source apportionment studies or other data analysis and modeling efforts. Disclaimer: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official agency policy.

7PA-2

MULTIYEAR EVALUATIONS OF PMCOARSE BY DIFFERENCE UTILIZING LOW AND HIGH VOLUME SAMPLERS AND COLLOCATED 50 DEGC TEOMS,

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Existing PMc by difference data is being used by regulators to help shape the future of the PMc standard. PMc by difference has been calculated by subtracting PM-2.5 from PM-10 from all available PM-2.5 and PM-10 data on the EPA AQS database. This paper examines the PMc determined in New York from data collected in 2002 and 2003 by three PM-10 measurement methods (TEOM, Reference High Volume and low volume samplers) and two PM-2.5 measurement methods (TEOM and FRM). The resulting PMc data is highly dependant on the sampling methodology used to obtain PM -2.5 and PM-10 ambient concentrations. High volume and 50 DegC TEOM samples tend to retain a smaller proportion of volatile components of the ambient matter; while low volume PM-10 and the PM-2.5 FRM samples retain a higher proportion of volatile matter. This is demonstrated by examining the seasonal bias that results from looking at PMc collected by different methods. Ambient concentrations of PM -10 are currently being monitored with three different methods in New York State; High Volume FRM instruments manufactured by Wedding and Associates, FEM TEOM instruments and low volume FRM PM-2.5 instruments that have been converted to PM-10. Two of these three methods are Reference methods for PM-10 while the third was proposed, approved and recently rescinded as a reference method. As demonstrated by comparisons of the data collected by these three different methods, the apparent concentration of PM-10 is highly dependant on the method used to collect this data. This is also evident when PM-10 data is compared to FRM PM-2.5 data. PM-10 data is important to State Agencies because the bulk of emissions permits that include PM are based on monitored ambient and source PM and PM-10 concentrations. It is not clear how States will handle the proposed change from a PM-10 to a PMc standard from a regulatory or a monitoring perspective. Differences among these monitoring methods will have implications for the future of the PM-10 NAAQS standard as well as the development of a NAAQS for PMc.

PMc: ambient particulate matter with an aerodynamic diameter in the size fraction from 2.5 through 10 microns.
TEOM: Rupprecht and Patashnick 1400AB Tapered Element Oscillating Microbalance.

7PA-3

FINE PARTICULATE MATTER MASS MEASUREMENTS AT THE ST. LOUIS – MIDWEST SUPERSITE,

JASON HILL, Jay Turner, Washington University, St. Louis, MO; Kevin Goohs, Thermo Electron, Franklin, MA

A battery of semicontinuous mass monitors has been operated at the St. Louis – Midwest Supersite core monitoring location in East St. Louis, IL, since its inception in April 2001. This site features a wide dynamic range of aerosol and environmental conditions (e.g. high wintertime nitrate concentrations, large organic carbon plumes of a few hours duration, periods of sustained high humidity). The initial deployment included an Andersen Continuous Aerosol Mass Measurement System (CAMMS) and a MetOne beta attenuation monitor (BAM) - operated by the Illinois Environmental Protection Agency - with various inlet heater configurations. This presentation will briefly summarize lessons learned from the first three years of fine mass measurements, which also included extensive filter mass data from Harvard Impactors and an FRM. Subsequently, this presentation will focus on the current fine mass measurement configuration which includes CAMMS, MetOne BAM, and a pre-production version of the TEI Synchronized Hybrid Ambient Real-time Particulate (SHARP) monitor. The SHARP monitor incorporates a high sensitivity light scattering photometer whose output signal is continuously referenced to the time-averaged measurements of an integral beta attenuation mass sensor. Emphasis will be placed on characterizing the SHARP, including its collocated precision and sensitivity to environmental parameters. The current performance evaluation is supported by: daily 24-hour integrated FRM mass measurements; semicontinuous measurements for fine particulate matter sulfate, nitrate, organic carbon, elemental carbon, and electrical charge integral; and on-site meteorology.

7PA-4

CONTINUOUS PM2.5 MASS MEASUREMENTS AT THE PITTSBURGH AIR QUALITY STUDY SUPERSITE,

ANN WITTIG, CUNY at City College of New York, New York NY; Allen Robinson, Spyros Pandis, Carnegie Mellon University, Pittsburgh PA

A Tapered Element Oscillating MicroBalance with sample equilibration (Series 1400a TEOM with SES, Rupprecht & Patashnick Co., Inc.) was evaluated during the Pittsburgh Air Quality Study (PAQS) from July 2001 to August 2002 (Wittig et al., 2004). The TEOM uses gravimetric methods to measure PM2.5 mass on a 5-minute average basis. The SES uses Nafion diffusion dryers to dehumidify the ambient air and aerosols before collection onto a 30 deg-C filter surface. This diffusion-based approach allows the TEOM to dehumidify the aerosol stream without use of heat, minimizing the loss of semi-volatile aerosol species that can occur when the instrument is operated in the typical configuration without a SES and with a filter maintained at 50 deg-C. The TEOM with SES was evaluated throughout the study period using collocated measurements of fine particle mass. Integrated 24-hour samples of PM2.5 were collected using a Partisol FRM Sampler (Model 2000 FRM, Rupprecht & Patashnick Co., Inc.) and Dichotomous Sampler (Series 241 Dichot, Thermo Anderson), both operated according to EPA guidelines. The filters collected by these samplers were conditioned and weighed in a humidity and temperature-controlled environmental chamber. Throughout the study period, the TEOM with SES performed reliably and with excellent data capture. Its measurements were well correlated to the collocated measurements, with major axis regression R2 values greater than 95%. Overall, the instrument bias was approximately +5% relative to the FRM and Dichot sampler measurements. However, on individual days during the winter or when the 24-hour average fine particle mass was less than 20 μg/m3, this bias was greater. The near-continuous TEOM with SES measurements have been used in conjunction with temporally resolved measurements of aerosol-bound water and inorganic and organic aerosol species to investigate the closure of the mass balance at the PAQS Supersite (Rees et al., 2004). Wittig AE, Anderson N, Khlystov AK, Pandis SN, Davidson C, Robinson AL, 2004. Pittsburgh Air Quality Study Supersite Program Overview. Atmospheric Environment 38:3107-3125. Rees S, Robinson A, Khlystov A, Stanier C, Pandis SN, 2004. Mass Balance Closure and the Federal Reference Method for PM2.5 in Pittsburgh Pennsylvania. Atmospheric Environment 28:3305-3318.

7PA-5

COMPARISONS OF MEASUREMENTS FOR SULFATE AND NITRATE IN THE AMBIENT ATMOSPHERE,

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The measurements of sulfate and nitrate by RP8400, dichotomous, and RP2000 were compared in this study, where the filters collected by dichotomous and RP2000 were analyzed by ion chromatography. The sampling inlets for RP8400 and RP2000 were of the same model. The durations for RP8400 were 10 minutes and those for dichotomous and RP2000 were six hours; thus, the comparisons among the three methods were for six-hour duration. Four RP8400s were used to evaluate the variations for RP8400 itself and the differences among the RP8400s were generally within 10% of average values for both sulfate and nitrate. The averages of the four RP8400s were used in the following comparisons. The correlation coefficients of nitrate were 0.88, 0.39, and 0.86, respectively, for the RP8400 vs. RP2000, RP8400 vs. dichot, and RP2000 vs. dichot; and those of sulfate were 0.80, 0.89, and 0.95, respectively. The relationships of linear regression analyses for nitrate were RP8400 = 0.446*RP2000 +0.66, RP8400 = 0.135*dichot+3.52, and dichot = 0.878*RP2000+1.42; those for sulfate were RP8400 = 0.620*RP200+3.06, RP8400 = 0.690*dichot+2.54, and dichot = 0.968*RP2000-0.38. For the paired comparisons, the differences for (RP2000-RP8400), (dichot-RP8400), and (dichot-RP200) were 4.95, 4.13, and 0.18 ug/m3, respectively, for nitrate and those for sulfate were 1.59, 0.99, and -0.87 ug/m3, respectively. Note that the average concentrations for nitrate and sulfate for RP2000 were 10.1 and 12.3 ug/m3. Therefore, good agreements between manual methods by RP2000 and dichotomous were observed, especially for sulfate with the average differences less than 5%. The concentrations measured by RP8400 were generally less than those by RP2000 and dichotomous. The differences were greater for nitrate than those for sulfate.

7PA-6

MEASUREMENTS OF WATER-SOLUBLE AEROSOL AND GASES DURING PITTSBURGH AIR QUALITY STUDY,

ANDREY Y. KHLYSTOV, Duke University, Department of Civil and Environmental Engineering, Durham, NC; Bhavesh V. Shah, Satoshi Takahama, Spyros N. Pandis; Carnegie Mellon University, Department of Chemical Engineering, Pittsburgh, PA

A modified Steam-Jet Aerosol Collector was operated within the Pittsburgh Air Quality Study during the period of July 2001 – September 2002. The modification consisted in operating the sampler without a denuder, such that both PM2.5 aerosol and water-soluble gases (HNO3, NH3, HCl) were collected simultaneously, providing the “total” (gas + aerosol) budget of the species. A comparison with collocated denuder-filter pack system has shown that the modified SJAC performed well during the campaign. However, during winter months, high SO2 concentrations were found to interfere with sulfate measurements. We have developed a method for correcting the sulfate measurements using an aqueous-phase chemistry model. The model was evaluated against measurements over two months on selected days, five days in January 2002 and six days in July 2002. The results of the simulations of the oxidation of sulfur dioxide to sulfate showed that the model reproduced well the experimental data provided by the SJAC and the corresponding measurement artifact. Additional simulations were performed to test the sensitivity of the sulfate production in the system to various parameters. Our results can be also used to correct the artifact sulfate in particle-into liquid samplers in the case of a denuder break-through at high SO2 concentrations. The measured concentrations of inorganic aerosol components and their gaseous precursors were used to assess the sensitivity of PM2.5 mass to changes in concentrations of sulfate and ammonia using the thermodynamic GFEMN model. The response of PM2.5 mass to the concentrations of these components was found to be non-linear. The modeling has indicated that availability of ammonia may affect effectiveness of PM control strategies. For example, in winter, when there is sufficient ammonia to form ammonium nitrate, ammonia reduction may be more effective on the per-mass basis than a reduction of sulfate.

7PA-7

IN-SITU CONCENTRATION OF SEMI-VOLATILE AEROSOL USING WATER-CONDENSATION TECHNOLOGY,

ANDREY KHLYSTOV, Duke University, Durham, NC; Qi Zhang, Jose-Luis Jimenez, University of Colorado, Boulder, CO; Charlie Stanier, University of Iowa, Iowas City, IA; Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA; Manjula R. Canagaratna, Aerodyne Research Inc., Billerica, MA; Philip Fine, Chandan Misra, Constantinos Sioutas, University of Southern California, Los Angeles, CA

The effect of concentrating semi-volatile aerosols using a water-condensation technology was investigated using the Versatile Aerosol Concentration Enrichment System (VACES) and the Aerodyne Aerosol Mass Spectrometer (AMS) during measurements of ambient aerosol in Pittsburgh, PA. It was found that the shape of the sulfate mass-weighed size distribution was approximately preserved during passage through the concentrator for all the experiments performed, with a mass enhancement factor of about 10 to 20 depending on the experiment. The size distributions of organics, ammonium and nitrate were preserved on a relatively clean day (sulfate concentration around 7 ug/m3), while during more polluted conditions the concentration of these compounds, especially nitrate, was increased at small sizes after passage through the concentrator. The amount of the extra material, however, is rather small in these experiments: between 2.4% and 7.5% of the final concentrated PM mass is due to “artifact” condensation. An analysis of thermodynamic processes in the concentrator indicates that the extra particle material detected can be explained by redistribution of gas-phase material to the aerosol phase in the concentrator. The analysis shows that the condensation of extra material is expected to be larger for water-soluble semi-volatile material, such as nitrate, which agrees with the observations. The analysis also shows that artifact formation of nitrate will be more pronounced in ammonia-limited conditions and virtually undetectable in ammonia-rich conditions.

7PA-8

CONTINUOUS PM2.5 SULFATE AND CARBON AT ADDISON IN RURAL NEW YORK STATE: MEASUREMENTS FROM AND EVALUATIONS OF THE THERMO 5020 SULFATE AND THE SUNSET LABS OCEC INSTRUMENTS,

JAMES SCHWAB, Olga Hogrefe, Kenneth Demerjian, Atmospheric Sciences Research Center, University at Albany - SUNY, Albany, NY; Oliver Rattigan, Dirk Felton, New York State Department of Environmental Conservation, Division of Air Resources, Albany, NY; Vicent Dutkiewicz, Liaquat Husain, Wadsworth Center, New York State Department of Health, Albany, NY

One important goal of the PMTACS-NY supersite program is the deployment and evaluation of PM measurement instrumentation with an eye for technology transfer and eventual routine deployment by states and local agencies in addition to research institutions. PM2.5 mass, sulfate, and carbon are particularly important target species for our location in the eastern U.S.; and our experience with continuous (and semi-continuous) PM2.5 mass monitors is the subject of a separate paper in this conference. Together, sulfate and carbon, along with their associated species, constitute a majority of the PM2.5 mass for most locations, and specifically, for Eastern U.S. locations like our site in Addison, NY. We have deployed a Thermo 5020 continuous sulfate particulate analyzer and a Sunset Labs semi-continuous OCEC analyzer at our research site in Addison, NY beginning in July of 2004. These instruments compliment the existing wide array of gas phase and PM measurement instruments at the site. We will present data from this site, laboratory evaluations of the Thermo 5020 sulfate analyzer, comparisons of both sulfate and carbon instruments with filter data; and more detailed comparisons of the sulfate and carbon data with other continuous and semi-continuous instruments during a month-long summer intensive. The filter comparisons will provide a benchmark for the continuous methods, and for sulfate, should allow a determination of the method accuracy. Given the difficulties and uncertainties associated with sampling and analysis of carbon, it may be overstating the case to contend that filter comparisons can establish accuracy, but such comparisons are an important step toward standardizing and understanding the measurement process. Laboratory tests of the sulfate analyzer will establish the conversion and detection efficiency for several sulfate compounds present in the lower atmosphere.

7PA-9

ANALYTICAL ADVANCES IN ANALYSIS OF SIZE AND TIME RESOLVED CONTINUOUS SAMPLES FROM ROTATING DRUM IMPACTORS,

THOMAS A. CAHILL, Steven S. Cliff, Michael Jimenez-Cruz, Lee Portnoff, DELTA Group, UC Davis, CA, Kevin D. Perry, Meteorology Dept, U. Utah, UT, Graham Bench, Center for Accelerator Mass Spectrometry, Lawrence Livermore NL, CA, and Roger Miller, Physics Dept, State University of New York, Potsdam, NY

Detailed information on aerosols by size and composition has long been known to be essential for understanding particulate sources, transport, transformation, and impacts on welfare, especially light scattering and visibility. In addition, in the past decade, new information has become available on the impacts of very fine (0.25 to 0.1 μm) and ultra-fine (< 0.1 μm) particles on human health. This includes the impact of highly toxic components of PM2.5 mass, such as diesel exhaust, in the < 0.25 μm mode. Detailed information on aerosols as a function of time is equally important, as dramatic differences in aerosol concentration occur in time scales less then the standard 24 hr average, especially in strong diurnal patterns but also in plume impacts of the worrisome very fine aerosols. Both problems have been long addressed via particle collection versus size on rotating drum impactors (Lundgren, 1967) in which a multi-stage inertial impactor collects particles on substrates on slowly rotating drums. However, lack of analytical options and cost of analyzing continuous samples from these units has usually limited their use to problems in which particle size was essential, largely atmospheric optics. The UC Davis DELTA Group was formed in 1997 to address these analytical problems, and in the past 7 years has developed a suite of compatible and non-destructive analytical techniques that now allows wider utilization of rotating drum impactors while achieving IMPROVE-pioneered 'integral redundancy' in data quality assurance. In this report, we describe the 7 operational methods used by the DELTA Group and its national and international associates; color photography and computer scanning of samples, mass (in air) by soft beta transmission, optical transmission and reflection by pulsed IR-vis-uv spectroscopy. mass (in vacuum) by scanning transmission ion microscopy (STIM) and hydrogen by proton elastic scattering analysis (PESA), often done together, and all elements sodium and heavier by synchrotron induced x-ray fluorescence (S-XRF). Additional methods, especially organic speciation by time of flight mass spectroscopy, are under development. While the first four methods can be done inexpensively at the home institution, STIM, PESA, and S-XRF all rely on access to accelerators, possible at CAMS, Lawrence Livermore NL, and the Advanced Light Source, Lawrence Berkeley NL, although other options are available in both cases. We present applications of these techniques including the Fresno Super-site, the 16 site NSF ACE-Asia program, aerosols from the World Trade Center fires, and visibility studies at Yosemite NP. We gratefully acknowledge developmental funding and support from the Vice Chancellor of Research, UC Davis, and DOE Advanced Light Source, Beam Line 10.3.1, Lawrence Berkeley NL and The Center for Accelerator Mass Spectrometry, LLNL.

7PA-10

MEASURING LIGHT ELEMENTS BY RUTHERFORD BACK SCATTERING TECHNIQUE, OMAR F. CARVACHO, Carlos M. Castaneda, Lowell L. Ashbaugh, Robert G. Flocchini and Jaspinder P. Singh, Janice C.S. Lam. University of California, Crocker Nuclear Laboratory, Air Quality Group. One Shields Avenue, Davis, California 95616

Crocker Nuclear Laboratory (CNL) routinely performs X-Ray Fluorescence (XRF) analysis of aerosol samples to measure the concentration of elements with Z>10. In order to allow a more complete reconstruction of the aerosol mass, we recently began testing a Rutherford Back Scattering (RBS) technique to measure carbon (C) and oxygen (O) from air samples on Teflon filters using the 76-inch cyclotron at Crocker Nuclear Laboratory. The detector used for the measurements is a surface barrier detector (Si) placed at 150 degrees to the beam axis. The detector has an area of 150mm2, collimated to 18.1mm2 (4.8mm in diameter), and is located 160mm from the sample. The thickness of the detector will stop the 4.5Mev proton beam. Its measured resolution is better than 25Kev. The objective of this presentation is to show the basic energies and channels used to measured C and O using this technique. For standards, we used a 0.3 mg/cm² carbon foil and a 6µm thick Mylar sheet with known areal density to establish the basis of the measurements. As a practical test, we analyze two Teflon (C2F4) filters: one as a blank to subtract the amount of C in the substrate, and the other impregnated with UREA (NH2CONH2).

7PA-11

MEASUREMENTS OF AMBIENT AMMONIA USING A TUNABLE DIODE LASER ABSORPTION SPECTROMETER AND AN AQUEOUS SCRUBBING-CHEMICAL DERIVATIVE TECHNIQUE AT URBAN AND RURAL NEW YORK LOCATIONS, YONGQUAN LI, Kenneth Demerjian, Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY 12203; Jian Hou1, Xianliang Zhou1,2. 1Department of Environmental Health and Toxicology, School of Public Health, State University of New York at Albany, and 2Wadsworth Center, New York State Department of Health, Albany, NY

Abstract A tunable diode laser absorption spectrometer (TDLAS) was deployed during the PMTACS-NY Supersite winter 2004 intensive field campaign at Queens College in New York City and 2004 summer Pinnacle State Park (Addison, NY) field campaign to measure ambient ammonia along with a collocated aqueous scrubbing-chemical derivative technique. These field measurements and follow up laboratory comparison studies with a certified ammonia standard have been used to evaluate the performance of the two methodologies. High time resolved (1 hertz) TDLAS ambient ammonia measurements performed at Queens College from January 11 to February 8 showed high variability, with NH3 concentrations ranging from below the detection limit (0.07 ppb) to maxima of 61 ppb with a mean value of 0.76 ppb over the winter campaign. A bimodal diurnal pattern believed to be associated with traffic exhaust, was observed over the measurement period. Ammonia measurements at Pinnacle State Park, performed from July 30 to August 12 reported values below the detection limit to maxima of 9.29 ppb with a mean value of 0.47 ppb. A diurnal pattern in ammonia concentration with a noontime peak value was observed at Pinnacle State Park. This pattern may be attributable to the thermal release of ammonia from one or more sources (e.g. ammonia-based fertilizers, biogenic species or ammonium nitrate aerosols). The field and laboratory instrument comparison studies of the two ammonia measurement methods showed reasonable correlations in the laboratory, but poor agreement over the field measurement campaigns.

7PA-12

ANALYSIS OF GAS-PHASE AMMONIA MEASUREMENTS MADE DURING THE 2002 ATLANTA AEROSOL NUCLEATION AND REAL-TIME CHARACTERIZATION EXPERIMENT (ANARCHE) AT THE 1999 ATLANTA SUPERSITE,

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Ammonia (NH3) is a gas-phase precursor of ammonium nitrate and ammonium sulfates, compounds that are important constituents of airborne fine particulate matter. Gas-phase ammonia measurements were made at the location of the 1999 Atlanta Supersite Experiment in July and August of 2002 during the Atlanta Aerosol Nucleation and Real-time Characterization Experiment (ANARChE) with two different Chemical Ionization Mass Spectrometer (CIMS) techniques. One used a low-pressure flow tube reactor (Georgia Institute of Technology, GT) and the other an atmospheric pressure ionization technique (NOAA-Aeronomy Laboratory). Both CIMS instruments used protonated ethanol cluster ions to detect NH3. The protonated ethanol cluster ions react selectively and sensitively with NH3 to form stable cluster ions. The instruments used independent PFA Teflon sampling inlets. Instrumental backgrounds were determined every fifteen minutes by scrubbing NH3 from ambient air using silicon phosphates that release phosphoric acid when exposed to ambient levels of humidity. Standard addition calibrations were performed every one to two hours using NH3 permeation devices. Though final data was reported for both instruments as 1-minute averages, the sampling intervals were 1s for the NOAA-AL instrument and 4s for the GT instrument. The 1s and 4s resolution data were used to evaluate the time response of each inlet and suggest that both pass the majority of a multiple ppbv calibration on the order of seconds. Fast-time response measurements, such as these, were critical for studying the influence of ammonia on short-lived nucleation events. The sensitivity for the NOAA-AL CIMS was 1 Hz per pptv of NH3 for 100 kHz of reagent ion while the GT CIMS sensitivity was 30 Hz per pptv of NH3 for 5 MHz of reagent ion. The instrumental background varied over days and typically ranged from 0.1 to 1 ppbv. Over the period of concurrent measurements the two instruments showed reasonable agreement within estimated uncertainties though at times the NOAA-AL CIMS data were higher. Correlations between the 1-minute NOAA-AL data and the 1-minute GT data yielded a slope of 1.013 with an intercept of 0.37 ppbv and an r2 of 0.72. The ambient measurements ranged from 0.4 to 13 ppbv and showed a diurnal profile possibly due to automobile traffic. The gas-phase NH3 observations along with fine particulate (PM2.5) inorganic composition (i.e., NH4+ and SO42-) measurements made by the GT Particle Into Liquid Sampler (PILS) instrument were used to determine if thermodynamic equilibrium exists between the gas and fine particulate phases. Preliminary observations made over the city of Atlanta in August of 2004 by a similar airborne CIMS instrument aboard the NOAA WP-3D during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study will also be discussed.

7PA-13

AN APPROACH TO MONITOR ULTRAFINE EC WITH A MODIFIED ACPM,

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An Ambient Carbonaceous Particulate Monitor (ACPM, R&P 5400) was modified in an attempt to monitor the concentration of elemental carbon in ultrafine aerosol particles. The adaptation consisted of placing a filter in one of the two sampling lines of this dual-channel instrument. In this line aerosols of all sizes are collected, while the standard impactor-sampler in the other line collects (only) particles larger than 0.14 um. The concentration of elemental carbon in particles smaller than this cut-off diameter is derived by difference. The performance of ACPM's was tested using a second instrument and the correlation in the data was better than 0.95 (R2) for a period similar to that in a subsequent campaign and at lower concentrations. The measuring campaign took place at a suburban site in Amsterdam, the Netherlands, during the winter season. The location was at a distance of more than 1 km from major thoroughfares. On average 35% of the elemental carbon was in particles smaller than 0.14 um, as deduced from the difference in concentration in the two lines of the instrument. Alternative explanations for the difference in concentration obtained via the two sampling lines can be excluded on the following grounds. The difference in the signals in the two channels could be a difference in the extent of oxidation: This extent should be a function of loading, which is not the case here. Another reason could be that less material is collected by the impactor, due to rebound of the presumably solid EC particles. However, Such bounce does not occur in the Netherlands because of the stickiness of the other co-depositing aerosol material, as evidenced in earlier published studies on the possible bounce of local aerosol in cascade impactors. The ACPM also provided data on ultrafine OC. The average concentration in the impactor line was less than half of that in the filter line. However this difference is to a large extent caused by an adsorption artefact as shown by tests in which the aerosol was removed at the inlet. Teflon-filters were used in these tests because they remove particulate carbon, but have negligible adsorptivity for adsorbing gaseous compounds. The conclusion of this study is that the modified ACPM for measuring ultrafine EC seems promising, but that a similar approach for OC is not warranted.

7PA-14

EVALUATION OF COARSE, FINE AND ULTRAFINE PARTICLES AS PART OF AN AIR POLLUTION EXPOSURE STUDY,

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Ambient PM is a complex mixture that includes bioactive and toxic compounds of natural and anthropogenic origin, several of which have been theorized to be causative or contributory to the adverse effects of PM inhalation. Numerous epidemiological studies have reported associations between exposure to ambient levels of particulate matter (PM) and various indices of cardiopulmonary morbidity and mortality. However, despite a decade of intensive study, much about the PM health effects problem is still not understood. Various physicochemical properties such as particle size and surface area have also been linked to the health effects of PM, and it has been hypothesized that toxicity of PM is related to particle size, proposing that smaller particles are relatively more potent than larger ones in producing health effects. Ultrafine particles (UF; particles less than 0.1 um) have been specifically associated with a worsening of pre-existing pulmonary diseases and have been shown to have a higher acute inflammatory potency than larger particles in animal instillation studies. The current and proposed National Ambient Air Quality Standard limits on permissible PM levels are set on a mass basis for two particle size fractions, particles between 2.5 and 10 um and for those less than 2.5 um in mean aerodynamic diameter. However, UF particles present a special problem in the regulation of ambient PM because they normally contribute relatively little to the total PM mass. Thus, it is possible that current and proposed regulation of ambient PM on a mass basis fails to adequately control levels of UF particles. In an effort to provide additional insight on this issue, the U.S. Environmental Protection Agency (EPA) has initiated an experimental assessment of the health effects of exposure to UF particles concentrated from ambient air in healthy young adult human subjects. A key component of this study is evaluation of subjects exposed to PM in a specially designed aerosol chamber. As part of this effort, it is necessary to document the size distribution and composition of the PM introduced to the chamber. A discussion on the design of the EPA particle concentrator chamber is provided along with methods used to collect and analyze coarse, fine and UF particles.

7PA-15

ULTRAFINE PARTICLE SIZING RESULTS AND PERFORMANCE OF AN ELECTRICAL AEROSOL DETECTOR AND PORTABLE CONDENSATION PARTICLE COUNTER DURING THE PMTACS-NY 2004 WINTER INTENSIVE,

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Two relatively new particulate instruments, the Electrical Aerosol Detector (EAD, Model 3070A, TSI Inc.) and a portable Condensation Particle Counter (CPC3007, Model 3007, TSI Inc.) were deployed during the PMTACS-NY 2004 Winter Intensive. Both field performance and particle counts from the portable, isopropanol-based CPC3007 are compared to those from a co-located, standard butanol-based CPC (CPC3022, Model 3022, TSI Instruments). The short lifetime of the isopropanol reservoir (ca. 6 hours) limited the relative usefulness of the CPC3007 for such a long-term ambient measurements. However, the portability of the unit proved useful in evaluating the effect of potential particulate sources located near the sampling site. The relative magnitude of particle counts and response to particle events for the CPC3007 and CPC3022 is also evaluated. The EAD measures total aerosol length of particles (mm/cc), and by combining this parameter with particle number counts from a CPC (#/cc) the mean of the particle size distribution can be calculated. Data from both the CPC3007 and the CPC3022 is used to calculate the mean of the particle size distribution from the EAD data. These results are then compared with the means of the particle size distributions determined by two co-located Scanning Mobility Particle Sizers equipped with nano-DMAs (SMPS, Model 3936 series, TSI, Inc.).

7PA-16

FIELD EVALUATION OF A TSI MODEL 3034 SCANNING MOBILITY PARTICLE SIZER IN NEW YORK CITY: WINTER 2004 INTENSIVE CAMPAIGN,

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A new “single box” Scanning Mobility Particle Sizer (TSI SMPS Model 3034) was deployed and operated during a period of four weeks as a part of a PMTACS-NY Winter 2004 intensive study in Queens College, New York City. The SMPS 3034 is an alternative to a conventional multi-component TSI SMPS and houses a Differential Mobility Classifier and butanol-based Condensation Particle Counter in one cabinet. The SMPS 3034 operates at 1 l/min sample flow rate (4 l/min sheath flow rate) and measures size distributions within a 10 nm - 487 nm size range. One size scan is produced every 3 min. Two conventional TSI SMPSs (with a Nano- and a Long Differential Mobility Analyzers) and a Condensation Particle Counter (TSI CPC Model 3022) were operated side-by-side with the SMPS 3034. Results from those measurements will be used to evaluate performance of the SMPS 3034.

7PA-17

REAL-TIME MEASUREMENT OF PARTICLE SIZE DISTRIBUTION AND CONCENTRATION IN DIFFERENT ENVIRONMENTS-THE EFFECT OF HUMIDITY ON AMBIENT AIR PARTICLES,

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Introduction Outdoor Air ELPI (OELPI, Electrical Low Pressure Impactor, Dekati Ltd) is a modified version of the standard ELPI instrument developed for ambient air particle size distribution and concentration measurements. The instrument operating range is 7nm – 10um, and the sample flow rate of the OELPI is increased from 10 to 30lpm to improve the instrument sensitivity and measurement accuracy also in low concentration areas. The OELPI unit itself measures particles in real-time, without any sample conditioning. This can lead to higher mass concentration values than those given by reference methods, such as gravimetric filter samples, since OELPI detects both the dry particle mass and the particle bound water. The amount of absorption of water depends on the hygroscopic properties of the particles. In some occasions the particle bound water may contribute more to the PM2.5 mass concentration than the actual dry particle mass. OELPI was chosen as a tool to study the effect of humidity on ambient air particles due to its ability to also measure the wet particle concentration. The unit was used during several different measurement campaigns, in different relative humidities, with and without a particle dryer to estimate the effect of humidity on particle size distribution and total PM2.5 concentration. The operation of the particle sample dryer was evaluated in previous studies and it was proven to be suitable for particle sample drying with the high OELPI sample flow rate. To verify the OELPI data, the results were compared to those given by other instruments, and a good correlation was found when the OELPI sample was dried. Results A clear effect of the humidity on particle mass concentration and size distribution was found. In environments with high humidity OELPI without the dryer (wet concentration) showed higher mass concentration values than other methods that removed water from the sample (dry concentration). The difference between the wet OELPI result and the dried mass results followed consistently the changes in the relative ambient humidity that was also monitored continuously. A slight decrease in the particle size was also found. Chemical analysis of the total collected particle mass was performed to determine the total amount of hygroscopic compounds. In the future studies, the size classified impactor samples collected with the OELPI can be further analysed to study the effect of hygroscopicity in the different particle size classes in more detail. Acknowledgements The authors would like to acknowledge Sergey Grinshpun, Dainius Martuzevicius and Tiina Reponen from the University of Cincinnati, and Timo Mäkelä and Risto Hillamo from the Finnish Meteorological Institute for their contribution in this work. References Hillamo, R., Mäkelä, T., Kerminen, V.-M., Keskinen, J. and Marjamäki, M. 2002. Use of Electrical Low Pressure Impactor (ELPI) in Atmospheric Aerosol Studies. Eurotrac-2 symposium. Garmisch-Partenkirchen, Germany, March 2002. U.S.EPA. 2003. Air Quality Criteria for Particulate Matter. Ojanen, J. 2003. The Effect of Relative Humidity on PM2.5 Mass Concentration. Master of Science Thesis, Tampere University of Technology.

7PF-18

SOURCE APPORTIONMENT OF BALTIMORE AEROSOL FROM COMBINED SIZE DISTRIBUTION AND CHEMICAL COMPOSITION DATA, DAVID OGULEI, Philip K. Hopke, Liming Zhou, Clarkson University, Potsdam, NY, J. Patrick Pancras, Narayanan Nair, John M. Ondov, University of Maryland at College Park, MD

The basic assumption in receptor modeling is that the measured ambient particulate matter (PM) concentrations are linear sums of constant profiles from all of the contributing sources. The assumption of constant profiles implies that for the same location and transit time, it is expected that the size distribution is stationary or quasi-stationary such that the number concentrations measured at the receptor site have a linear relationship with both the number and mass contributions from all sources. If indeed this relationship exists, then it should be possible and useful to combine size distribution and chemical composition data into a single multivariate analysis so as to obtain a better understanding of source-receptor relationships for the environmental situation under consideration. This problem has been recently explored for the Pittsburgh Supersite (Zhou et al., J. Geophys. Res., in press, 2004). In this work, Partial Least Squares (PLS) is used to investigate the relationship (linearity) between number concentrations and PM2.5 mass concentrations of all chemical species measured at the Baltimore Supersite. The size distribution and chemical composition data are then simultaneously analyzed by Positive Matrix Factorization (PMF). The resolved sources are identified using information from number and mass contributions from each source (source profiles) as well as meteorological profiles. Complete results from this work will be presented.

7PF-19

ATMOSPHERIC AEROSOL OVER TWO URBAN-RURAL PAIRS IN ALABAMA AND GEORGIA: CHEMICAL COMPOSITION AND POSSIBLE SOURCES, Wei Liu, Yuhang Wang, Armistead Russell and Eric S. Edgerton

Positive matrix factorization (PMF) was used to infer the sources of PM2.5 observed at four sites in Mississippi and Florida. One pair of urban and rural sites in each state is used to examine the regional and urban influence on PM2.5 concentrations in the Southeast. Eight factors were resolved for the two urban sites and seven factors were resolved for the two rural sites. Spatial correlations of factors were investigated using the square of correlation coefficient calculated from the resolved G factors. Fourier transform was also used to define the temporal characteristics of PM2.5 factors at these sites. Factors were normalized by using aerosol fine mass concentration data through multiple linear regression to obtain the quantitative factor contributions for each resolved factor. Common factors include: (1) secondary sulfate dominated by high concentrations of sulfate and ammonium with a strong seasonal variation peaking in summer time; (2) nitrate and the associated ammonium with a seasonal maximum in winter; (3) “coal combustion/other” factor with presence of sulfate, EC, OC, and Se; (4) soil represented by Al, Ca, Fe, K, Si and Ti; and (5) wood smoke with the high concentrations of EC, OC and K. The motor vehicle factor with high concentrations of EC and OC and the presence of some soil dust components is found at the urban sites, but cannot be resolved for the two rural sites. Among other factors, two similar industry factors are found at the two sites in each of the same state. For the wood smoke factor, different seasonal trends are found between urban and rural sites, suggesting different wood burning patterns between urban and rural regions. For the industry factors, different seasonal variations are also found between urban and rural sites, suggesting that this factor may come from different sources or a common source may impact these two sites differently. Generally, sulfate, soil, and nitrate factors at the four sites showed similar chemical composition profiles and seasonal variation patterns reflecting the regional characteristics of these factors. Regional factors such as sulfate, nitrate, soil have predominantly low frequency variations while local factors such as coal combustion, motor vehicle, wood smoke, and industry factors have high frequency variations in addition to low frequency variations.

7PF-20

PSEUDO-DETERMINISTIC MULTIVARIATE RECEPTOR MODEL FOR USE WITH HIGHLY-TIME RESOLVED DATA, JOHN M. ONDOV, Joseph Patrick Pancras, Seung Shik Park, Gregory Beachley, Melissa Rury, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

A new pseudo-deterministic hybrid receptor model (PDRM) is being developed for determining emission rates of pollutants emitted from individual sources using highly time-resolved ambient air data collected at a fixed receptor site. Such data contains inherent information on the location of sources, e.g., observed plume width varies with distance and, more importantly, combined with meteorological data, it reveals the direction of the source, when the time-scale for changes in wind direction are comparable to the measurement periods. In PDRM the basic factor model terms are interpreted as the products of pollutant (i) emission rates (ERi)) and meteorological dispersion factors (X/Qj) for stationary sources (j) known to be located in the modeling domain. A Gaussian plume model is used to constrain solutions to the X/Qjs by appropriately filtering contributions from sources according to their angle with respect to prevailing winds. Model outputs are i) average ERis for each source for the modeling period, ii) time dependent X/Qjs, and iii) resolved source contributions to ambient concentrations. Accurate solutions are obtained with data collected in <24 hours. The model has been used with great success using 30-min element and SO2 concentrations collected during the Tampa Bay Regional Aerosol Chemistry Experiment (BRACE) in May 2002 wherein emission rates for SO2 were predicted to within 6% of values derived from continuous emission monitors. More recently, the data has been applied to Pittsburgh, i.e., a domain characterized by rough terrain. Herein, we describe the model, discuss its sensitivity with respect to constraint ranges and methods of application, and present preliminary results for data collected at the Baltimore Supersite, a highly complex urban source area.

7PF-21

PM10 AND PM2.5 SOURCE APPORTIONMENT AT THREE URBAN BACK GROUND SITES IN THE WESTERN RUHR-AREA, GERMANY, H. FISSAN Process and Aerosol Measurement Technology, University Duisburg-Essen,47057 Duisburg, Germany. T.A.J. Kuhlbusch, U. Quass, K.G. Schmidt IUTA e.V., Department Airborne Particles, Bliersheimerstr. 60, 47229 Duisburg, Germany. M. Koch ECOFYS, 50933 Cologne, Germany. P. Bruckmann, U. Pfeffer North Rhine-Westphalia State Environmental Protection Agency , 45133 Essen, Germany

INTRODUCTION PMX mass concentrations, chemical compositions as well as particle number size distributions were measured at one central site in Duisburg for one year to obtain information on sources and their contribution to PM10 and PM2.5, respectively (184 days valid data). PM10 and PM2.5 were measured with HiVol-samplers (DIGITEL DHA 80) and additionally PM10 and PM2.5 online with two TEOM®. Two additional urban back ground sites in the main wind direction to the central site (up and down wind), Kaldenhausen (southwest) and Styrum (northeast; overall 16 km apart) were included in the measurement program for two intensive field campaigns (together 78 days valid data). PM10 and PM2.5 were measured at the satellite stations with HiVol-samplers (DIGITEL DHA 80) or LowVol-samplers (LVS 3, Derenda). PM10 online data were also recorded at those two stations. A special cascade impactor (3 stages: 0.2-1 μm; 1-2.5 μm, and 2.5-10 μm) for sampling directly onto carriers for subsequent TXRF-analysis was employed in addition to the manual filtration samplers. Overall 24 different elements and chemical compounds were analysed. METHODS The available data on PM10 and PM2.5 including the chemical composition were investigated with Positive Matrix Factorisation (PMF; Paatero 1997) to derive information on sources and source processes influencing the mass concentration. Generally, PMF gives two matrices; a) an F-matrix, which contains the information on the composition of the factors (source profiles) and b) a G-matrix, which contains the factor loadings. The prior matrix is the main matrix for source identification since it gives the chemical composition of the factor. The latter matrix with the factor loadings gives the mass concentration of the factors for each analysed sample, in our case each 24 hour sample. PMF resolved 8 factors for PM10. The data set comprised the chemical composition data of the three investigated sites. These factors were subsequently analysed in various steps. A correlation study of the factor loadings between the three investigated sites based on 78 samples was conducted to identify the source areas of the factor. A super regional source area can be assumed for a given factor if slopes and correlation coefficients are all close to 1. Correlation coefficients (R^2) between 0.3 and 0.8 with varying slopes indicated mixed source areas from local to super regional scale. Even lower regression coefficients indicated local sources. That information was used to corroborate the source identification based on the F-matrix. A further analysis was based on wind direction and backward trajectories. That information also gives valuable indication of specific source areas and hence can be used a) to identify the source areas and b) to corroborate the source identification. PMF was also employed on the separate PM2.5 data set. 6 factors were resolved in this case. A comparison of the PMF-factors for PM2.5 with the PMF-factors for PM10 gives important information a) on the robustness of a factor, b) indication on the quality of the resolution of a factor, and c) on the PM2.5 to PM10 mass ratio. CONCLUSIONS The results of the PMF source apportionment for the central urban background site in Duisburg showed that about 30% of the PM10 mass concentration is attributed to traffic. The next important factors identified were Secondary 1 (mainly ammonium nitrate, 23%) and Secondary 2 (mainly ammonium sulphate; 14%). Minor contributions were allocated to wind erosion (earth crust), sea salt and two local sources linked to industry. Wind direction analyses combined with the identified source factors gave clear indication on the local source areas and, linked with PMF, a quantitative estimate of their contributions. The PM2.5/10 ratios between similar factors obtained with PMF for the PM2.5 and the PM10 data set show a reasonable range for the sources with a ratio around 1 for the Secondary 1 factor and e.g. a low ratio of around 0.35 for the sea salt / Holland factor. PMF source apportionment results for PM10 and PM2.5 will be presented for three urban background stations and the source factors discussed in more detail.

ACKNOWLEDGEMENTS We thank the Ministry of Environmental Protection of North Rhine-Westphalia for the support of this work. We also thank all co-workers involved in this study for their enthusiasm and help. REFERENCES Paatero, P. (1997). Least squares formulation of robust non-negative factor analysis, Chemometrics and Intelligent Laboratory systems, 37, 15-35. Quass, U., Kuhlbusch, T.A.J., Schmidt, K.G., Fissan, H. (2004). Quellenzuordnung für die Feinstaubfraktion, report to Ministry of Environmental Protection of North Rhine-Westphalia, IUTA-Bericht LP 10/2004

7PF-22

COMPARISON BETWEEN MEASURED AND ESTIMATED UNCERTAINTIES FOR SOURCE APPORTIONMENT OF THE SPECIATION TRENDS NETWORK DATA, EUGENE KIM, Philip K. Hopke, Clarkson University, Potsdam, NY; Shelly Eberly, US EPA, Research Triangle Park, NC

Beginning in 2000, the U.S. EPA established the Speciation Trends Network (STN) to characterize PM2.5 (particulate matter less than 2.5 micrometers in aerodynamic diameter) composition, to estimate long-term trends in constituents of PM2.5, and to support source apportionment modeling for identification and quantification of sources impacting areas out of attainment of the PM2.5 national ambient air quality standards. One of the regularly used source apportionment models, Positive Matrix Factorization (PMF), uses estimated uncertainties in concentration data to resolve sources and their respective contributions. Concentrations with larger uncertainties have less influence on the resulting solution. A general uncertainty, basically based on a percentage of concentration and method detection limit, may be specified for each species. Alternatively, uncertainties may be specified for each sample for each species, if such detail is available. The objective of this study is to examine the impact to PMF results of using general uncertainties versus sample-species specific uncertainties for two selected STN sites, one in Elizabeth, New Jersey and the second in Baltimore, Maryland. Comparisons between the source compositions and source contritubions will be made. The results of this study will be important for several reasons. First, it is important to understand whether sample-species specific uncertainties provide better results. Second, if the results are better if using sample-species uncertainties, then it will be critical to develop and maintain sample-species specific uncertainties for source apportionment modeling. Disclaimer: Although this work was reviewed by EPA and approval for publication, it may not necessarily reflect official Agency policy.

7PF-23

SOURCE IDENTIFICATION OF PM2.5 MEASURED AT THE SPECIATON TRENDS NETWORK SITES IN NORTHERN NEW YORK AREA, EUGENE KIM, Philip K. Hopke, Clarkson Universtiy, Potsdam, NY

Ambient PM2.5 (particulate matter less than 2.5 micrometer in aerodynamic diameter) data collected at the three U.S. EPA Speciation Trends Network (STN) monitoring sites located in northern New York area were analyzed by positive matrix factorization (PMF): Burlington, VT, Buffalo, NY, and Rochester, NY. Particulate carbon was analyzed using the thermal optical method that divides carbon into total OC and total EC. The number of samples at each site ranged from 87 to 271 samples and 26 to 35 variables measured between 2001 and 2003 were used in these analyses. Estimated OC blank values were subtracted and the estimated error structures for the STN data were successfully applied. PMF provided reasonable source separations maximizing the utilization of existing STN data. PMF identified six to seven sources including secondary sulfate aerosol, secondary nitrate aerosol, motor vehicle, airborne soil as main sources. Potential source directions, weekday/weekend variations, and seasonal trends were examined.

7PF-24

DETECTION AND CHARACTERIZATION OF A SMOKE PLUME FROM CANADIAN FOREST FIRES DURING THE PITTSBURGH SUPERSITE EXPERIMENT,

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Over a three day period (July 6th – 8th, 2002) during the Pittsburgh Supersite experiment, a smoke plume, originating from a series of boreal forest fires in the Canadian province of Quebec, was detected and measured by a single particle mass spectrometer, RSMS-3, and a high-volume sampler. Temporal variation in the distribution of single particle positive ion mass spectra amongst the identified particle classes was monitored over a two month period (June-July) to isolate the detection of these fire events. The fraction of particles belonging to the EC/OC/K class, a single particle fingerprint for biomass burning, increased by a factor of eight on July 7th and by a factor of four on July 6th and July 8th, as compared to the other days. Hourly resolution of the EC/OC/K class indicates that the bulk of the plume rapidly mixed to the surface early in the morning on the 7th and then slowly dissipated over the next 48 hours. Similarly, 24 hour total PM2.5 and PM10 mass concentrations of potassium, determined by ICP-MS analysis of high-volume samples, were monitored over the same two month period. Results from this analysis indicate an approximate four fold increase in potassium mass concentrations on July 7th and 8th, for both PM2.5 and PM10, as compared to the average of the other days. Images taken by MODIS on the Terra satellite not only confirm the existence of this smoke plume over the Pittsburgh area, and most of the east coast, but can also trace its origin back to the Quebec wild fires. Back trajectories, calculated using HYSPLIT, reveal strong subsidence of the air mass from mid-tropospheric transport altitudes at the point of injection (Quebec, July 5th) to the top of the boundary layer at the point of detection (Pittsburgh, July 6th-8th), as well as validate the path from source to receptor. In addition, RSMS particle size data for the temporally resolved classifications of both positive and negative ion single particle mass spectra was used, in conjunction with SMPS data and back trajectories, to capture certain aspects of the physical and chemical evolution of the observed particles during this event.

7PF-25

IDENTIFICATION OF SOURCES OF ATMOSPHERIC PM AT THE PITTSBURGH SUPERSITE: RSMS III AND FILTER-BASED POSITIVE MATRIX FACTORIZATION,

NATALIE PEKNEY, U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, PA; Cliff Davidson, Carnegie Mellon University, Pittsburgh, PA; Keith Bein and Anthony Wexler, University of California, Davis, Davis, CA; Murray Johnston, University of Delaware, Newark, DE

During the Pittsburgh Air Quality Study (PAQS), July 2001-September 2002, two collocated samplers measured elemental composition in ambient particulate matter (PM). One sampler, the RSMS III, counted single particles classified by size and chemical composition. Possible sources of PM detected by the RSMS were identified using information on the wind direction as well as particle size and composition. The second technique involved collection of PM on cellulose filters using a high-volume (hi vol) sampler, followed by microwave-assisted digestion and analysis by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Positive Matrix Factorization (PMF) was used to identify possible source categories. A MOUDI sampler also operated during the PAQS to obtain filter-based size distribution measurements of PM. Several dates of MOUDI filters were selected for microwave-assisted digestion and analysis by ICP-MS. Comparing the two sets of data is complicated by the different time resolution of each (45 minute resolution with the RSMS, 24 hour averages with the filter sampling), as well as the different size cuts (1.5 µm for the RSMS, 2.5 µm for the hi vol filter sampling). The strengths of each method are combined to arrive at best estimates of source types for various elements, and thus obtain information on the contribution of each source type to ambient PM in Pittsburgh. Some findings include: 1. The RSMS individual particle data weighted by d3 (where d = particle diameter) are consistent with the ICP-MS data for bulk elemental composition and size distributions obtained from the MOUDI filter analysis. 2. The lack of Ti in RSMS data compared with appreciable Ti concentrations in the ICP-MS data reflects a significant amount of Ti between 1.5 and 2.5 µm. 3. Ni and V are from both coal and oil; although these two sources cannot be separated using the PMF analysis, differences in characteristics of individual particles can separate these sources using the RSMS data. 4. Mo and Cr are found together in both a PMF source category and in individual particles identified by RSMS. 5. Zn, Fe, and Mn are found in a single source category by PMF, but the RSMS data suggest that these elements are not associated with the same particles. 6. Ga is associated with coal combustion, and is found in abundance according to both the ICP-MS and RSMS data. However, elements associated with Ga in the RSMS data include Si, K, and Fe. The coal combustion source category for PMF includes Ni, Cu, V, and As along with Ga. Reasons for the differences are explored. 7. Na, K, Zn, and Pb are found together in individual particles according to the RSMS. These elements are associated with a number of difference source categories based on the PMF results. 8. Pb is associated with most individual particles detected by the RSMS; in contrast, Pb is found in its own source category with no other elements according to the PMF results. Reasons are explored. 9. The ICP-MS shows an abundance of Se, although this is not seen in the RSMS data. Reasons are explored.

7PF-26

IDENTIFYING SOURCES OF PM2.5 IN PITTSBURGH USING PMF AND PSCF,

NATALIE PEKNEY, U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, PA; Cliff Davidson, Carnegie Mellon University, Pittsburgh, PA; Liming Zhou and Philip Hopke, Clarkson University, Potsdam, NY

The concentrations of atmospheric fine particulate matter in Pittsburgh, Pennsylvania are largely affected by regional transport of PM2.5 as well as from local source emissions. Positive Matrix Factorization (PMF), a source-receptor model, was used with data collected during the Pittsburgh Air Quality Study (PAQS) to determine the most significant sources of PM2.5 in the Pittsburgh region, both for chemical composition of PM2.5 from sources as well as the contribution of each source to the ambient PM2.5 levels. Ambient data used include concentrations of particulate sulfate, nitrate, organic carbon, elemental carbon, trace elements, and several organic carbon species. Eleven sources were identified, including secondary sulfate, secondary nitrate, wood combustion, coal combustion, vehicle emissions, steel production, specialty steel production and processing, crustal material, a selenium source, a cadmium source, and a lead source. The potential source contribution function (PSCF) analysis combines the PMF-modeled source contributions with air parcel back trajectories to locate the source areas and to evaluate each source as being regional or local. For sources determined to be local, a conditional probability function (CPF) estimates the most probable direction of the source such that the local source can be identified.

7PF-27

SOURCE IDENTIFICATION FOR FINE AEROSOLS IN THE MAMMOTH CAVE NATIONAL PARK,

WEIXIANG ZHAO, Philip K. Hopke, Department of Chemical Engineering, and Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY

A relationship between human mortality/morbidity and particulate matter concentrations has been observed. Also, the evidence for a significant role of traffic-related emissions on public health has been reported. Thus how to effectively identify the possible sources including the diesel/gasoline emissions becomes more and more important. In this study, Positive Matrix Factorization (PMF) was applied to the chemical composition data of the ambient PM2.5 matters collected at the Mammoth Cave National Park, a rural IMPROVE site in Kentucky. The objectives were to identify the aerosol sources in that area and to demonstrate the feasibility of using carbon fractions to resolve the motor vehicle sources in the upper Mid-western rural area. Eight individual carbon fractions, four organic carbons (OCs), pyrolyzed organic carbon (OP) and three elemental carbons (ECs) were provided to the analysis. Nine sources including the well distinguished gasoline emission and diesel emission were identified. Also, the back trajectories indicated the crustal factor in this study was likely caused by Saharan dust storms in the summer. The apportionment of nine sources was: gasoline emission (6.7%), diesel emission (3.1%), summer secondary sulfate (49.0%), winter secondary sulfate (0.6%), OP-rich secondary sulfate (16.2%), secondary nitrate (2.8%), Intercontinental dust plus soil (4.9%), wood smoke (13.6%), and aged sea salt (3.2%). The results of this study will help regularize the pollution control strategies in rural areas of Kentucky and the upper mid-western US.

7PF-28

INVESTIGATION OF SOURCES FOR AMBIENT AEROSOLS IN INDIANAPOLIS, IN, WEIXIANG ZHAO, Philip K. Hopke, Department of Chemical Engineering, and Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY

One of the aims for EPA to establish the Speciation Trends Network (STN) is to characterize PM2.5 chemical composition in urban areas and to investigate sources of the ambient aerosols in urban areas. The purpose of this study is to identify the sources of the ambient aerosols in Indianapolis, IN. The samples for analysis were collected from 12/10/2000 to 11/14/2003. STN data have a number of measurement problems. Organic carbon (OC) in the STN data was not blank corrected. The STN uses the samplers from five different manufacturers at different sites and the different XRFs have different MDLs and reported errors. The STN did not provide uncertainty values to most species measurements. These problems make the study on STN data a challenge. The data pretreatment for these three problems will be discussed in detail. Positive Matrix Factorization (PMF) is applied to determine the source profiles and contributions. The results of this study will help regularize the pollution control strategies for the Indianapolis urban area. The results will also be compared with the source resolutions of other STN sites, which may help provide a panorama of aerosol sources of different urban areas.

7PG-29

MODELING THE FORMATION OF PHOTOCHEMICAL AIR POLLUTION IN SÃO PAULO, BRAZIL: A CASE STUDY, Odón R. Sánchez-Ccoyllo, Maria de Fátima Andrade, Leila D. Martins, RitaYuri Ynoue, Department of Atmospheric Sciences, Institute of Astronomy Geophysics and Atmospheric Sciences, University of Sao Paulo - Brazil

The high episode of surface ozone concentrations in the Metropolitan Area of Sao Paulo (MASP), Brazil, for the period of 13 -15 March 2000 was modeled with the California Institute of Technology (CIT) three-dimensional photochemical model. For this period, four different emission scenarios were used as input. The base case scenario was simulated using the CETESB (State Environmental Protection Agency) emission inventory for the year 2000. The second scenario considered the implementation of an air pollution control program by motor vehicles, called PROCONVE. The third scenario consisted of the hypothetical situation in which the PROCONVE was not implemented but the vehicles were submitted to new technologies. The fourth case consisted of a scenario without PROCONVE and with vehicles with an older (before 1989) technology. Impacts of these different emission inventories on ozone concentrations and other pollutants such as Carbon Monoxide (CO), Nitrogen Oxide (NOx) and non-methane hydrocarbon (NMHC) were analyzed. More elevated troposphere ozone concentrations were predicted for emission inventory scenario without PROCONVE (technology before 1989) and emission inventory scenario without PROCONVE but with technologic evolution than the emission inventory scenario with PROCONVE. This study is important concerning the evaluation of air quality improvement in the mega-city of São Paulo.

7PG-30

A PARTICULATE MATTER AIR QUALITY FORECAST MODELING SYSTEM FOR THE NORTHEAST U.S. – COMPARISONS WITH PMTACS-NY FIELD MEASUREMENT CAMPAIGNS AND PM NETWORK DATA, C. CAI, C. Hogrefe and K. L. Demerjian. Atmospheric Sciences Research Center, University at Albany, Albany, NY

An air quality forecast modeling system (AQFMS) used to demonstrate reliable 24-hr oxidant air quality forecasts for the Northeast United States, has been further developed to consider the prediction of PM air quality in the region. The AQFMS operates with forecasted meteorological fields derived from an ETA type mesoscale meteorological model (University of Athens). The meteorological fields are used to drive the Comprehensive Air Quality Model with Extensions (CAMx), a photochemical air quality simulation model. This prototype system has recently been upgraded to incorporated SMOKE emission module, National Emission Inventory 1999 and CAMx4.0 with the secondary formation mechanism for sulfate, nitrate and organic particulate matter since 2004. Archived meteorological forecasts for July 2001, have been used to re-run the forecasts with updated emissions generated by the SMOKE emission model and the modified chemical mechanism within the CAMx model. In this paper we evaluate the performance of the PM air quality forecast modeling system using data collected during summer (July 2001) and winter (January-February 2004) intensive field campaigns of the PMTACS-NY EPA “Supersite” program. Model comparisons of PM mass, PM chemical speciation and associated precursor gases measured during these campaigns are presented. In addition, representative monthly means of PM mass and composition for each season in 2003 are compared across the modeling domain using measurement data from IMPROVE and STN monitoring sites.

7PG-31

THE DYNAMICS OF MULTICOMPONENT ATMOSPHERIC NANOPARTICLES, JAEGUN JUNG, Peter Adams, Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA

Atmospheric aerosols are multicomponent particles with sizes ranging from a nanometer to tens of microns. New particles are introduced to the atmosphere either by direct emission or in-situ formation (nucleation). Nucleation is not well understood because of both experimental and theoretical difficulties. We describe the development and evaluation of a computationally efficient new multicomponent aerosol dynamics model that simulates the full aerosol size distribution starting at 0.8 nm. The model uses a two-moment sectional algorithm that describes both the aerosol number and mass distributions. Three chemical components, sulfate, ammonium and non-volatile organics are currently simulated. The model is evaluated first against analytical solutions of the coagulation and condensation equation and then against ambient measurements from the Pittsburgh Air Quality Study. The model is able to reproduce the details of a real nucleation event. The model can also explain why freshly nucleated particles smaller than 33 nm are quite acidic during at least some of the nucleation events. The low CPU time requirements of the model make it suitable for incorporation in three-dimensional chemical transport models.

7PG-32

COMPARISON OF OBSERVED AND CMAQ SIMULATED ATMOSPHERIC CONSTITUENTS IN THE SOUTHEAST IN THE PROJECTED FACTOR SPACE,

Wei Liu, Yuhang Wang, Amit Murmur, Armistead Russell and Eric S. Edgerton

In this paper, in order to evaluate the performance of CMAQ model, observation and CMAQ simulated gas and particle data were compared on the basis of SEARCH observations in Atlanta, Birmingham, Centreville, and Yorkville for 2000 and 2001. For most of the species, the simulated data from the rural sites are agreed better with the measured data than that from the urban sites. The SO2 and NOy fraction data were analyzed to investigate the accuracy of CMAQ gas/particle portioning mechanism. The results imply that the CMAQ transfer mechanisms of gas phase SO2 to particle phase sulfate is not as sensitive as the real situation and that CMAQ apportioned too much gas phase N to particle phase nitrate during cold seasons. In addition to the direct comparison, PMF was used to evaluate the simulation results from CMAQ model. For both of the simulation data and the observational data, five factors were resolved from each of the four sites (two urban sites and two rural sites). The resolved factors include (1) secondary sulfate, (2) secondary nitrate, (3) mixed factor characterized by EC, OC, and CO, (4) SO2, and (5) motor vehicle factor characterized by EC, OC, CO, NO and NOy. The correlations between the resolved factor contribution from the observations and the simulated data were investigated. The seasonal variations for sulfate and nitrate factors were similar between the simulated and the observational data. On average, for all of the four sites, CMAQ sulfate factor contribution concentrations were well simulated and CMAQ nitrate factor was overestimated especially in winter. The correlation is very poor for the motor vehicle and mixed factors between the CMAQ and the observation data, reflecting source errors in the CMAQ model.

7PG-33

PROTECTION OF BUILDINGS AGAINST ACCIDENTAL OR DELIBERATE RELEASES OF HAZARDOUS BIOLOGICAL AND RADIOLOGICAL PARTICULATES,

D. NORRIS, S.M. Ghiaasiaan, S.M. Jeter, Georgia Institute of Technology, Atlanta, GA

The protection of residential and commercial buildings against accidental or deliberate releases of hazardous biological and radiological particulates is expected to gain increasing importance in the future. This study is meant to establish a computational simulation-based methodology for the analysis of buildings, where the vulnerability to the spread, deposition, and inhalation of released hazardous particulates are simultaneously considered. The developed methodology will be based on three levels of analysis. At the first level, a two dimensional HVAC energy simulation of a commercial medical facility (Georgia Tech Student Health Center), using the state-of-the-art building code EnergyPlus, will calculate building heating, cooling, lighting, ventilating, and other energy flows at various building locations. In these computations, the biological activities of building residents will be accounted for, such as internal moisture loads. Subsequently the boundary conditions, such as convection heat transfer coefficients and nominal room air temperatures, are used in the second level of analysis. At the second level, detailed and local (room-scale) particulate transport patterns will be obtained using the computational fluid dynamics code FLUENT. The third level includes inhalation and dose calculations for various building locations, and these doses will be compared to regulatory limits. This three-level analysis can identify locations best fitted for early detection or shelter, and it can be used for devising simple defensive action plans based on short-term manipulations of the building HVAC and other systems that would mitigate the spread of particulates.

7PG-34

TRANSPORT DISPERSION AND DEPOSITION OF ONE MINUTE PARTICLE SIZE DISTRIBUTIONS BETWEEN 5 AND 560 NANOMETERS NEAR A MAJOR INTERNATIONAL TRADE BRIDGE CONNECTING THE U.S. AND CANADA: A MODEL COMPARISON WITH EXPERIMENTAL RESULTS, PETER JAQUES, Kambiz Nazridoust, Goodarz Ahmadi, Philip Hopke, Andrea Ferro and Timothy McAuley. Clarkson University; 5805 Biology; 8 Clarkson Avenue; Potsdam NY

The Peace Bridge Plaza Complex (PBC), located in Buffalo, New York, is the busiest U.S. - Canada border crossing in northeastern U.S.A. The PBC provides a line-source of typically constant commercial traffic of heavy diesel trucks, and prevailing wind trajectories transporting emitted particles into an adjacent residential community. To date, no known data characterizing the general air quality, nor the transport, dispersion and deposition of atmospheric particles from this line-source of mobile emissions has been reported in peer-reviewed literature. This study applies time- and size-resolved particle number concentrations measured in the area of the PBC to a Lagrangian particle tracking model. During the summer of 2004, housed in a mobile lab, an Engine Exhaust Particle Sizer™ (EEPS™; TSI Inc.) spectrometer measured particles from 5.6 to 560 nanometers every minute. The EEPS™ uses an “inside-out” differential mobility analyzer to measure concentrations of multiple particle sizes simultaneously. Wind data was gathered from both a meteorological tower less than 1 kilometer upwind of the PBC, adjacent to the shoreline of the Niagara River, and a portable system housed on the mobile lab. Particle number concentration measurements were made within a 1 kilometer area to the east of the PBC, which is predominantly downwind. The transport, dispersion and deposition of particulate pollutants near the Peace Bridge in the City of Buffalo are modeled using an unstructured computational grid of the Peace Bridge area and its vicinity and the wind flow is simulated. Experimentally measured data for wind speed is used in the analysis. A Lagrangian particle-tracking model is used for simulating the transport, dispersion and deposition of particulate emission from the motor vehicle exhaust on the bridge and in the Peace Bridge custom area. The pollutant transport model used accounts for the drag and Brownian forces acting on the particles, in addition to the gravitational sedimentation effects. For particulate emission in the size range of 0.01 to 50 um, the corresponding concentrations in different areas are evaluated and the deposition rates on various surfaces studied. For particles between 5 and 560 nanometers, the simulation results will be compared with the experimental data and discussed.

7PG-35

A SECOND-GENERATION MODEL OF THE FORMATION OF SECONDARY ORGANIC AEROSOL IN THE ATMOSPHERE, TIMOTHY LANE, Spyros Pandis, Neil Donahue, Carnegie Mellon University, Pittsburgh, PA

A Second-Generation Model of the Formation of Secondary Organic Aerosol in the Atmosphere Timothy Lane, Spyros Pandis, Neil Donahue Department of Chemical Engineering, Carnegie Mellon University ABSTRACT Secondary organic aerosol (SOA) is formed when condensable products produced from the oxidation of volatile organic compounds (VOCs) in the gas phase partition into the aerosol phase. SOA is an important component of atmospheric particulate matter, posing health hazards and contributing to global climate change. The goal of this research is to develop a state-of-the-science SOA model taking advantage of the results of recent laboratory studies. NOx (NO and NO2) has been shown to effect SOA concentrations; however, its effect is not yet well understood and the current SOA models are relatively insensitive to NOx levels. In this research, two condensable products were included in each VOC reaction using the yields and vapor pressures estimated from smog chamber experiments. The lumped biogenic VOC “species” was split into actual compounds and the biogenic emissions rate was split using estimated summertime monoterpene fluxes in the West Coast from Geron et al. [1]. Also, condensable products were added to the photooxidation of isoprene since Claeys et al. [2] provided evidence that the oxidation of isoprene may be a substantial source of SOA. Using the new SOA mechanism in the Secondary Organic Aerosol Model (SOAM), the updated model was applied to air pollution episodes in California (Summer 1987) and in Pittsburgh (July 2001). For California, simulations for the 24 trajectories, one for each hour of the day, were used to predict the 24-hour average SOA concentration and the contributions from each VOC. The SOA results were in agreement with the estimates from Turpin and Huntzicker [3]. The addition of SOA products to the photooxidation of isoprene did not significantly effect the overall SOA concentration but did produce 6% of the biogenic SOA. This new model predicts that SOA concentrations are also dependent on the NOx emissions and follow similar trends observed by Pandis et al. [4]. The SOA concentration is also dependent on the VOC emission rates. Decreasing the VOC emissions by 50% leads to a reduction of the predicted SOA by 55%. Also, decreasing the VOC emissions by 25% has a similar effect on total SOA as reducing the NOx emissions by around 90%. The results for Pittsburgh will also be discussed.

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7PG-36

SIMULATION OF THE ATMOSPHERIC AEROSOL SIZE/COMPOSITION DISTRIBUTION IN A THREE-DIMENSIONAL CHEMICAL TRANSPORT MODEL,

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Atmospheric pollutants have been implicated in the development of adverse effects on human, animal, and plant health, the formation of acid rain and acid fogs, visibility reduction, and influence on the energy balance of the planet. Models that accurately describe the physical and chemical atmospheric processes these pollutants undergo are necessary to determine how changing emissions will affect downwind airborne concentrations and how best to go about controlling air pollution. Improvements and additions have been made to ENVIRON's chemical transport model (CTM) CAMx (v. 4.02) to create a research grade CTM PMCAMx+ (v. 4.0). These improvements focus on the treatment of the aerosol and aqueous-phase processes. The first addition was a hybrid mass transfer approach to determine partitioning between the gas and aerosol phases for volatile and semi-volatile inorganic species. Here bulk equilibrium is assumed for fine particles, and mass transfer equations are solved for larger particles using the trajectory-grid approach (Gaydos et al., 2003). Second, to simulate the behavior of secondary organic aerosol (SOA) components and their interactions with inorganics, an SOA model was also integrated into PMCAMx+ (Koo et al., 2003). Finally, in an effort to describe cloud and fog processing of pollutants, a variable size resolution aqueous-phase chemistry module also was incorporated into the model (Fahey and Pandis, 2003). We will present an overview of our additions to PMCAMx+ and explore the accuracy and efficiency of these additions. The performance of PMCAMx+ will be evaluated with respect to data collected largely in 2001 at Pittsburgh and other supersites. References Fahey, K., and Pandis, S. (2003). Size-resolved aqueous-phase atmospheric chemistry in a three-dimensional chemical transport model. Journal of Geophysical Research 108, 4690 (doi:10.1029/2003JD003564). Gaydos, T., Koo, B., Pandis, S., and Chock, D. (2003). Development and application of an efficient moving sectional approach for the solution of the atmospheric aerosol condensation/evaporation equations. Atmospheric Environment 37, 3303-3316. Koo, B., Ansari, A., and Pandis, S. (2003). Integrated approaches to modeling the organic and inorganic atmospheric aerosol components. Atmospheric Environment 37, 4754-4768.

7PG-37

HOX BEHAVIOR IN THE WINTER URBAN ATMOSPHERE IN NEW YORK CITY,

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Hydroxyl (OH) and hydroperxy (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) winter 2004 intensive campaign in New York City. Much lower levels of OH and HO2 were observed in comparison to those in summer 2001 due to weak solar radiation and low ambient temperature in the winter. On average the maximum daytime mixing ratios were 0.06 pptv for OH and 0.8 pptv for HO2. Small levels of OH and HO2 were also observed at night, indicating the importance of OH oxidation in nighttime chemistry. A zero-dimensional box model based on regional atmospheric chemical mechanism (RACM) was used to calculate steady state OH and HO2 concentrations and to study HOx behavior in this urban environment. The model was constrained to the observed concentrations of O3, NOx, CO, SO2, HONO, HNO3 and VOCs. Detailed measurement-model comparison is made. HOx budget analysis shows that the main HOx sources were O3+alkenes reactions and photolysis of HONO and HCHO. Instantaneous O3 production and the formation rates of gas-phase HNO3 and H2SO4 are also discussed based on the observations.

8A-1

TOWARDS A GLOBAL AEROSOL PHENOMENOLOGY: CONTRASTING THE PHYICAL AND CHEMICAL CHARACTERISTICS OF AEROSOLS GLOBALLY, Jean-Philippe Putaud, JULIAN WILSON, Institute for Environment and Sustainability, Joint Research Centre, Ispra, Italy; Urs Baltensperger, Paul Scherrer Institute, Villigen, Switzerland; Wolfram Birmili, Institute for Tropospheric Research, Leipzig, Germany; Mario Cerquiera, University of Aviero, Portugal; Byoung-Cheol Choi, Korean Meterological Agency, Chung-Nam, Korea; Sarah Guibert, Michael Schultz, Laboratoire des Sciences du Climat et de l'Environnement, Gif-sur-Yvette, France; S. Gerard Jennings, National University of Ireland, Galway, Ireland; Anne Kasper-Geibl, Technical University of Vienna, Austria; Carrie Lillyman, Atmospheric Environment Service, Ontario, Canada; Willy Maenhaut, University of Ghent, Belgium; Bill Malm, Colorado State University, Fort Collins, CO; Noer Nurhyati, Meteorological and Geophysical Agency, Jakarta, Indonesia; Xavier Querol, University of Barcelona, Spain; Patricia Quinn, NOAA Pacific Marine Environmental Laboratory, Seattle, WA; Sjaak Slanina, Peking University, Peking, China; Kjetil Toreseth, Norwegian Institute for Air Research, Kjeller, Norway

Aerosols affect health, climate, regional acidification and visibility. Improved awareness of the similarities and differences in aerosol physical and chemical properties globally, is thus relevant for co-ordinating global policy responses to these problems. The European Aerosol Phenomenology reported by Putaud et al. (2004) and Van Dingenen et al. (2004), reported on these aspects in within Europe. We have initiated a follow up global study in order to answer the following basic questions: What are the main contributors to PM mass? What are the main contributors to light extinction by PM? What are the main contributors to PM number concentrations? and following from these, we will examine problems such as What are the proportions of these properties that are regionally as opposed to locally derived? and What are their sources? The study is identifying, cataloguing and assembling both long term data sets and informative shorter duration datasets from 1990 onwards, that of known quality and can be shown to be internally consistent. We are thus working with already published/ worked up data sets of two or more, of the following parameter classes: 1. At least one of: TSP, PM10, PM2.5 and PM1. 2. Chemical Speciation of PM masses. 3. Number Size distribution, 4. Optical Properties – (wavelength specific) light absorption and scattering We have defined a minimum set of meta-data required to establish comparability between different networks and measurement techniques, and have set as a minimum duration 1 month of data, continuous data (defined as >50% coverage) and 3 months (seasonal) data for periodic sampling data sets. We will use appropriate standardised data exchange formats for automated processing, NASA AMES 1001 in Europe, and we encourage the use of the NARSTO DES, elsewhere. Data contributors and users will have a dedicated web based forum to access the data and results of the analyses. We are particularly keen to involve regional experts in reviewing and analysing the data sets, through both formal and informal collaboration agreements as appropriate. The intended outcomes of the entire study would be a series of EU/WMO reports or monographs on the data evaluations and peer-reviewed publications detailing the principal results, together with the underlying data used in the study which would ideally be made available through the Global Atmosphere Watch World Data Centre for Aerosols. The presentation will report on the progress in the project.

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8A-2

INCORPORATING HEALTH AND ENVIRONMENTAL BENEFITS INTO SELECTION OF COMPLIANCE STRATEGIES, LAURAINE CHESTNUT, David Mills, Stratus Consulting Inc., Boulder CO

States, local air quality management districts, and private sector organizations face an array of standards and regulatory programs related to various types of particulate matter (PM) sources and aerosol and ozone precursors. These include the National Ambient Air Quality Standards (NAAQS) for PM and ozone, the regional haze rule, the acid rain program (Title IV), the prevention of significant deterioration (PSD) process, and others. These efforts are motivated by the desire to protect human health and environment, but there is nothing that assures that the regulated community’s pollution control expenditures are being allocated in a way that maximizes the potential health and environmental benefits. This paper presents a conceptual framework that regulatory agencies could use to choose among alternative control strategies that takes into account the benefits of different types and locations of emissions reductions. In other words, it shows how to get the biggest bang for the buck. For example, state and local decision makers have choices about the mix of control strategies they are going to use for meeting the requirements of the NAAQS during the State Implementation Plan (SIP) process. By focusing only on selecting the least-cost strategies for meeting the NAAQS requirements, they may be missing an opportunity to more effectively focus their resources on improving the environment while at the same time meeting the standards. For example, SO2 contributes to the formation of PM2.5 and its associated effects on human health, visibility degradation and acid deposition. NOx also contributes to PM2.5 formation and its associated human health effects, visibility degradation, and acid deposition, but at different rates than SO2. NOx also contributes to ozone formation (and its associated effects on human health and vegetation), and contributes to nitrogen deposition and its effects on water and soil nutrient loadings and eutrophication. Taking all these into account may change the optimal mix of control strategies. This paper will (1) state the issue to be addressed, (2) explain why and how “least cost” compliance strategies may not generate as much health and environmental benefits as might be attained at nearly the same cost, (3) offer some ideas for performance measures and indices that may help identify benefit-enhancing compliance strategies, and (4) suggest areas for future research and analysis to develop practical tools to assist decision makers.

8A-3

HIGHLIGHTS AND LESSONS LEARNED: PM2.5 TECHNOLOGY ASSESSMENT AND CHARACTERIZATION STUDY IN NEW YORK – PMTACS-NY SUPERSITE PROGRAM, KENNETH L. DEMERJIAN, J. Schwab, G. Lala, O. Hogrefe, Y. Li, S. Weimer ,Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY; D. Felton, G. Boynton, T. Lanni, B. Frank Division of Air Resources, NYS Department of Environmental Conservation, Albany, NY; F. Drewnick, Cloud Physics and Chemistry Department, Max-Planck-Institute for Chemistry, Mainz, Germany ; D. Orsini, K. Rhoads, Chemistry Department, Siena College; Loudonville, NY; L. Husain, X. Zhou, V. Dutkiewicz, Department of Environmental Health and Toxicology, University at Albany/SUNY, Albany, NY; W. Brune, X. Ren, R. Lesher, Pennsylvania State University, College Station, PA; D. Worsnop, C. Kolb, M. Zahniser, J.T. Jayne, Aerodyne Research, Inc., Billerica, MA; P. Hopke, P. Venkatachari, Clarkson University, Potsdam, NY; H. Patashnick, J. Ambs, Rupprecht & Patashnick Co., Inc., East Greenbush, NY; J. Jimenez, Z.Qi, University of Colorado, Boulder, CO.

Four years of routine PM2.5 mass, composition and precursor data as well as four intensive field measurement campaigns have been carried out under PMTACS-NY program, a U.S. EPA “Supersites” Program. The study utilized conventional and advanced instrumentation technologies to characterize physical and chemical composition of particulate matter and related precursors. During intensive field campaigns teams of scientists from university, state, and private sector organizations deployed research grade instrumentation and emerging commercial measurement technologies to provide detailed real-time chemical and physical characterization of the urban PM2.5/co-pollutant complex under summer and winter conditions to assist in the 1) elucidation of the operative gas-to-particle transformation processes occurring in these environments; 2) enhancement of chemical source signature database in support of source attribution studies; and 3) performance testing and evaluation of emerging measurement technologies and their comparison with EPA mandated PM federal reference methods currently operational as part of the New York State and national PM2.5 monitoring networks. The intensive field programs allowed for the study of urban-rural and summer-winter contrasts of the physical and chemical composition of particulate matter and related precursors. These results are discussed, as are their implications to potential mitigation strategies for addressing PM2.5 nonattainment in the region. The program overview also provides a summary of the data collected and selected highlights of the findings and conclusions as they relate to program objectives.

8A-4

CONCEPTUAL MODEL OF FINE PARTICULATE MATTER SOURCES, FORMATION AND ACCUMULATION IN SOUTHEAST TEXAS, GARY McGAUGHEY, Matthew Russell, David Allen, University of Texas, Austin, TX; Donald Collins, Texas A&M University, College Station, TX; Matthew Fraser, Rice University, Houston, TX

Daily, seasonal, and spatial trends in fine particulate matter concentrations, compositions, and size distributions were examined using data collected through the regulatory fine particulate matter monitoring network in Southeast Texas and during the Gulf Coast Aerosol Research and Characterization Study (GC-ARCH or Houston Supersite). PM2.5 mass concentrations and compositions are generally spatially homogeneous throughout Southeast Texas when averaged over annual or seasonal time periods. There is relatively little seasonality to mean total PM2.5 mass and mean PM2.5 composition throughout the region, although slightly higher concentrations of total mass tend to occur in the spring and late fall. High FRM PM2.5 mass (>20 µg/m3) occurs both when there is high spatial variability among sites and low spatial variability among sites. This suggests that both local and regional emission sources contribute to PM2.5 in Southeast Texas. Sulfate ion (32%), organic carbon (30%), and ammonium ion (9%) are the largest components on average of PM2.5 by mass. Mean diurnal patterns for PM2.5 mass concentrations throughout the region show a consistent morning peak and a weaker and slightly less consistent peak in the late afternoon to early evening. High hourly averaged PM2.5 mass concentrations (>40µg/m3) tend to be associated with daily average PM2.5 above the annual NAAQS of 15 µg/m3. These high hourly PM2.5 concentrations also tend to occur on days with high diurnal variation, indicative of elevated, short-lived PM2.5 events. In contrast to mass concentrations, particle size distributions are not spatially homogeneous throughout Southeast Texas. Industrial sites have higher concentrations of freshly emitted, primary particles than more residential sites. Because the freshly emitted particles generally have diameters of 0.1 µm or less, these primary emissions do not have as large an impact on PM2.5 mass or bulk composition as they have on the number density of fine particles.

8A-5

RELATIONSHIPS BETWEEN OZONE AND PM DURING CRPAQS, BETTY PUN, Christian Seigneur, Atmospheric and Environmental Research, Inc., San Ramon, CA

The relationships of ozone and PM and its components were explored using ambient monitoring data obtained during the California Regional PM Air Quality Study (CRPAQS). We first characterized when and where high ozone corresponded to high PM2.5 concentrations. Seasonal effects are discussed. Next, we investigated the relationships between ozone and key secondary PM2.5 components, including nitrate and secondary organic aerosols. Several hypotheses were tested using the ambient data, including local photochemical formation of secondary organic aerosols, daytime vs. nighttime formation of nitrate at surface and upper air monitoring sites, and the heterogeneous formation of sulfate and nitrate during fog events.

8B-1

COMPARISON OF PM2.5 LEVELS AND CHEMICAL SPECIATION AT URBAN AND RURAL AREAS, KAREN MAGLIANO, Kasia Turkiewicz, Theresa Najita, California Air Resources Board, Sacramento, CA

Concentrations of PM2.5 mass and its most abundant chemical species are compared for urban and rural sites in the San Joaquin Valley. Over 80% of PM2.5 mass at urban as well as rural locations can be attributed to carbon and ammonium nitrate. While most of the carbon is directly emitted into the atmosphere as a particle, ammonium nitrate is formed in the atmosphere from precursor gases (ammonia, oxides of nitrogen (NOx), and Volatile Organic Carbons (VOCs)). Since carbon as well as precursor gases, except ammonia, are more abundant in the urban than rural locations, urban sites experience high concentrations sooner than rural. However, during a prolonged episode, rural sites can reach concentrations similar to urban sites in magnitude, but different with respect to chemical composition. Rural concentrations are usually heavily dominated by ammonium nitrate with a much smaller carbon contribution than urban. The difference in the chemical composition is related to the fact that gases (ammonium nitrate precursors) are transported more efficiently than particles (carbon) from the urban into the rural environment where they can react with ammonia and form ammonium nitrate.

8B-2

ELEMENTAL COMPOSITION OF PM2.5 AEROSOLS MEASURED DURING THE PM2.5 TECHNOLOGY ASSESSMENT AND CHARACTERIZATION STUDY-NEW YORK (PMTACS-NY), VINCENT A. DUTKIEWICZ(1,2), Sumizah Qureshi (2), Kamal Swami(1), Karl X. Yang(1), Liaquat Husain(1,2), James J. Schwab(3), and Kenneth J. Demerjian (3), (1) Wadsworth Center, New York State Department of Health, Albany, New York (2) Department of Environmental Health and Toxicology, State University of New York at Albany, Albany NY and (3) Atmospheric Sciences Research Center, State University of New York, Albany, NY

As a part of the PM2.5 Technology Assessment and Characterization Study-New York (PMTACS-NY) daily aerosol samples were collected from July 2001 - December 2004 at three NY sites; urban Queens, and rural Pinnacle State Park, and Whiteface Mountain. All samples were analyzed for sulfate by ion chromatography. The 2001 and 2002 samples also had 15 metals determined by Inductively-coupled plasma mass spectroscopy (ICP-MS) after a rigorous micro-wave digestion (total). Elements included, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Cd, Sb, and Pb. Because elements with high solubility can be more readily bio-activated in the lungs and thus may be potentially more harmful for humans, samples collected through June 2002 had ICP-MS analysis run on a water extraction aliquot to specifically determine the soluble fraction. An overview of the elemental composition of PM2.5 aerosols at the three sites over the 18 months will be presented. This will include a comparison of seasonal changes in aerosols composition, including solubility at these sites: and with the aid of air trajectories provide some insight into potential sources impacting Queens. The solubility measurements on the 15 elements at the three sites can be divided into three general groups. The largest group of elements have solubility > 70%. This group includes Mg, V, Mn, Ni, Zn, As, Se, Sb, and Pb. The day to day variations of the solubility for elements in this group was also relatively small and well within uncertainties. Elements with intermediate solubility that averaged between 40% and 70% includes Ca, Fe, and Co. For this group, however, there were some days with very low solubility (10- 30%) particularly for iron. These days occurred sporadically but most often in spring. The third group which includes Al, Cr, and Cd, has generally low solubility ~ 10%, but it can also be highly variable. For Queens, Co, Ni, Zn, and Pb have the strongest seasonal trends as the cold (October - March)/warm (April - September) concentrations ratios were 1.7, 2.1, 1.5, and 1.6, respectively. Vanadium, As, and Se had moderate trends with ratio of 1.2, 1.2 and 1.4, respectively, however, this may just be due to unusually low concentrations in the spring quarter. The remaining elements showed no clear trends but may have been influenced by special events. The details of several unique trace element events noted at the three sites will be presented: e.g., impact from World Trade Center collapse on aerosol composition at the Queens site; impact from 2002 Quebec wild-fire smoke. Taking advantage of the large daily elemental data base the radial concentration profiles utilizing surface and 1 km air trajectories were computed for warm and cold months separately for all three sites, however, this presentation will focus on the profiles for the urban site. The profiles are used to glean insight into source regions impacting Queens including an evaluation the relative importance of local emissions versus transport from regional sources.

8B-3

SPATIAL VARIATIONS OF PM2.5 IN THE PITTSBURGH REGION, Wei Tang, US EPA, Research Triangle Park, NC; Timothy Raymond, Bucknell University, Lewistown, PA; Beth Wittig, City College of New York, New York, NY; CLIFF DAVIDSON, Spyros Pandis, Allen Robinson, Carnegie Mellon University, Pittsburgh, PA; Kevin Crist, Ohio University, Athens, OH

The Pittsburgh Air Quality Study (PAQS) included sampling for 15 months beginning in July 2001, with intensive runs during July 2001 and January 2002. The study was organized to characterize airborne particles with respect to size, morphology, and chemical composition, and to identify sources, transport pathways, and atmospheric transformations of these particles. In this paper, we use data from the PAQS for three specific objectives: (1) to identify the spatial variability in concentration of the different chemical components of PM2.5 across the Pittsburgh region throughout the year, (2) to evaluate the relative contributions of regional and urban sources influencing PM2.5 in summer and in winter, and (3) to explore the role of meteorology in influencing PM2.5 concentrations. Sampling sites from west to east were Florence (PA), three sites within the city of Pittsburgh (PA), and Greensburg (PA). In addition, limited data were obtained at Athens (OH). The Florence site was in a rural area about 50 kilometers west of Pittsburgh without any major sources nearby. The Greensburg site was in a suburban area close to roads and about 55 kilometers east of Pittsburgh. The Athens site was in a small city about 270 kilometers southwest of Pittsburgh. Results for summer 2001 show that 24-hour PM2.5 total mass, sulfate, ammonium, and organic carbon at these sampling locations have similar concentrations within experimental error. Measurable differences among the six sites were observed for nitrate and elemental carbon during the same time period. In contrast, measurable differences were observed for total mass and all five chemical species at the same sites during winter 2002. The differences in regional homogeneity between summer and winter are attributed to the importance of photochemistry in summer, which results in production of secondary species over relatively long time periods and spatial scales. The fractions of secondary PM are smaller in winter, and thus the influences of local sources in the city are expected to be greater. Meteorological back-trajectories show that concentrations can steadily increase along an airmass trajectory. Data obtained when winds were from the west show PM concentrations as smallest at Florence, intermediate for the three sites in Pittsburgh, and highest at Greensburg. In contrast, when winds were easterly, the opposite was observed with the highest concentrations measured at Florence. The data thus show that regions downwind of a city such as Pittsburgh may be affected by emissions from the city; however, PM2.5 levels measured within the city may not be significantly affected by local emissions if background levels are sufficiently high.

8B-4

SEASONAL VARIABILITY OF ORGANIC MASS CONTRIBUTION TO PM2.5 WITHIN METRO ATLANTA AND FURTHER DOWNWIND,

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PM2.5 mass and composition, as well as main aerosol gases NH3, HNO3, HONO, SO2, and light organic acids (LOA, i.e. acetic, formic and oxalic) were measured at Jefferson Street in downtown Atlanta during EPA's Supersite Experiment in August 1999 (ASSE99), and during the July 2001 and January 2002 intensives of the Fall-line Air Quality Study (FAQS), that coincided with EPA's Eastern Supersites Program (ESP). Inclusion of PM2.5 data from the ASACA (Assessment of Spatial Aerosol Composition in Atlanta) and Georgia's regulatory monitoring networks, allowed the investigation of the seasonal differences in the urban-rural gradient of PM2.5 mass and individual species. The FAQS site near Griffin, GA, approximately 40 miles south from Jefferson Street served here as the more rural site. PCM sampling was supported by continuous measurements of various meteorological parameters and gas-phase indicator species (CO, NO, NOx, NOy, SO2 and O3) at both sites. In all cases, sulfate and organic carbon (OC via TOT) were the main contributors to overall PM2.5 mass, which was regionally highest in summer, although decreasing from summer to summer. The underlying parameters causing ozone and PM2.5 formation (stagnant periods associated with high temperature, relative humidity, and UV radiation) varied between the different summers, correlating with the observed pollutant concentrations. Also at each site, the organic mass (OM) was estimated as an upper limit from mass closure principles. The observed OC/EC and OM/OC followed a trend towards higher values with increased distance from the urban core in summer, while the wintertime OM/OC ratios were generally lower. An Ozone Production Efficiency (OPE) interpreted and derived from the slopes of least square linear fits of [O3] versus [NOz] (NOy-NOx) of carefully selected data yielded ~4 ±0.2 molecules of O3 produced per NOx oxidized during ASSE99, whereas the OPE during ESP01 was only ~3 ±0.3. The lower atmospheric oxidative capacity in summer 2001 was furthermore indicated by a lower O3 background concentration of 38 ±2.7 ppbv compared to 59 ±1.5 ppbv in August 1999. Lower and upper estimates of the OPE in the air masses arriving at the Griffin receptor site, ranged between 3 ±0.3 and 14 ±0.6, indicating more photo-chemical activity and larger abundance of peroxy radicals (RO2) as the Atlanta urban plume was advected over BHC-rich terrain, transitioning to a more NOx-limited regime. Possible links to the observed increase in OC/EC and OM/OC ratios as indicators for the formation of SOA and more highly oxygenated POC, during this advective outflow are being discussed in conjunction with influences from prescribed burning and wild fire occurrences in the different seasons.

8B-5

SOURCE APPORTIONMENT OF PM2.5 IN THE SOUTHEASTERN UNITED STATES,

SANGIL LEE, Michael Chang, Karsten Baumann, Armistead Russell, Georgia Institute of Technology, Atlanta, GA

The EPA Speciation Trends Network (STN) monitoring sites of PM2.5 are distributed throughout the southeastern United States. They provide inorganic chemical speciation (inorganic ionic species and trace metal elements) and elemental and organic carbon fine particle (PM2.5) concentrations. Using this data, PM2.5 source apportionment was conducted for 24 sites using CMB 8.0 covering a 13 month period from January 2002 to November 2003. Prior to the source apportionment, primary organic carbon (POC) was estimated by using the primary OC/EC ratio obtained from using the elemental carbon tracer approach (Castro et al., 1999). The primary OC/EC ratios are variable across the locations. The lower OC/EC ratios (2~3) appear in urban areas which are heavily impacted by motor vehicle sources, whereas the higher primary OC/EC ratios (3~7) in are found in rural/suburban areas. Secondary organic carbon (SOC) was calculated by subtracting POC from total OC. Estimated SOC by using this method shows a clear seasonal variation, that is, SOC is higher in summer than winter. Overall, SOC is estimated to be about 40 to 60 % of total OC. The estimated SOC also shows a positive relationship with organic mass (unidentified mass + OC) to OC ratio indicating more oxygenated organic carbon during summer time. Source apportionment was conducted using the POC estimates. Extensive spatial analysis between stations provides a picture as to the regionality of specific source impacts. Similar to other studies in the region, motor vehicles and wood burning are found to be the two major primary sources. However, there is significant spatial variability among sites. Motor vehicles in urban areas contribute about 20% (~3.0 ug /m3) of PM2.5 concentrations whereas in other rural/suburban areas they comprise less than 10% (~1.5 ug / m3). Unlike the motor vehicle source, more wood burning appears in rural/suburban areas (>10%; 1.5 ug /m3) than urban areas (<10%; 1.5 ug /m3). Other primary sources also show significant spatial differences even though their contributions are less than 1 ug /m3. For example, the contributions of oil combustion at Savannah, GA and mineral production (i.e. cement kilns) at Macon, GA are significantly different from other sites. Four sites in Tennessee, two sites in Georgia, and one site in Alabama are impacted by coal power plants much more than other sites. These results provide information as to the representativeness of one site for characterizing a region, e.g. for policy or health effects analysis, and also can be compared to the emissions inventories for the region to suggest possible incongruities.

8C-1

WATER-BASED CONDENSATION PARTICLE COUNTERS FOR ENVIRONMENTAL MONITORING OF ULTRAFINE PARTICLES,

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Abstract Around the globe, air quality standards for particulate matter (PM) are based on mass. In recent years, however, there has been growing concern about the role that ultrafine particles have on human health effects. While current PM measurement techniques are capable of accurately determining the mass of larger, coarse and fine aerosol particles, they are incapable of measuring the ultrafine particles which have the highest fraction of number concentration, but least amount of mass. Environmental monitoring stations in Switzerland, the South Coast Air Quality Management District in California, the Greater London area in the UK, and several U.S. supersite monitoring stations have deployed condensation particle counters (CPCs) and scanning mobility particle sizer™ (SMPS™) spectrometers to monitor particle number (PN) concentration levels of ultrafine particles along with their size distribution in order to collect both temporal and spatial data of ultrafine particles. A new group of CPCs have been developed and are well suited for environmental monitoring applications. Their unique design incorporates the use of water as the working fluid instead of alcohol. Water is odor-free, readily available, and eliminates the problem of water condensation and absorption into the alcohol working fluids during humid periods. From the performance of early General Electric expansion-type, water-based condensation particle detectors, it is known that the measurement response varies for hydrophilic and hydrophobic particles. In this study, the measurement performance of TSI water-based CPCs (WCPC) were characterized for several aerosol compositions, including sucrose, salt, DOS, DOP, emery oil, silver, and ambient aerosol particles from several locations. Sucrose and oil particles were generated in the laboratory using an electrospray aerosol generator (TSI 3480). Salt and silver particles were generated using a tube furnace. All particles, including ambient aerosol, were size-selected using a nano DMA (TSI 3085) to create monodisperse challenge aerosols. The challenge aerosol was split and delivered to both a WCPC and an aerosol electrometer (TSI 3068A) or an ultrafine butanol-based CPC (TSI 3025) to determine the counting efficiency. For the TSI model 3785 WCPC, the D50 (i.e., the size with 50% counting efficiency) was determined to be 3.1nm for salt particles, 4.7nm for sucrose and ambient particles, 5.6nm for silver particles, and > 50nm for ultra-pure oil particles. However, the WCPC exhibited much better sensitivity to smaller oil particles (< 10nm) when a slight amount of contamination was introduced into the oil. Similar tests were performed on the TSI 3786 ultrafine WCPC (UWCPC) using size-classified ambient, silver, and salt particles. For ambient and silver particles, the D50 is approximately 2.5nm and 2.7nm, respectively. For salt particles, the D50 is below 2.5nm and much better than we could actually measure using the TSI 3025 or aerosol electrometer as the reference. Ambient measurements comparing the PN concentration levels of the WCPCs and traditional CPCs were also performed. Results show excellent agreement between PN concentration measurements for the two types of instruments. Both types of CPCs were able to detect ultrafine particle events.

8C-2

A FAST-RESPONSE, NANOPARTICLE WATER-BASED CONDENSATION COUNTER,

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A thermally diffusive, laminar-flow, water-based condensation particle counter (WCPC) has been developed to measure number concentrations for nanometer and ultrafine particles. Particles are enlarged by water condensation in a laminar flow using a “growth tube” technology that explicitly takes into account the high diffusivity of water vapor. The supersaturation necessary for particle activation and growth is produced in a warm wet-walled condenser. Because the mass diffusivity of water vapor exceeds the thermal diffusivity of air, the flux of water vapor to the centerline is faster than the heat flux from the walls. The first version of this instrument has an unsheathed sample flow of 1 L/min and saturator and condenser temperatures of 20C and 60C respectively. Its lower cutpoint, defined as the particle size detected with an efficiency of 50% is 4.5 nm for non-hydrophobic aerosols, including salts, organic acids and ambient aerosols. Reported here is a second, nanoparticle version of the instrument. The nano-WCPC utilizes a 50% sheath flow with an aerosol flow of 0.3 L/min, and saturator and condenser temperatures of 10C and 70C respectively. Tests with ambient, tunnel and laboratory generated aerosols show that the effective cutpoint is approximately 2.7 nm. The time response is approximately 300 ms, excluding the flow-enduced lag. The relatively high aerosol sampling rate yields significantly better counting statistics, allowing much faster size distribution scans that previously possible.

8C-3

PERFORMANCE EVALUATION OF A RECENTLY DEVELOPED WATER-BASED CONDENSATION PARTICLE COUNTER, SUBHASIS BISWAS, Philip M. Fine, Michael D. Geller, and Constantinos Sioutas,* , University of Southern California, LA, CA. Susanne V. Hering, Aerosol Dynamics, Inc. Berkley, CA.

This study focuses on the intercomparison of the performance of a newly developed water-based condensation particle counter (WCPC) and a butanol-based reference CPC (TSI 3022A). Four test aerosols (ammonium nitrate, ammonium sulfate, adipic acid, glutaric acid) were generated in the laboratory before the instruments were deployed at four field locations (USC/downtown LA, I-710 Freeway, Pacific coast/ ocean aerosol, LAX Airport). Both instruments sampled the same incoming aerosol. Selected experiments utilized a differential mobility analyzer (DMA) to select a particle size upstream of the CPCs. Evaluation of performance was based on response of the instruments, particle composition, number and size. The results indicated good correlation between the two CPCs, with R2 values ranging from 0.91-0.99. The size fractionated experiments were performed after selecting a particular size with a scanning mobility particle sizer (SMPS). The WCPC performed better for laboratory particles with small mobility diameters (10-50 nm) due to the hygroscopic nature of these particles and relative lower detection limits of the WCPC. The particle number concentration has a pronounced impact on the performance of WCPC. It demonstrated better detection of particle concentrations between 0 and 40,000 particles/cm3, with WCPC/ TSI 3022A ratio between 1-1.4. Due to differences in the photometric mode calibration of these instruments, the ratio drops to 0.6 -0.8 between 40,000-100,000 particles/cm3. However, the ratio rises again for lab aerosols to1.0-1.1 after 100,000 particles/cm3. The TSI 3022A-CPC appears to have a lag period of 2-3 s from the WCPC as determined from time response and correlation plots. This lag may be caused in part by the difference in the time constant, a dynamic characteristic relating to the time required for a particle to clear the measurement zone of an instrument. Time constants were measured to be 0.78s and 9.5s for the WCPC and the TSI-3022A CPC, respectively. Results of this evaluation show that the WCPC is a reliable particle counting technology for particle concentrations in many normal ambient environments (< 40,000/cm3).

8C-4

THE SJAC-MOI FOR MEASURING THE COMPOSITION OF UF-AEROSOL, HARRY TEN BRINK, Rene Otjes, Energy Research Centre of the Netherlands (ECN), Petten, NL

A SJAC (Steam Jet Aerosol Collector) was extended with a series of pre-impactors for on-line measurement of the composition of size-resolved PM. Analysis of the aerosol collected in the SJAC occurs with several aqueous-phase techniques. The time resolution depends on the specific analysis instrumentation used and varies from continuous detection for ammonium and OC, to one analysis per 15 minutes for components analysed with IC. The new tool is known as SJAC-MOI, in which MOI stands for the use of the stages of a commercial Micro Orifice Impactor. The performance of the stages in their single stage application was checked with test-aerosols and found to be equivalent with their performance in a cascade setting. The actual stages in the SJAC-MOI are preceded by a stage with a larger cut-off to remove larger particles. The SJAC-MOI allows on-line sampling and analysis of aerosols down to a diameter of 7 nm. A further advantage is that the wet-analysis instrumentation also measures refractory aerosol components. A prototype SJAC-MOI was used in a summer campaign of two months on top of a 200 m high meteo-tower in the centre of the Netherlands for on-line measurement of the ionic composition of the regional fine and ultrafine PM. The instrument was operated in a fully automated way and appeared to most optimally work for nitrate. The average concentration of this component in the submicron aerosol fraction was 3.4 ug m-3, which is equal to the average value interpolated for the site from data stemming from the dense national network. The nitrate is present in the form of ammonium nitrate. On average half of the ammonium nitrate was in particles smaller than 0.3 um in diameter, of which again 30% was in particles smaller than 0.18 um. The concentrations of sulphate, chloride and ammonium were also determined, but detection limits for sulphate and ammonium were higher than that for nitrate, which leads to some uncertainties in the concentration of these components in the ultrafine aerosol fraction. In this fine mode the average ratio of nitrate to sulphate seems close to one. The concentration of chloride was almost negligible compared to that of the two other components. In an earlier campaign, at the institute, the concentration of OC as a function of size was determined. A coming development is the use of an impactor stage of 0.1 um for which the pressure drop seems a problem.

8C-5

USE OF SPECIATION SAMPLERS TO PROVIDE INFORMATION ON INDIVIDUAL PARTICLE CHARACTERISTICS,

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The U.S. Environmental Protection Agency (EPA) has established a speciation network to quantify PM2.5 mass concentrations of trace elements, geological material, sulfate, nitrate, ammonium, organic carbon and elemental carbon. Data of this nature are needed to better understand the sources leading to elevated PM2.5 concentrations. The requirement for data on elemental composition, anions/cations and carbon requires the use of "speciation" samplers designed with multiple and independent sampling channels allowing for simultaneous sampling on different filter media. Presently, the samplers used in the EPA speciation network collect PM2.5 on Teflon filters to determine mass concentration via gravimetry and elemental concentrations using X-ray fluoresce (XRF); nylon filers for anions and cations (e.g., SO4, NO3, NH4, etc.); and quartz filters to determine elemental carbon and organic carbon (EC/OC) using thermal optical methods. As part of the National Ambient Air Quality Standard (NAAQS) for particulate matter (PM) promulgated 1997, the EPA realized that sampling for speciation purposes is an evolving science and encouraged creative approaches to speciation sampling and analysis. The EPA has also stated that special measurement needs may include determining individual particle size, morphology and composition using microscopic methods. In an investigation of PM2.5 conducted by the Department of Energy (DOE) National Energy Technology Laboratory (NETL), a sampling and analysis site was established at NETL Pittsburgh facility to improve the understanding of the components and characteristics of PM2.5. Ambient PM2.5 samples were collected using a four channel Andersen RAAS speciation sampler. To enhance the knowledge on PM2.5, a polycarbonate (PC) filter was utilized in addition to Teflon and quartz filters in the speciation sampler to permit analysis using electron microscopy techniques. For each speciation experiment, four different flow channels were used: two at the standard FRM rate of 16.7 L/min and two at a flow rate around 7 L/min. One of the higher flow channels utilized a standard Teflon filter whereas the other had a carbon denuder followed by a quartz fiber filter followed by a carbon impregnated quartz filter. The Teflon filter was use to determine mass concentration and elemental constituents and the EC/OC analysis was performed on the quartz filter set. The two lower flow channels were used for collecting PM2.5 on PC filters for computer controlled scanning electron microscopy (CCSEM) analysis. Through experimentation, it was determined that a flow rate of around 7 L/min produced the most appropriate particle loading for electron microscopy examination. Each of these two channels had upstream carbon denuders to remove acid gases from the air, followed by PC filters on Typar fiber backing pads (more uniform air flow through the PC filter and more even particle dispersion) followed by nylon membrane filters. The nylon filters were subsequently analyzed by ion chromatography to determine levels of nitrate and/or sulfate lost from the primary particles collected on the PC filters. An overview of this speciation program is provided along with results comparing bulk analysis results to individual particle data obtained through electron microscopy techniques.

9A-1

AEROSOL MASS SPECTROMETRY: AEROSOL CHEMICAL AND MICROPHYSICAL PROPERTIES,

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Assessment of atmospheric aerosol impacts on air quality and health effects requires detailed study of aerosol chemical and microphysical properties, including size dependent chemistry and morphology. A recently developed Aerosol Mass Spectrometer (AMS) measures size and compositionally resolved mass loadings of ambient aerosol. Sub-micron particles are aerodynamically focused into high vacuum. Aerodynamic diameter is determined via particle time-of flight measurement. Flash vaporization followed by 70 eV electron impact ionization mass spectrometry provides universal and quantitative determination of mass loading for the non-refractory components (that vaporize at 600-900C). Mass spectra clearly separate inorganic (sulfate, nitrate, ammonium, chloride) and organic components. Additional beam width and light scattering probes measure shape and optical properties. These measurements provide correlation of sub-micron particle size, shape and chemical composition. Combining physical mobility diameter (measured via SMPS) provides detailed information of particle morphology and density. Size resolved measurements have chemically analyzed the growth of new particles in urban and forested regions. Study of fractal soot particles demonstrates these capabilities in the lab, in vehicle plumes and in ambient observations. Variation in mass spectral signatures of organics can distinguish hydrocarbon (primary) from oxygenated (secondary) aerosol. New results for organic analysis utilizing vacuum ultraviolet photo-ionization will be presented.

9A-2

DEVELOPMENT OF A SONIC VIRTUAL IMPACTOR,

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Virtual impactors are widely used for particle concentration from a carrier gas for further analysis. The general mechanism involves separation based on particle inertia ─ The flow is divided into major and a minor flow, the high inertia particles fail to turn and are therefore concentrated into the minor flow. The principal parameter governing this concentration is the particle Stokes number. A low cut point virtual impactor requires either high velocities or small orifices. However, there are very few studies on high velocity impactors. The objective of this work is to design a sonic slit virtual impactor with high efficiency. In this work, the sonic flow through the slit impactor is simulated using the CFD code FLUENT, and the corresponding particle trajectories are studied. This work seeks to understand and identify the parameters that govern focusing in a sonic impactor. The work is then extended to optimize the design for high efficiency and transmission rates, for application in single particle analysis instruments.

9A-3

FIELD EVALUATION OF THE VACES PARTICLE CONCENTRATOR COUPLED TO THE RSMS-3 SINGLE PARTICLE MASS SPECTROMETER,

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A field evaluation of Versatile Aerosol Concentration Enrichment System (VACES) coupled to Rapid Single-particle Mass Spectrometer (RSMS-3) was conducted as part of the U.S. Environmental Protection Agency (EPA) Supersite program in Pittsburgh during March 2002. RSMS-3 hit rate increases were measured and possible particle composition changes introduced by the VACES were examined in the single particle mass spectra. The hit rates increased by 5-20 times at particle sizes ranging from 40 to 640 nm. VACES only enhances the hit rate by about a factor of 2 for large particle sizes because the RSMS-3 flow rates for these particles did not match the optimum operating condition of VACES. During the three days of measurements, most of the particles were a mixture of carbonaceous material and ammonium nitrate with a variation across the spectrum from particles that were mostly carbonaceous to particles that were mostly ammonium nitrate. Both ambient and concentrated carbonaceous and ammonium nitrate composition distributions were indistinguishable with RSMS-3 suggesting that VACES introduces an insignificant artifact for those particles.

9A-4

SIZE-RESOLVED CHEMICAL CLASSIFICATION OF DUAL POLARITY SINGLE-ULTRAFINE-PARTICLE MASS SPECTROMETERY DATA COLLECTED DURING THE PITTSBURGH SUPERSITE EXPERIMENT,

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Approximately 236,000 single particle mass spectra were collected throughout the duration of the Pittsburgh Supersite experiment using RSMS-3, a third generation single particle mass spectrometer. The instrument was operated semi-continuously for 306 days, sampling particles with aerodynamic diameters in the range of 30 – 1100 nm and collecting both positive and negative ion spectra, particle size and time of detection for each particle measured. The entire data set has been fully processed and analyzed. Spectra have been clustered into 20 distinct particle classes based on the distribution of their positive ion mass peaks. Negative ion spectra were classified independently within each positive ion class. Frequency of occurrence versus particle size, month of the year and wind direction has also been calculated for the full data set, as well as within each class. Results indicate a rich array of multi-component ultrafine particles. Approximately 54% of all the particles measured fell into the carbonaceous ammonium nitrate (CAN) class. These particles were observed in all size bins and from most wind directions for the entirety of this study. Ubiquitous sources throughout the area, including vehicular emissions and secondary organic aerosol formation, are considered to be responsible for a large fraction of these particles. In terms of particle number, metal containing aerosol dominated the remainder of the particle classes identified. These particles were rich in K+, Na+, Fe+, Pb+, and to a lesser extent, Ga+ and Zn+. They tended to be smaller in size and were highly correlated with specific wind directions, facilitating the isolation of specific sources.

9A-5

SIZE AND TIME RESOLVED FINE AND ULTRAFINE SINGLE PARTICLE COMPOSITION IN BALTIMORE, MARYLAND,

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The real time single particle mass spectrometer RSMS-3 was deployed for an eight month period (April-November 2002) at the Particulate Matter Supersite in Baltimore, MD. The supersite was located to the east of the city, northwest to many of the industrial sources of pollution. Over 381,000 particles in the aerodynamic size range of 50-750 nm were analyzed during this time period. The resulting positive and negative ion spectra for each particle were classified using two complementary approaches to study time and size dependent changes in chemical composition. Single particle chemical composition can be interpreted either in the context of a specific particle source or a specific chemical component. In the particle source viewpoint, each particle contains a specific combination of chemical components that is related to its origin. These chemical components are determined by the emission characteristics of the source as modified by physical or chemical transformation processes. In this viewpoint, the main goal is to classify each particle in a manner that traces back to a unique emission source and/or transformation process. This approach was implemented using the ART2-a algorithm. Over 99% of the particles could be classified into 10 major composition types that were further grouped as regional processed aerosol, local processed aerosol, and local unprocessed aerosol. Ambient number concentrations were determined for each type and correlated with particle size, wind direction and time of day/year. In the chemical component viewpoint, the goal is to identify all particles containing a specific chemical component and then determine how that component is distributed within the aerosol. This viewpoint is useful in the context of exposure to specific toxic compounds or studying atmospheric processes associated with a particular species. It was implemented by first sorting particle mass spectra on the basis of a marker ion (for example, 56 m/z for iron), then performing ART2-a on the selected particles to distinguish particle classes that contain the species of interest from those that contain isobaric interferences. As above, ambient number concentrations were determined for each type and correlated with particle size, wind direction and time of day/year. Examples from this type of analysis of the Baltimore aerosol include determining the total number concentration of particles containing a specific transition and/or heavy metal (useful for identifying point source emissions) and elucidating ultrafine particle events associated with nitrate cycling in the atmosphere. This presentation will focus on the complementary aspects of the two approaches and how together they provide a coherent view of time and size dependent changes in aerosol chemical composition.

9B-1

LOCAL AND REGIONAL SECONDARY ORGANIC AEROSOL FORMATION: INSIGHTS FROM A YEAR AT PITTSBURGH AND COMPARISON WITH LOS ANGELES AND ATLANTA,

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An automated semi-continuous thermal-optical transmittance (TOT) carbon analyzer was used to measure 1-4 hr average particulate organic and elemental carbon concentrations (OC and EC, respectively) in Claremont, CA, Long Beach, CA, Atlanta, GA, and Pittsburgh, PA. Measurements were made for over one year in Pittsburgh, while the other studies were 4 -8 weeks in duration. The quantity of secondary organic aerosol formed was estimated for each study using an EC tracer method. Strong diurnal variations were seen in Los Angeles Basin OC and EC. During summertime photochemical smog episodes (Claremont) EC peaked around 7 am and OC exhibited peaks both near 7 am and in the late afternoon. EC is considered a tracer for combustion-generated OC. The additional afternoon OC that did not correspond to EC was most likely secondary organic aerosol. Daily peak concentrations of calculated secondary organic aerosol tracked peak ozone concentrations during photochemical smog episodes. The strong diurnal nature of these secondary OC formation events suggests that formation occurred locally in the afternoons when conditions were favorable. In contrast to Los Angeles Basin measurements, OC and EC in Atlanta and Pittsburgh showed only modest diurnal variations. Some events were observed in which secondary formation appeared to occur locally. However, much more frequent were secondary organic aerosol estimates that increased and stayed elevated over several days, suggesting formation during regional transport. Occasionally nighttime peaks in ozone and secondary organic aerosol occurred, consistent with down mixing of aged air from aloft. These data suggest that secondary organic aerosol is the dominant contributor to Los Angeles Basin particulate carbon only during the peak hours of photochemical smog episodes. In contrast, secondary organic aerosol accounts for 30-40% of monthly average OC from June to November in Pittsburgh and 44% in Atlanta in August. At times, 1-4 hr average secondary organic aerosol contributions were as great as 70% in all locations. Results suggest that secondary organic aerosol formation is particularly important in locations that are recipients of long distance transport, e.g. the eastern US. One might speculate, based on other research, that acid-catalyzed oligomerization and/or in-cloud processes could contribute to regional formation in the eastern US.

9B-2

CHARACTERIZATION AND COMPARISON OF URBAN AND RURAL PARTICULATE MATTER ON A MEDITERRANEAN ISLAND,

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Levels of PM10 were determined at three receptor sites representing urban traffic, residential and rural background on the very dry Mediterranean island of Cyprus to describe the dominant patterns showing a significant influence on the levels and composition of PM10. From November 2002 to September 2003 a total of 515 24h PM10 samples were taken on 50 mm filters at the three sites and analysed in the lab. All together 15 elements (Cr, K, Na, Ti, Mg, Mn, Fe, Zn, Cu, Pb, Ba, S, Ca, Al, Si) were detected by X-RFA (X-Ray Fluorescence Analysis), 5 ions (NO3-, SO4-2, NH4+, Na+, Cl-) by Ion Chromatography and additionally 5 elements (Pb, Cd, Ni, As, Cu) were analysed by GFAAS (Graphite Furnace Atomic Absorption Spectrometry). The average PM10 concentrations at the urban traffic and residential sites were 40.1 and 45.5 µg/m³ respectively, slightly exceeding the EU annual limit value of 40 µg/m³, while at the rural site the average PM10 concentration was 15.8 µg/m³. A significant seasonal trend with high winter values was obtained at the urban traffic site whereas several peak concentrations were observed also in summer and spring at all sampling sites. Special events e.g. long range transport of Saharan dust were recorded over urban as well as rural areas in the order of 5-7 events per year, with a major frequency in the summer and spring periods. To determine the origin of the ambient air particles the PM10 composition was compared with the soil composition around the sites which had been analysed before in detail. The results show that enrichment factors change considerably for some elements when calculated by using real soil data instead of literature data. The influences of different sources on the PM10 load was investigated using factor analysis based on the element composition. A strong correlation was found between PM10 components and local soil dust suggesting strong contribution of resuspended local mineral dust to PM10 at the urban traffic site. The elemental composition of PM10 was compared in three typical sites. The results demonstrate that at the urban traffic site local mineral dust, anthropogenic and sea-salt components accounted for a mean of 19%, 33% and 15% of PM10 mass respectively and at the urban residential site these accounted as 23%, 20% and 15% respectively whereas at the rural site local mineral dust and sea-salt accounted for a mean of 39% and 21% respectively. Peaks of mineral dust and sea-salt contribution to PM10 were recorded during Saharan dust events. Thus, because of the dry conditions on the island resuspension of local mineral soil particles contribute decisively to the PM10 load at rural as well as at urban sites. Finally, the results demonstrated that at the urban traffic site the largest contribution to PM10 is traffic (exhausted and resuspended particles) while at the rural background site, local soil dust together with sea-salt source types have the largest contribution to PM10 considered as being of natural origin.

9B-3

PM2.5 EPISODES USING SEMI-CONTINUOUS INSTRUMENTS AT THE BALTIMORE SUPERSITE AT PONCA STREET, Seung Shik Park, David Harrison, Narayanan P Nair, JOHN M ONDOV, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742; Jan Kleissl, Vijayant Kumar, Dept of Geography and Environmental Engineering, The Johns Hopkins University, Baltimore, MD

Highly time-resolved measurements of PM2.5 nitrate, sulfate, and elemental and organic carbon (EC and OC) were made at intervals ranging from 10 minutes to 1 hour from February 14th through the end of November, 2002, at the Baltimore Supersite at Ponca St. using commercial and prototype semi-continuous instruments. Additionally, particle size distributions (9 nm to 20 µm), criteria gas (CO, NO/NO2, and O3), and meteorological data were measured at 5-10 minutes intervals. During the entire study period, a total of 13 PM2.5 pollution episodes, each in which 24-h averaged PM2.5 mass concentrations exceeded 30.0 µg/m3 for one or more days, were observed. Herein, 6 of these episodes (A-F) were identified as follows: A, C, and E, regional transport combined with elevated O3 levels; B, Canadian Forest Fires; D, a mixture of regionally transported and local traffic emissions; and F, local traffic dominated stagnation period. During these events, PM2.5 elevations were often due largely to elevations in the concentration of one or two of the major species. The most pronounced features during the regional haze episodes (A, C, D, and E) were multi-day incursions of air masses with elevated sulfate concentrations. For example, in Episodes A, C, and D, maximum hourly sulfate (assumed to be ammonium sulfate) accounted for up to ~80% of the maximum hourly PM2.5 mass. Organic matter, accounting for up to 60% of the PM2.5 mass, was on average the second largest contributor in these episodes. Short-term excursions in OC, EC, nitrate, CO, and NOx levels were often observed in the morning hours. For example, during the second highest hourly PM2.5 excursion (87 µg/m3) of the study period, OC (as organic matter) was ~65% of PM2.5 mass and was observed along with very high EC, CO, and NOx levels. The results described herein show that concentrations of PM2.5 and its major constituents vary enormously on time scales ranging from <1 hr to several days, thus imposing a more highly complex pattern of pollutant exposure than can be captured by 24-hr integrated methods, alone. Lastly, local sources are shown to be important contributors to PM2.5 episodes and transients, especially, in cooler months.

9B-4

INFLUENCE OF URBAN EMISSIONS ON RURAL GAS AND PM CONCENTRATIONS, ERIC S. EDGERTON Atmospheric Research & Analysis, Inc., 410 Midenhall Way, Cary, NC 27513. Benjamin E. Hartsell Atmospheric Research & Analysis, Inc., 720 Ave. F, Ste. 220, Plano, TX 75074. John J. Jansen Southern Co., 600 18th Street N, Birmingham,AL 35291. Callie J. Waid Atmospheric Research & Analysis, Inc., 720 Ave. F, Ste. 220, Plano, TX 75074

The SEARCH network includes 8 research sites in four rural-urban pairs. Each site is equipped with an array of equipment to measure meteorological variables, dry light scattering and trace gases (O3, CO, NO, NO2, HNO3, NOy and SO2) with 1-minute time resolution. PM2.5 mass, black carbon, organic carbon, ammonium, nitrate, and sulfate are measured with 24-hour (filter based) and hourly, or better, time resolution. The network configuration and measurement density permit examination of air mass movement and exchange on a variety of temporal and spatial scales. This presentation will look at the influence of urban emissions on regionally representative sites. Two site-pairs will be discussed: one inland and one near the Gulf of Mexico. The inland pair includes Yorkville, GA and Jefferson Street (Atlanta), GA, while the near-coastal pair includes OLF, FL and Pensacola, FL. Yorkville is rural-agricultural and located about 55 km WNW of downtown Atlanta. The meteorology of north GA is such that air mass transport form Atlanta to Yorkville occurs several times per week. This is evidenced by substantial increases in CO and NOy concentrations (primary pollutants) and sometimes by modest increases in HNO3 and O3 concentrations (secondary pollutants). Depending on time of year, the CO:NOy ratio may be appreciably higher than observed at Jefferson Street, indicative of photochemical processing. PM concentrations may also increase at the same time as CO or NOy. In some cases, incremental PM is largely carbonaceous, while in other it is largely ammonium nitrate. Analysis of short-term data suggests the carbonaceous material is transported to Yorkville, while the ammonium nitrate may be formed through reaction between transported HNO3 and locally emitted NH3. OLF is a suburban site located approximately 20 km NW of downtown Pensacola, FL. The meteorology of this area is typical of the Gulf Coast and is more or less dominated by land breeze/sea breeze circulation. Depending on the synoptic meteorology, the sea breeze may advect air from Pensacola to OLF, or it may advect relatively clean air from the Gulf of Mexico to OLF. This fairly subtle difference in transport direction allows us to examine the influence of Pensacola on OLF. As for Yorkville, influence of the urban air mass is detected by increased CO and NOy concentrations; however, shorter transport times limit processing and consequent production of secondary species between Pensacola and OLF. PM exhibits small (1-3 ug/m3) increases during CO excursions and increment mass is generally associated with carbonaceous matter.

9B-5

AIR QUALITY MONITORING STRATEGY IN DENMARK,

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The air quality monitoring strategy in Denmark is based on measurements of many parameters in different representative environments, i.e. local (”hot spots”, streets), urban background, rural background and real background (remote, elevated from surfaces). The objectives are to determine the contribution from different sources, e.g. traffic, general urban sources, regional pollutants and large scale and natural background pollutants. The measurement set-up can be considered as a “super site” The data obtained from such “super sites” are useful for application of receptor modelling and for assessment of possible measures to reduce air pollution effectively. The use of more types of sites in an area is used to give the super sites another dimension, which facilitates the use of measurement data. E.g. subtraction of urban background data from street pollution data are used for determination of the traffic contribution to PM, NOx etc. The large-scale background is estimated by measurements in a bridge tower 250 m above ground. The data are analysed by using advanced receptor models for determination of source contributions in different scales.

9C-1

SEASONAL AND SPATIAL TRENDS IN PARTICLE NUMBER CONCENTRATIONS AND SIZE DISTRIBUTIONS AT THE CHILDREN'S HEALTH STUDY SITES IN SOUTHERN CALIFORNIA,

MANISHA SINGH, Harish C. Phuleria, Constantinos Sioutas, University of Southern California, Los Angeles, CA; Kenneth Bowers, California Air Resources Board, Sacramento, CA

Continuous measurements of particle number, particle mass (PM10) and gaseous copollutants (NOx, CO and O3) were obtained at eight sites (urban, suburban and remote) in Southern California during years 2002 and 2003 in support of University of Southern California Children's Health Study. We report the spatial and temporal variation of particle numbers and size distributions within these sites. Higher average total particle number concentrations are found in winter (November to February), compared to summer (July to September) and spring (March to June) in all urban sites. Contribution of local vehicular emissions is most evident in cooler months, whereas effects of long-range transport of particles are enhanced during warmer periods. The particle size profile is most represented by a combination of the spatial effects eg. sources, atmospheric processes and meteorological conditions prevalent at each location. Afternoon periods in the warmer months are characterized by elevated number concentrations that either coincide or follow a peak in ozone concentrations, suggesting the formation of new particles by photochemistry. Results show no meaningful correlation between particle number and mass, indicating that mass based standards may not be effective in controlling ultrafine particles. The study of the impact of the Union worker's strike at port of Long Beach in October 2002 revealed statistically significant increase in particle number concentrations in the 60-200 nm range ($p<0.001$), which are indicative of contributions of emissions from the idling ships at the port.

9C-2

IN-CABIN COMMUTER EXPOSURE TO ULTRAFINE AND NANOPARTICLES IN LOS ANGELES ROADS AND FREEWAYS: MEASUREMENTS WITH A NEW WATER-BASED CONDENSATION PARTICLE COUNTER.,

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High concentrations of ultrafine (UF, dp<100nm) and nanoparticles (NPs, dp<50nm) have been observed on or near freeways in urban areas by a number of investigators. A component of fine particles (PM2.5), UF particles are toxic to lab animals and are able to enter the circulatory system when inhaled. Thus, it is reasonable to expect that, as a result of increasing traffic congestions and commute times occurring worldwide, in-cabin exposure may constitute the most important route of exposure to toxic PM. Despite these findings, limited in-cabin information is available for human exposure to PM while traveling on congested freeways, or walking on sidewalks of city streets with high volume of traffic. We report the first set of in-cabin observations of particle number concentration (#/cm3) acquired with an all new water-based condensation particle counter (WCPC) while driving in Los Angeles roads and freeways. A TSI Inc. model 3785 WCPC, sensitive to fast-changing aerosol concentrations ranging from ca 10 nm to over 3 µm in diameter, was used to test two vehicles in this study: A model 2002 1.8T Jetta Wagon and a model 2004 Audi A4 1.8T passenger car, each equipped with a factory-installed high efficiency particulate matter filter (HEPA) followed by a bed of activated carbon. The driver and a passenger drove in typical high-traffic Los Angeles freeways and roadways, with varying fractions of heavy duty diesels vehicles, under a variety of in-cabin test vehicle parameters and operating conditions including open or closed windows, engagement of the vehicle air conditioning system and intake air, vehicle speed, and traffic conditions. In-cabin carbon monoxide (CO) concentrations were measured at one-minute intervals on a continuous basis by a TSI Model 8550 Q-Trak monitor. Our results show that, in general, while driving on freeways and surface streets, carbon monoxide (CO) concentration and particle number concentration went up and down together. Relatively low CO concentrations with high particle number concentrations were observed on freeways with free flow traffic. Dramatic increase in particle number concentration occurred when the vehicle went from local streets onto freeways. The highest on-board cabin particle number concentration, about 3.0e5 particle/cm3, was observed while driving on the I-710 (a major truck route with up to 25% heavy-duty diesels) and I-105 freeway with all windows open when traffic was moving at ~65 mph. The lowest particle number concentration, ~2,000 particle/cm3, was observed while the vehicle was at a shopping center's parking lot with the engine off and windows closed. The factory installed standard HEPA filter offers good protection against PM. Differences between observed highest and lowest particle number concentrations in this study were ca 130 times.

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9C-3

VOLATILITY AND CHEMICAL CHARACTERISTICS OF PM IN THE PROXIMITY OF A LIGHT-DUTY VEHICLE FREEWAY,

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Volatility properties of ultrafine particles were analyzed next to State Route 110 (Pasadena freeway, CA), a light-duty vehicle freeway, where heavy-duty traffic is prohibited. In addition, mass concentration and chemical composition of particulate matter (PM) were measured in coarse, accumulation, and ultrafine modes. On weekdays from May 17 to June 4 2004, measurements were performed in two locations, one very close to the freeway (within 2.5 m from the curb) and one at a distance of about 50 m to the freeway. For measurement of mass and chemical composition, the study employed in each location a Micro-Orifice Uniform Deposit Impactor (MOUDI) and a modified high-volume sampler. Both instruments sampled with the same size cut-points: a coarse mode from 2.5 µm to 10 µm, an accumulation mode from 0.18 µm to 2.5 µm, and an ultrafine mode of particles less than 0.18 µm in aerodynamic diameter. Alternately, a tandem differential mobility analyzer (TDMA) was used at the two sites. The first DMA selected particles of a certain diameter. A heater between the two DMAs evaporated volatile material from this monodisperse aerosol. The second DMA analyzed the losses of volatile components. The ultrafine number concentrations next to the freeway were 38300 1/cm3 on average during the sampling period. The MOUDI ultrafine mass concentration, nitrate, and EC were higher next to the freeway than at the background site, farther from the freeway. The other components analyzed in the ultrafine mode had similar concentrations next to the freeway and at the background site. Volatility ranged from about 65% volume losses of 120 nm particles heated to 110 °C, to 95% of 20 nm particles. The 20 nm aerosol was only internally mixed, whereas increasing non-volatile fractions were found for 40 nm (6% next to the freeway), 80 nm (20%), and 120 nm (28%) aerosols.

9C-4

DIURNAL VARIATION OF SUBMICRON PM SIZE DISTRIBUTIONS AND GASEOUS POLLUTANT CONCENTRATIONS DURING A YEAR 2004 IN PRAGUE, POLLUTION SOURCE ESTIMATION,

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Urban air quality is result of emissions both gaseous and particulate pollutants from numerous local sources, long range transport and meteorology conditions. Our three-years monitoring of gaseous components and meteorology parameters in urban atmosphere in Prague-centre revealed frequent (>30% of days) bi-modal pattern of diurnal variations of CO, NO, NO2, NMHC and partially SO2. The first mode appears between 8-9 a.m. and the second mode between 8-10 p.m. The gaseous pollutant concentrations within the peak time intervals are two to six times higher than their daily averages reaching 300 ppb for NOx in several cases. While the first peak is clearly associated with morning rush hour, the cause of the second peak is more difficult to apportion because there is no usual rush hour in Prague in the late evenings. To reveal whether bimodal pattern is reflected also in aerosol characteristics we conducted continuous measurement, besides gaseous components, of 5 minute integrates of aerosol size distributions (13.8 – 723 nm) during the second half of 2004 year. Aerosol number size distributions recorded during the first peak in the morning are monomodal (mean diameter - GMD near 40 nm) or in several cases bi-modal (40 nm and 70 nm GMD). Aerosol number size distributions recorded during the second peak are monomodal (near 70 nm GMD) in most cases. The appearance of the bi-modal pattern of diurnal variation is more frequent during calm air conditions but independent of wind direction or sun radiation. Therefore, the modes are not solely caused by emission from one point source or gas-to–particle process in ambient air. With regards to ultrafine sizes of particle emitted during these peak episodes, direct emissions from high–temperature processes have to be considered. Possible linkage between temporal variation of natural gas consumption in heating plants or apartments in the neighborhood and the bi-modal pattern of diurnal variation pollutant concentrations is also discussed. Acknowledgment The study was supported by GACR grant No. 205/03/1560

9C-5

INSIGHTS INTO THE CHEMISTRY OF NEW PARTICLE FORMATION AND GROWTH EVENTS IN PITTSBURGH BASED ON AEROSOL MASS SPECTROMETRY,

QI ZHANG, Jose-Luis Jimenez, CIRES, University of Colorado, Boulder, CO; Charles Stanier, University of Iowa, IA, Manjula Canagaratna, John Jayne, Douglas Worsnop, Aerodyne Research Inc., MA; Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA

New particle formation and growth events have been observed in several urban areas, and are of concern due to their potential negative effects on human health. The main purpose of this study was to investigate the chemistry of ultrafine particles during the growth phase of the frequently observed nucleation events in Pittsburgh (~ 100 events per year 1), and therefore infer the mechanisms of new particle growth in the urban troposphere. An Aerodyne Aerosol Mass Spectrometer (AMS) and two SMPS systems were deployed at the EPA Pittsburgh Supersite during September 2002. Significant nucleation events were observed in three out of the sixteen days of this deployment, including one of the 10 strongest nucleation events observed in Pittsburgh over a period of 15 months. These events appear to be representative of the climatology of nucleation events in the Pittsburgh region. Distinctive growth of sulfate, ammonium, organics and nitrate in the ultrafine mode (33 – 60 nm in vacuum aerodynamic diameter or ~ 18 – 33 nm in physical diameter) was observed during each of these 3 events, with sulfate always being the first, and the fastest, species to increase in size and mass. Ultrafine ammonium usually increased 10 – 40 min later than sulfate, causing the ultrafine mode particles to be more acidic during the initial stages of the nucleation events. Significant increase of ultrafine organics often happened after 11:00am, when photochemistry is more intense. This observation, coupled with a parallel increase of ultrafine oxygenated organic compounds, indicates that secondary organic species contribute significantly to the growth of particles at a relatively later time of the event. Among all these four species, nitrate was always a minor component of the ultrafine particles and contributed the least to the new particle growth.

10A-1

TIME RESOLVED ORGANIC MOLECULAR ANALYSIS BY PHOTOIONIZATION AEROSOL MASS SPECTROMETRY (PIAMS),

MURRAY JOHNSTON, Michael Tolocka, Matthew Dreyfus, Berk Oktem, University of Delaware, Newark, DE

A new method has been developed for rapid analysis of organic compounds in aerosols between about 40 and 500 nm in diameter. Particles enter the mass spectrometer through an aerodynamic focusing inlet and deposit on a probe inside the source region. After a sufficient amount is collected, the sample is irradiated with a pulsed infrared laser beam to flash evaporate semi-volatile organic (and inorganic) components. The vaporized components are photoionized with 10.5 eV radiation from a second laser and then characterized by time-of-flight mass spectrometry. The photoionization energy is large enough to permit detection of most organic compounds, but sufficiently low to inhibit molecular fragmentation. Experiments with test aerosols show that both aliphatic and aromatic hydrocarbons give intense molecular ion signals. Aromatic compounds give little or no fragment ions whereas aliphatic compounds do exhibit some fragmentation. A linear relationship between signal intensity and amount deposited on the probe is observed. For a given amount of analyte sampled, the signal intensity is independent of particle diameter. Preliminary studies using off-line sampling of specific particle sources show that each yields a unique signal intensity distribution that is consistent with previous GC-MS work. Diesel exhaust from an idling bus showed a number of peaks that can be attributed to unburned fuel droplets consisting of high molecular weight hydrocarbons. Gasoline exhaust from an automobile loaded with 93 octane gasoline showed peaks corresponding to a variety of semivolatile alkyl aromatics. Meat cooking aerosol showed peaks corresponding to cholesterol, palmitic acid and stearic acid among others. Wood smoke showed enhanced signals corresponding to levoglucosan, 4-ethylsyringol and 4-propylsyringol. Cigarette smoke showed an enhanced signal corresponding to nicotine. The time resolution for ambient measurements with PIAMS is determined by the time required to deposit a detectable amount of material. Current molecular detection limits with PIAMS are in the low pg range. A particle concentrator and high-flow rate aerodynamic focusing inlet are being installed to increase the effective aerosol flow rate to 30 L/min. With these devices, it should be possible to detect organic compounds at the 1 ng/m3 level with a 1 minute sample collection period. Experiments to explore this possibility will be performed in early 2005. PIAMS has also been used to study the ozonolysis kinetics of organic compounds in smog chamber experiments and to study the formation and growth of carbonaceous particles in flames. Each of these applications will be discussed.

10A-2

PARTICLE SAMPLER FOR ON-LINE CHEMICAL AND PHYSICAL CHARACTERIZATION OF INDIVIDUAL ORGANICS,

HACENE BOUDRIES, Kenneth A. Smith, Massachusetts Institute of Technology, Cambridge, MA; John T. Jayne, Douglas R. Worsnop, Aerodyne Research, Inc., Billerica, MA

In this presentation, an innovative particle sampler for sampling and collecting sufficient sub-micron aerosol mass in an artifact-free manner for analysis of organics species by GC/MS will be presented. Aerosols are crucially important due to their role they play in affecting the Earth's climate, including their influence on perturbations of the earth's direct radiative balance and cloud microphysics, and their impact on human health effects. The main purpose of this particle sampler is to improve the measurements of individual organic compounds present in/on aerosol particles. This prototype particle sampler offers the capability to collect both laboratory and ambient particles, thermally desorb and efficiently transfer the desorbed chemical species to any attached gas phase analytical detector for on-line quantification and speciation of particulate organic composition. This particle sampler system will provide on-line measurement with improved time resolution (less than 1 hour) size-resolved chemical speciation of organics aerosol composition. Vacuum techniques separate the particles from the gas phase via an aerodynamic lens to focus the aerosol beam and a particle velocity selector device to size resolve the particles to be collected and sampled. The collected particle mass is then thermally desorbed and analyzed with appropriate analytical detectors. This approach greatly minimizes artifacts due to evaporation and condensation compared with current filter collection and extraction techniques used for identification and quantification of individual organic species present in/on aerosols and will make use of the wide array of gas phase analytical methods. Different classes of organic aerosol will be collected using collection times varying between 1 (for laboratory generated aerosols) and 45 minutes for ambient air. Samples tested will include laboratory generated aerosols of oleic acid, diesel fuel, lubricating oil and ambient aerosols.

10A-3

USING AEROSOL CIMS TO INVESTIGATE THE ROLE OF PARTICLE SUBSTRATE EFFECTS IN DETERMINING THE REACTIVITY OF ORGANIC AEROSOLS,

John D. Hearn, Amanda J. Lovett, GEOFFREY D. SMITH, University of Georgia, Athens, GA

Aerosols in the atmosphere are often composed of internally-mixed particles containing many different species. Such complicated mixtures may significantly alter the reactivity of individual components with trace gases by affecting particle morphology and properties such as diffusion and solubility. As such, laboratory measurements of reactive uptake by pure liquid films or pure liquid droplets may not be relevant to the atmosphere. We have begun to explore the interaction between different types of particle constituents and the subsequent effects on their reactivity. The reaction between gas-phase ozone and particles containing a mixture of unsaturated (reactive) and saturated (unreactive) species is used as a model system. These viscous (even solid) particles are believed to more closely resemble organic particles found in the troposphere. Furthermore, these reactions are representative of the oxidative processing which may potentially alter many critical properties of organic particles, including hygroscopicity and the ability to act as cloud condensation nuclei. We measure the rates of reaction of internally-mixed organic particles with ozone using our Aerosol CIMS (chemical ionization mass spectrometry) instrument. This technique provides online, quantitative information about the composition of particles as well as the gas phase. It is particularly well-suited to the study of organic species since the chemical ionization affords mass spectra with very little fragmentation as well as the flexibility to detect many different types of molecules. The reactive loss of unsaturated organics, such as oleic acid, are monitored in internally-mixed particles also containing substrates of various saturated organics, such as stearic acid. The measured rate of reaction is investigated as a function of both the amount and identity of the substrate molecules. In addition, the simultaneous appearance of reaction products is monitored, and the volatility of these species is measured as a function of particle composition. The findings of these studies will be discussed in the context of using specific molecular markers in the source apportionment of particulate matter.

10A-4

CHARACTERISTICS OF PRIMARY AND OXYGENATED ORGANIC AEROSOLS IN MULTIPLE URBAN, RURAL, AND REMOTE ATMOSPHERES,

QI ZHANG, Jose-Luis Jimenez, Katja Dzepina, Edward Dunlea, Alex Huffman, CIRES, University of Colorado, Boulder, CO; M. Rami Alfarra, James Allan, Paul Williams, Hugh Coe, Keith Bower, The University of Manchester, Manchester, UK; Douglas Worsnop, Manjula Canagaratna, Aerodyne Research Inc., MA; Frank Drewnick, Max Planck Institute, Mainz, Germany; Silke Weimer, Ken Demerjian, SUNY-Albany, NY; Alice Delia, Scripps Institution of Oceanography, CA

A recently developed procedure (Zhang et al., this conference) was applied to Aerodyne Aerosol Mass Spectrometer (AMS) data to estimate the mass concentrations and size distributions, and extract the mass spectra (MS) of primary and oxygenated organic aerosols (POA and OOA respectively) in multiple locations throughout the world. Urban locations include Pittsburgh, Mexico City, New York City, Houston, Boulder, Manchester UK, and Edinburgh, UK. Rural and remote locations include Storm Peak (Colorado), Duke Forest (North Carolina), Trinidad Head (California), Cheju Island (Korea), and Mace Head (Ireland). In this presentation, the mass concentrations and fractions, temporal variations, extracted MS, and size distributions, of POA and OOA from these locations will be discussed and compared. Results from three US EPA Supersites – Pittsburgh, Houston, and New York City – will be emphasized. Primary (combustion) aerosols represent a significant fraction of the organic aerosol in cities, although OOA is often larger, especially in the summer. OOA may comprise both secondary organic aerosol (SOA) and products of the oxidation of primary aerosol. Freshly-emitted combustion POA appear as a distinct mode at small vacuum aerodynamic diameters at all urban locations, which is confirmed by “chase studies”, during which an AMS sampled the emissions of individual vehicles. OOA is generally concentrated in the accumulation mode, even in cities, indicating that most SOA condensation occurs on regional rather than urban scales. Organic aerosols at rural and remote locations are almost always dominated by OOA. While the material measured as OOA may contain the products of the oxidation of primary aerosols, the diurnal profiles and size distributions of OOA suggest that at least a significant fraction of this component is secondary in origin. These data also indicate that OOA is possibly internally mixed with sulfate. The mass spectra and size distributions of primary and oxygenated aerosols extracted with this procedure will be compared at the locations above.

10A-5

DEVELOPMENT AND APPLICATION OF A MASS SPECTRA-VOLATILITY DATABASE OF COMBUSTION AND SECONDARY ORGANIC AEROSOL SOURCES FOR THE AERODYNE AEROSOL MASS SPECTROMETER,

Brenda Klingbeil, Sulekha Chattopadhyay, PAUL ZIEMANN, University of California, Riverside, CA; Alex Huffmann, Jose-Luis Jimenez, University of Colorado, Boulder, CO; Douglas Worsnop, John Jayne, Aerodyne Research, Billerica, MA

This talk describes research being performed as part of the US EPA STAR Program on Measurement, Modeling, and Analysis Methods for Airborne Carbonaceous Fine Particulate Matter (PM2.5). In this project, we are developing and applying a thermodenuder-Aerodyne Aerosol Mass Spectrometer (TD-AMS) technique for ambient organic fine particle analysis, which through its application will improve the understanding of organic aerosol formation mechanisms and sources, and add valuable new data for use in source apportionment modeling. The objectives of this project are the following: (1) construct and couple a thermodenuder to the AMS and evaluate and optimize its performance, (2) use the TD-AMS technique in laboratory studies to develop a mass spectra-volatility database for the major atmospheric sources of combustion aerosol (including gasoline and diesel fuel, wood, and meat cooking) and secondary organic aerosol (formed by oxidation of anthropogenic and biogenic compounds), and (3) apply the database to a TD-AMS study of organic aerosol in the Los Angeles Air Basin. To date, progress has been made on system development and evaluation, laboratory studies of organic aerosol sources, and field measurements. A thermodenuder system has been designed and constructed based on a model published by Wehner et. al, 2002. The first tests were designed to confirm that the instrument was working according to specifications set by the authors of the design. The heating tube was tested for performance, and optimized to flatten the temperature profile over the desired heating stage. Based on results indicating that vapor re-condensation could introduce significant errors into the analysis, some aspects of the system are being re-designed to keep the temperature elevated to an optimal level until the point at which the vaporized material is able to interact with the activated charcoal adsorbing media. Passing efficiencies were also measured to verify that particles were passing through the instrument with minimal losses due to diffusion and thermophoresis. These tests outlined areas of sub-optimal temperature and passing performance that are being further investigated. Although the design of the thermodenuder is not yet optimal, it operates sufficiently well that it was deployed alongside an AMS as a part of the NEAQS-ITCT at Chebogue Point, Nova Scotia for three weeks in July 2004. This was the first time the TD-AMS system was used for ambient particle analysis. In addition to using the study to add the volatility dimension to the data set, it was important to employ the instrument under field study conditions to help determine design aspects that could be improved. During the study, we determined that the time for switching to lower temperatures is too long for our needs, and we are now redesigning part of the heating unit to speed up the temperature ramp. Overall, however, the thermodenuder worked well in the field, and produced reasonable particle volatility results. Recently, the thermodenuder has also been interfaced to a thermal desorption particle beam mass spectrometer (similar to an AMS) at the University of California, Riverside to obtain mass spectra-volatility information on secondary organic aerosol formed in environmental chamber reactions.

10B-1

ESTIMATION OF UNCERTAINTIES IN AEROSOL SIMULATIONS DUE TO EMISSION INVENTORY UNCERTAINTY USING CMAQ-DDM,

Di Tian, Yongtao Hu and Armistead G. Russell, School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA

Emission-based models are often used to understand the complex relationships between emission sources and air pollutant concentrations in the atmosphere. However, due to the details and tremendous work involved in developing emission inventories, and the limitations in resources, emission inventories are always uncertain to some extent. This study aims to evaluate the impact of emission inventory uncertainty on aerosol simulations using CMAQ-DDM, which can calculate, simultaneously, the aerosol concentrations and sensitivities of aerosol concentrations to different emission sources. Emission inventory uncertainties in this study are based on literature review of other studies and expert elicitation when no detailed studies for some emission sources are available. Uncertainties of aerosol prediction due to these uncertainties are propagated through first order approximation method with consideration of correlation between some emissions sources (e.g. NOX and VOC emissions from mobile sources). The method introduced by this study will provide a practical way to quantify uncertainties in aerosol prediction and the results will serve as necessary information for policy making.

10B-2

IMPLEMENTATION OF THE DIRECT DECOUPLED METHOD (DDM) INTO THE CMAQ MODEL FOR AEROSOL SPECIES, SERGEY NAPELENOK, Dan Cohan, Ted Russell, Yongtao Hu, Georgia Institute of Technology, Atlanta, GA

The Direct Decoupled Method in three dimensions (DDM -3D) for computing aerosol sensitivities was integrated into the EPA's air quality model CMAQ. This work was an extension to a previous effort to implement DDM for gas-phase species by Cohan, et al., 2003. The DDM method directly calculates the three-dimensional, time-resolved sensitivities by solving the coupled, non-linear, partial differential equations that govern the formation, transport, and removal mechanisms for aerosols and gas species. This is done at each model time-step using the same subroutines already in place in the model to calculate concentrations. CMAQ processes that are important for aerosol sensitivities include transport algorithms, gas phase chemistry, aerosol chemistry and dynamics, and cloud chemistry and dynamics. ISORROPIA was used as the basis for computing sensitivities of aqueous species equilibrium. When feasible, the analytical derivatives of those processes are directly calculated. In the case of the inorganic equilibrium calculated by ISORROPIA, it is possible to take the derivative of the resulting matrix governing mass conservation and thermodynamic equilibrium of the various species. Sensitivities of sulfate, nitrate, ammonium, organic and elemental carbon, anthropogenic secondary organics, and biogenic secondary organics in both Aitken and accumulation modes are computed by this method. Here we apply the method to assess sensitivities of PM composition to emissions of gas species such as SO2, NOx and VOCs, as well as initial and boundary conditions. This can be done at a domain-wide scale as well as for individual point and area sources. This method has been tested by comparing to a more traditional brute force approach. The comparison shows that while there is room for improvement, it can be a time-efficient alternative to computing sensitivities using CMAQ via the brute force approach. --- Cohan, D., Hu, Y., Hakami, A., Russell, A., "Sensitivity Analysis of Ozone in the Southeast." Models-3 Users Workshop, October 27, 2003.

10B-3

PREDICTED RESPONSES OF INORGANIC PM TO EMISSION CHANGES FOR A CHEMICAL TRANSPORT AND AN OBSERVATION-BASED MODEL, SATOSHI TAKAHAMA, Robert W. Pinder, Cliff I. Davidson, Spyros N. Pandis, Carnegie Mellon University, Pittsburgh, PA

To meet air quality standards for PM2.5, it is desirable to evaluate the effectiveness of different emission control strategies. In the eastern United States, PM2.5 is primarily anthropogenic, with inorganic species accounting for approximately 50% of the mass (USEPA, 1996), and it is on this fraction that we focus for this study. PMCAMx is a 3-D chemical transport model that is conceptually ideal for this purpose, as it links emissions to PM2.5 concentrations through a mechanistic description of the atmospheric processes. However, uncertainties in the required inputs (emissions and meteorological variables) and its inherent complexity give rise to large uncertainties in the predictions (Seigneur, 2000). Observation-based approaches have been proposed as alternatives (West et al., 1999; Blanchard and Hidy, 2003). The Thermodynamic Model with Removal (TMR) is a semi-empirical box model that uses atmospheric measurements as inputs, simulates the partitioning and removal of semi-volatile inorganic compounds and predicts the inorganic PM2.5 mass concentration (Vayenas et al., 2004). The change in inorganic PM2.5 concentration to changes in emissions can be represented as the product of two responses: 1) the change in inorganic PM2.5 mass with respect to change in precursor concentrations and 2) the change in precursor concentrations with respect to emissions. TMR can be used to estimate the first component if suitable measurements are available. As an example, we calculate responses for 10, 30, and 50% reductions in sulfate, total ammonia, and total nitrate (total = PM2.5 + gas) for Pittsburgh for the summer of 2001 and winter of 2002. We simulate scenarios with the same magnitudes of reductions of emissions of SO2, NH3, and NOx directly with PMCAMx and compare the two predictions of the response of inorganic PM2.5 to emissions. The comparisons of simulation results from PMCAMx and TMR are analyzed in the context of evaluating emission control strategies for these inorganic compounds.

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10B-4

UNCERTAINTY ANALYSIS OF CHEMICAL MASS BALANCE RECEPTOR MODEL,

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Chemical mass balance (CMB) modeling is one of the more widely used receptor-oriented approaches for source apportionment with both scientific and air quality management applications. It is able to quantify not only source contributions but also associated uncertainties of the estimated impacts by incorporating input uncertainties from ambient measurement and source profiles. However, the calculated uncertainties are based on assumptions about the uncertainty structure, and do not include physical constraints. Here, we used data from 8 EPA STN monitoring sites that are distributed throughout Georgia to conduct an uncertainty analysis. These measurements include inorganic chemical speciation (inorganic ionic species and trace metal elements) and elemental and organic carbon fine particle (PM2.5) concentrations. Using this data, PM2.5 source apportionment was conducted for those sites by using CMB 8.0 covering a 23 month period from January 2002 to November 2003. These results serve as our best current estimation of source impacts. Probability distributions for ambient measurement and source profile data were developed for each species and profile assuming lognormally distributed data. Uncertainties in the source profiles were constrained by noting that the sum of individual components can not be greater than one. Random sampling from each distribution was done using midpoint Latin hypercube sampling (LHS) method, which gives more uniform sampling than Monte Carlo sampling method. CMB model was run about 300 times for each data point with 300 different input data from LHS. Total uncertainty of each source contribution was estimated from 300 model runs and then compared with those from the original source apportionment. Uncertainty contributions of each species to total uncertainty were also estimated to understand which species drive total uncertainty. This study provides information as to uncertainty of CMB model estimation for policy analysis, policy decision making, and health effect analysis of PM2.5, and which species and profiles are of greatest importance in the process as applied to the Southeast.

10B-5

UNCERTAINTY IN THE HEALTH DAMAGES FROM SO2,

VLADIMIR HLASNY

In regulating the amount of SO2 emissions from electric generators, the Environmental Protection Agency faces uncertainty regarding many factors of the production, emission stream and the associated health damages. This paper evaluates how SO2 emissions enter the calculation of damages, and how sensitive is the ranking of regulatory policies to the uncertainty in the damage function. The model uses a numerical simulation with empirical data to estimate plants' production and emissions-abatement cost functions, demand by energy consumers, transportation pattern of emissions, and damages caused by the resulting concentrations of SO2. Information on current power-generation and emissions-cleaning technologies, electricity demand, coal supply, and weather patterns is used to predict realistic behavior under all information and regulatory-instrument scenarios. Recent literature has estimated benefits from the Title IV of the Clean Air Act of two to ten times the costs of emission abatement. The great difference between the costs and damages stems from the ex ante uncertainty about the effects of the regulation, and from the political process of implementation. The broadness of the range of estimates stems mainly from the uncertainties in the valuation of emission damages. The medical literature estimates concentration responses for various health effects per small increase in the air concentration of SO2. The economic literature has taken these to imply linear response functions. This contrasts with the classical literature treating damages as step functions with a threshold of safe levels. The existence of "safe" concentration levels is indeed uncertain as the EPA itself acknowledges. In evaluating the sensitivity of the benefits from regulation and the ranking of policies, I use different parameters for the curvature of the response functions that satisfy the point estimates in the medical literature. I estimate the critical values for the curvature of the externality damages at which alternative policies dominate the system of marketable allowances in the net benefits. Surveys of medical literature report lower and upper bounds on many estimates. This uncertainty can be uniform for all receptor regions, or can enter non-uniformly. In the first case, our estimated damages are uniformly shifted, and our choice of policy instrument is unaffected. If the shock differs across plants, either stochastically or in coordination with other characteristics of the plants, our ranking of policy choices may change. If heterogeneity in the plants' cost functions is inadvertently related to the heterogeneity in the emission damages, the losses from a wrong policy may be substantial. Using the partial equilibrium framework for the energy market, I use the current state of restructuring in the energy industry and plants' cost and demand schedules to derive the equilibrium emissions at each plant. Given the large estimated health benefits of the Title IV, it seems appropriate to pay more attention to the externality damage function. If the true damage function is nonlinear in emissions or if it varies across regions, the Title IV may not be the best policy. There is curvature at which marketable permits would perform no better than the emission taxes. I test the sensitivity of the aggregate damages to the curvature of the damage function and demarcate the critical values, at which marketable permits perform as well as the competing policies.

10C-1

INVESTIGATING THE RELATIVE VALUE OF SPATIAL AND TEMPORAL DATA COLLECTION FOR EVALUATING AIR QUALITY MODELS USING THE GAS RATIO AS AN INDICATOR OF THE INORGANIC SYSTEM,

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A critical use of regional models of fine particulate matter is to predict changes in mass associated with changes in emissions. A related study showed that the Gas Ratio (GR) can be a useful construct to guide inquiry about the inorganic system and the potential nonlinearity of its response. Both gas and particle measurements are needed to define the GR, but these measurements are not routine. This study analyzes the relative value of spatial and temporal measurements of GR components with regard to evaluating air quality models and assessing changes in the future state of the inorganic fine particle system. Analysis with the Community Multi-scale Air Quality model, CMAQ, indicates there is a strong diurnal variation in total-nitrate and total-ammonia, but not sulfate, which may affect GR's and system response. A related study shows that GR's developed from monthly averaged data are not reliable indicators of change. While the calculation of GR's based on 24-hour average gas and fine particulate concentrations contains quality information, GR's based on 1-hour average concentrations provide a more accurate indication of system state throughout the day. As shown for the Pittsburgh supersite, hourly average concentrations are necessary to probe differences between model-derived and observation-derived GR's. Yet, information at a single site is not necessarily regionally representative. Analyses with CMAQ indicate there is strong spatial variability in GR's across the (Eastern) U.S. We are expecting significant changes in the near future in SO2 and NOx emissions. It is important that measurements be made that support the calculation of the GR to evaluate the regional air quality models and to track the reasons for future inorganic fine particle mass change, or lack of change. This study explores the spatial and temporal (monthly to daily to hourly) trade-offs for monitoring the constituents of the GR. Disclaimer: The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) under agreement number DW13921548. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

10C-2

SPATIAL INHOMOGENEITIES IN PM 2.5 CONCENTRATIONS AND THEIR EFFECT ON THE PERFORMANCE OF THE AIR QUALITY MODEL,

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The performance of an air quality model is typically judged from the relative agreement between simulated and measured pollutant concentrations. The goal of this paper is to determine if the spatial inhomogeneity of particulate matter could significantly affect the performance of air quality models and our performance expectations. For this purpose, we have conducted a series of analyses using simulated and observed pollutant concentration data in the United States: 1.Spatial inhomogeneities of particulate matter are analyzed in the Atlanta area for two years (2002-2003), and in the United States for two months (July 2001 and January 2002 -- ESP01/02) using performance metrics between measured concentrations at the monitoring site, and concentrations in surrounding areas. In the Atlanta area, we take advantage of two on-going campaigns where PM2.5 composition is being measured on a daily basis (SEARCH and ASACA). For the U.S., we us the STN results. 2.Effects of spatial inhomogeneities on the performance of the air quality models are investigated by classifying each station as one of four groups based on the statistical analysis of how the simulated pollutant concentration compares to the observation at a site and how the pollutant observation that site compares to surrounding sites. Sites are classified as a true positive(TP) group if the model performance is good with and without considering the spatial variation. Sites are classified as a false positive(FP) group if the performance of the model is good, but is shown to be poor when the spatial inhomogeneity is considered. Sites are classified as a false negative (FN) group if the performance of the model is poor, but is suggested to be good when the spatial inhomogeneity is considered. Sites are classified as a true negative(TN) group if the performance of the model is poor with or without considering the spatial variation. Results from the analysis of the spatial inhomogeneity show that in the Atlanta area, mean fractional errors are 6~16%(sulfate), 35~100%(nitrate), 14~22%(ammonium), and 5~36%(total carbon). At the larger scale, across the United States, spatial variability errors are 20%(PM2.5 mass), 28%(sulfate), 52%(nitrate), 37% (ammonium), 56%(elemental carbon), 55%(organic carbon), and 61%(crustal element). Mean fractional errors between observed and simulated concentrations in the United States are also calculated, and errors are larger for carbonaceous species and nitrate, which have relatively greater spatial inhomogeneities, suggesting that the spatial inhomogeneity might increase the disagreement between observed and simulated concentrations even if the model is correctly simulating the pollutant levels, i.e., the sites have a significant amount of "representativeness error". Such an error is important when assessing health effects. When percentages of wrongly judged sites(FP+FN) are examined by species, the fraction of wrongly judged sites is also larger for carbonaceous species and nitrate. In conclusion, this study shows that the comparison between observed and simulated concentrations itself is not enough to represent the performance of the air quality model in the presence of spatial inhomogeneity. Therefore, when an air quality model is evaluated, the spatial inhomogeneity should be analyzed in addition to the performance metrics between observed and simulated concentrations.

10C-3

EVALUATION OF A MODEL FOR PREDICTING FINE PARTICLE CONCENTRATIONS, ARI KARPPINEN, Mari Kauhaniemi, Jari Härkönen, Jaakko Kukkonen, Finnish Meteorological Institute, Helsinki, Finland; Anu Kousa, Tarja Koskentalo, Helsinki Metropolitan Area Council, Helsinki, Finland

Urban particulate matter originates from local mobile and stationary sources, from regional and long-range transport and from the suspended dust. Particles are also continuously formed, transformed and depleted by various physical and chemical processes. The atmospheric dispersion of vehicular emissions is evaluated using a roadside dispersion model, CAR-FMI (Härkönen, 2002). The model takes into account the effect of the non-exhaust vehicular emissions and particulate matter suspended from the street surfaces, using empirical correlations. The total contribution originated from traffic can be written as a sum of three terms: the contribution from exhaust emissions, the contribution of non-exhaust PM emissions and the contribution from cold start and cold driving emissions. The vehicular PM2.5 emissions were modelled to be dependent on vehicle travel velocity, separately for the main vehicle categories. The contribution of non-exhaust emissions was estimated using results presented in Tiitta et al., 2002. The influence of cold-start and cold driving emissions was modelled by estimating the cold start and cold driving emission separately in 283 areas in the Helsinki Metropolitan Area. The long range transport (LRT) contribution is evaluated on the basis of a statistical model utilising as input values the daily sulphate, nitrate and ammonium ion concentrations at the EMEP stations. (Karppinen et al., 2004) For comparing the model results with measurements, we utilized the hourly time-series of PM2.5 concentrations measured at the urban traffic station of Vallila in 2002. The station is located in central Helsinki and is part of the municipal air quality monitoring network of the Helsinki Metropolitan Area Council (YTV). On an yearly basis, the estimated contribution from regionally and long-range transported origin to the observed PM2.5 varies from less than 50 % in the centre of Helsinki to nearly 100 % in the outskirts of the metropolitan area. In winter (T < 0), cold starts and cold driving increased the amount of the exhaust emissions originated from local traffic approximately by 40 %. The resulting squared correlation coefficient between modelled and measured daily concentrations at Vallila is R2 = 0.60 while the bias between observed and modelled values was less than 5 %. The comparison of the daily averaged values with the corresponding measurements showed a satisfactory agreement. However, the model presented has several limitations. The accuracy of the LRT model depends critically on the chemical composition of long range transported PM2.5. Also the evaluation of the contribution from combustion and non-combustion emissions originated from local traffic causes big uncertainties. The term representing the contribution of non-exhaust PM emissions was estimated here to be directly proportional to the concentrations that originate from exhaust local vehicular emissions; however, the suspension caused by the traffic flow actually depends strongly on numerous other factors.

10C-4

ANNUAL MODELING OF INTERCONTINENTAL TRANSPORT OF PARTICULATE MATTER AND OZONE, CAREY JANG, US EPA

There is increasing evidence that air pollutants originating from regions outside of North America such as Asia could impact U.S. domestic air quality. At the same time, the U.S. is both an importer and exporter of air pollutants. A pioneer modeling project, the “Intercontinental Transport and Climatic Effects of Air Pollutants” (ICAP) project, has been undertaken at U.S EPA to help understand and assess these impacts associated with the intercontinental transport of air pollutants, including particulate matter (PM), ozone (O3), and mercury (Hg). The on-going modeling efforts include a series of modeling (108-km grid resolution) and emissions related activities over the pacific regions, including a 2001 Base year simulation, 2030 scenarios (IPCC’s A1B and B2 scenarios), and several sensitivity studies (e.g., removal of man-made Asian emissions and North America emissions, etc.). The trans-Atlantic modeling effort has also been under way. The key modeling tool used in this project is the Models 3/ Community Multi-scale Air Quality (CMAQ) modeling system developed at EPA. The trans-Pacific modeling results revealed that PM 2.5 and O3 can be transported across the Pacific Ocean over a time period of 5 to 10 days before reaching North America and the U.S. A sensitivity study by removing the Asian man-made emissions showed that the impact of Asian man-made emissions on North America appeared to be persistent through the entire year, although exhibiting seasonal variations. The spring (April) had higher impact for PM 2.5, up to 2 ug/m3 (monthly average) in the western U.S. and up to 1 ug/m3 in the eastern U.S., while the summer (July) and spring (April) has comparable impacts for O3, up to 5~6 ppb (daily max) in the western U.S. and up to 2 ppb in the eastern U.S. The results of future scenarios modeling indicated that sustainable development (IPCC B1 case) will have significant improvement over the continued growth (IPCC A1B case) on the air quality across the Pacific regions.

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10C-5

UNCERTAINTIES IN POLLUTANT TRANSPORT AND THEIR INFLUENCES ON AIR QUALITY MODEL PERFORMANCE,

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In 3-D air quality modeling, large errors are often found between the predicted and observed concentration fields at certain sites and time which can hardly be explained by the source and sinks or chemistry of the model. In time series and spatial plots we find that these large errors occur when the predicted and observed fields are out of phase. It strongly suggests that pollutants transport has not been predicted accurately. This is a clear indication of discrepancies between the predicted and actual wind fields that move the pollutants. It could be due to either the wind speed or wind direction or both. In this study a numerical experiment has been carried out to illustrate the influence of phase errors generated by inaccurate wind field on air quality model performance. It is found that at any downwind site model prediction could easily be off by a factor of 2-3 with only a few hours phase shift in the predicted time series. The accuracy of the source and sinks and chemistry in the model affects essentially the predicted pollutant amplitude but rarely the phase shift. Given the current understanding of the air quality science, the influence of amplitude error is likely much smaller than that of the phase error on model performance. Thus, improving model dynamics is the key to the success of air quality model predictions.

11A-1

USE OF FIELD DATA TO ESTIMATE EMISSION RATIOS OF PARTICULATE AND GASEOUS SULFUR, NITROGEN AND CARBON FROM BIOMASS BURNING IN THE SOUTHEASTERN U.S.,

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Biomass burning is an important source of atmospheric particles and gases in many parts of the world. Extensive burning occurs in the southeastern U.S. during fall and winter, both as a source of heat and also as a means of disposal for accumulated stocks of carbonaceous material. Relatively large fires, which can last several days or longer, provide opportunities to measure combustion products and to gain an understanding of emissions for a range of particles and gases. SEARCH is a long-term research program investigating spatial and temporal variability of fine particulate matter, and gases across the southeastern U.S. The SEARCH network includes 8 research sites in four rural-urban pairs. Each site is equipped with an array of equipment to measure meteorological variables and trace gases (CO, NO, NO2, HNO3, NOy and SO2) fine particulate mass, elemental carbon, ammonium, nitrate, and sulfate with 1-minute temporal resolution; CO2, fine particulate organic carbon and total carbon with hourly time resolution. This paper uses data from SEARCH to estimate emissions ratios for carbon (CO2, elemental carbon, organic carbon), nitrogen (NO, NOx, particulate nitrate and ammonium) and sulfur (SO2 and particulate sulfate) in several biomass-burning events. Emissions ratios are calculated relative to CO, since this is a relatively stable tracer species and because it is measured with high sensitivity and frequency. Resulting emission ratios are compared across events and then with non-biomass sources (e. g., urban and point source plumes) to evaluate robustness and uniqueness of signatures. Similarities and differences between observed ratios and those from other types of biomass burning (e.g., rain forest and savannah) are discussed.

11A-2

CASE STUDY OF LOCAL ACCUMULATION OF PM2.5 FROM PRESCRIBED BURNING WITH CONSEQUENCES FOR ATTAINMENT,

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During a three-week period in the fall of 2001 the 24h NAAQS for PM2.5 of 65 g m-3 was exceeded on five different days at a research monitoring site (OLC) at Columbus, GA operated as part of the Fall line Air Quality Study (FAQS). The worst exceedance occurred at a peak concentration of 448 µg/m3, and contributed to an annual mean of 16.9 µg m-3, which is 1.9 µg m-3 above the NAAQS. Exclusion of these five exceedances yields an annual mean of 14.4 µg m-3, achieving attainment. These high PM pollution levels were not observed at the other FAQS sites across Georgia, and even not at the two regulatory monitoring sites within the city of Columbus itself, although the two sites are only about 5 km and 11 km north of OLC, respectively. At both sites, the 24-h integrated PM2.5 mass concentration measurements followed the Federal Reference Method (FRM), and due to the one in three day sampling schedule, the main pollution episodes were missed. Witnessed by local residents and confirmed by burn records, all episodes could be attributed to emissions from large wild fires and prescribed burn activities originating on the military installation extending from 2 to 30 km east of OLC. The wild fires here occurred similar to prescribed burns, in that only the 2-3 year rough and needle brush in the forest’s understory burned. Examination of local measurements, in particular highly resolved PM2.5 mass, trace gas species and various meteorological parameters point to an important influence of local meteorological conditions. For example, local wind speed and daily maximum and minimum air temperature indicate significant nighttime cooling and give rise for a stably stratified nocturnal boundary layer (BL), inhibiting effective dilution of surface emissions such as smoldering biomass. A Principal Component Analysis (PCA) of various parameters and variables was performed, combining the location and size of the pollution source (wild and prescribed fires), OLC receptor measurements of pollutants (PM2.5 mass) and meteorology (wind speed, max/min air temperatures), with products from sub-regional weather forecasts (BL height, smoke dispersion index, plume trajectory, and average speed of advected air mass). Results of the PCA are presented and compared with results from CMB source apportionment of gas-phase organic compounds (VOC) and particle-phase organic species (POC) measured at OLC in winter/spring of 2003, utilizing experimentally determined source profiles of the near-by prescribed burning source. Both VOC and POC contributions from the prescribed burn-type fires were highest at nights under conditions that favored the formation of shallow nocturnal BL under clear skies and effective radiative cooling of the ground, inducing weak catabatic flows along two creeks across the military installation and toward OLC. Therefore, surface emissions such as the flaming and smoldering of prescribed fires can accumulate near the ground at night, and potentially carry pollutants emitted from still smoldering burns to relatively distant ambient receptor sites, here as far as 30 km. From the sensitivities established between the emissions sources and the forecasted meteorological parameters, strategies for minimizing local pollutant loads and optimizing the burn forecasts are elaborated.

11A-3

ORGANIC COMPOUND CHARACTERIZATION OF EMISSIONS FROM PRESCRIBED BURNS, WILDLAND FUELS, AND RESIDENTIAL WOOD COMBUSTION,

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Biomass combustion emissions arising from naturally occurring wildfires, anthropogenically generated prescribed burns, and residential wood combustion contribute greatly to atmospheric fine particulate matter (PM2.5). Wildland fire emissions are different from emissions of residential wood combustion due to differences in fuel composition and biomass structure, season of occurrences, time of day, and the local environment such as the slope of the ground, ambient temperature, and wind velocity. These environmental factors lead to some differences in ratios of known molecular markers, thus apportionment of wildland smoke using residential wood smoke source profiles may miss-represent the impact of smoke during the wildfire season. To provide new insight to biomass combustion emissions, sampling was conducted in several types of conditions. Carefully controlled conditions were employed for the simulation of residential wood combustion using a fireplace and a dilution sampling system at the Desert Research Institute. Additionally, controlled biomass combustion sampling was conducted at the USFS Fire Sciences Laboratory Combustion Facility to examine the emissions of several wildland fuels, including conifer needles, wildland grasses, and sagebrush. In-field open-area prescribed burning sampling was also conducted in the Mariposa Sequoia Grove within Yosemite National Park, in central rural Nevada, where desert brushes were the dominate species, and in the Toiyabe National Forest of the Sierra Nevada, where conifer trees are the dominate species. In all cases semi-volatile organic compounds (SVOC) samples were collected using a PM2.5 cyclone and Teflon-impregnated glass fiber (TIGF) filters followed by polyurethane foam (PUF) and XAD resin sandwich cartridges. Additional samples were collected using 47mm quartz and Teflon membrane filters for carbon analysis by thermal optical reflectance (TOR) method and gravimetric measurements, respectively. Semi-volatile organic characterization was conducted by gas chromatography coupled with mass spectrometry (GC/MS) using internal standard quantitation methods with addition of several deuterated internal standards prior to extraction. Variability of organic compounds found in biomass combustion emissions were examined in this study. Organic makers such as levoglucosan, methoxylated phenols, methoxylated organic acids, and resin acids vary considerably for wildland fuels. Comparison of these fuels and prescribed burn emissions to residential wood combustion indicate a large difference in the mass percentage of marker compounds such as levoglucosan. Thus, source profiles specific for wildland fires are needed to understand the true influence of these emissions to the ambient environment.

11B-1

INVERSE MODEL ESTIMATION OF SEASONAL NH3 EMISSIONS, ALICE GILLILAND, Robin Dennis, Shawn Roselle; National Oceanic and Atmospheric Administration, Air Resources Laboratory, Atmospheric Sciences Modeling Division (on assignment to National Exposure Research Laboratory, U.S. Environmental Protection Agency, RTP, NC); Rob Pinder Department of Engineering and Public Policy, Department of Civil and Environmental Engineering, Carnegie Mellon University, Pittsburgh, PA

The formation of ammonium nitrate aerosols is often limited by ammonia (NH3), and sulfate aerosols are predominantly in the form of ammonium sulfate. While NH3 plays a central role in the prediction of nitrate and sulfate aerosols, inherent uncertainty exists in NH3 emissions because of the predominant sources, animal husbandry and fertilizer application. The temporal variability in fertilizer application and the meteorological dependence of NH3 volatilization from animal waste suggest that a strong seasonal variability should be expected in the emissions. Current work by Pinder et al. [2004] provides the first farm-level model for NH3 emissions from dairy cattle, and Goebes et al. [2003] provides a seasonally varying fertilizer inventory for NH3. Top-down estimates of NH3 seasonally varying emissions for all combined source types have been developed by Gilliland et al. [2003] using an inverse modeling method. Currently, these studies provide the most comprehensive information available for seasonally distributing NH3 emissions for air quality modeling. Combining this information, we have constructed a best prior estimate of seasonal scaling factors for NH3 emissions. These emissions were then used in an annual 2001 simulation using the USEPA Community Multiscale Air Quality (CMAQ) model for a contiguous United States domain. The objective of this study is to evaluate the reasonableness of these prior NH3 emission scaling factors and then test the inverse modeling method used to produce revised top-down seasonal scaling factors for the modeling domain. First, we will describe the approach used to generate our best prior estimate of NH3 seasonal scaling factors and present the posterior inverse modeling emission estimates. Evaluation results against precipitation chemistry and speciated aerosol data will then be presented with a primary focus on monthly and seasonal time scales. Based on these results, we will then consider whether the inverse modeling results provided substantial improvements to the model performance and whether modifications are needed to the current inverse method for this application.

11B-2

IMPROVEMENTS TO REGIONAL AIR QUALITY MODELING FROM RECENT ADVANCES IN AMMONIA EMISSION INVENTORY DEVELOPMENT, ROBERT W. PINDER, Peter J. Adams, Carnegie Mellon University, Pittsburgh, PA; Alice B. Gilliland, Atmospheric Sciences Modeling Division, Air Resources Laboratory, NOAA, RTP, NC

Ammonia emissions from agricultural activities have significant temporal and spatial variation due to differences in climate and farming practices. However, most ammonia emission inventories used as input to regional air quality models do not explicitly account for these variations. Since ammonium nitrate aerosol is sensitive to changes in ammonia concentrations, the discrepancies between model-predictions and measurements can be large. Recent approaches have focused on two different techniques for calculating the seasonal variation in ammonia emissions: process-based emission modeling and inverse modeling. Process-based emission models contain a detailed representation of the physical and chemical processes that govern ammonia emissions from livestock. Emissions are predicted as a function of climate variables and farming practices (Pinder et al., 2004). In the inverse modeling approach, measured wet concentrations of NH4+ and predictions from a regional air quality model are used to adjust emissions such that the model-measurement error is minimized (Gilliland et al., 2003). Both methods predict large seasonal differences in emissions. This research seeks to identify the similarities and differences in model predictions of aerosol nitrate from using these two different approaches to calculating ammonia emissions. Ammonia emissions are estimated using a process-based approach, the results of inverse modeling, and a temporally constant control inventory. These inventories are used as input to PMCAMx, a three-dimensional, regional air quality model. Time periods in January, April, July, and October are selected to identify seasonal differences. The air quality model output is compared to measured aerosol sulfate, nitrate, and ammonium from the Speciation Trends Network (STN). We also estimate the gas phase ammonia and nitric acid concentrations using a model of aerosol thermodynamics, and compare those estimates to the regional model predictions. Furthermore, we discuss the limit of improvements to ammonia emission inventories that can be expected from comparisons to aerosol measurements, and how these limitations can be mitigated by measurements of total ammonia (NH3+NH4) from PM supersites. References: Gilliland AB, Dennis RL, Roselle SJ, Pierce TE. (2003) Seasonal NH3 emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method. Journal of Geophysical Research – Atmospheres. 108 (D15): Art. No. 4477 Pinder RW, Strader R, Davidson CI, Adams PJ. (2004) A temporally and spatially resolved ammonia emission inventory for dairy cows in the United States. Atmospheric Environment. 38 (23): 3747-3756

11B-3

EVALUATION OF THE PRIMARY ORGANIC CARBON EMISSION INVENTORY FOR THE EASTERN UNITED STATES,

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PMCAMx+, a three-dimensional, chemical transport model, is used to simulate fine particle concentrations for July 2001 and January 2002 intensive periods. The modeling domain is the eastern half of the United States and the inventory is based on EPA National Emission Inventory. PMCAMx+ has been configured to track different types of organic and elemental carbon by source class such as diesel vehicles, gasoline vehicles, and wood smoke. The performance of PMCAMx+ for total organic particulate matter concentrations is been evaluated using data from the EPA Supersites and related studies, the EPA speciation trends network (STN), and the IMPROVE network. This talk compares the source-classified predictions of PMCAMx+ to receptor model predictions of the contribution of different primary sources to organic carbon in Pittsburgh, PA. The comparisons focus on the following source categories: gasoline vehicles, diesel vehicles, biomass combustion, and natural gas combustion. These categories represent more than 80% of primary organic carbon and elemental carbon emissions in the inventory. Receptor model predictions of source of primary organic carbon are made using the chemical mass balance model applied to a large data set of organic molecular markers. Comparisons are also made between the source-classified predictions of PMCAMx+ and molecular marker concentrations measured in Pittsburgh. Literature source profiles are used to estimate molecular marker concentrations from the source contributions predicted by PMCAMx+. Large discrepancies exist between the source-classified PMCAMx+ results and the receptor model predictions. For example during the summer predicts that more than 20% of the primary OC is from natural gas combustion versus essentially none in the receptor model results. Similarities and discrepancies between the emission-based and receptor-based predictions are discussed.

11B-4

STATIONARY SOURCES OF AIRBORNE LEAD: A COMPARISON OF EMISSIONS DATA FOR SOUTHERN CALIFORNIA,

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In the South Coast Air Basin of California (SOCAB), there are three distinct institutions which attempt to quantify the emissions of airborne lead and lead compounds from stationary sources. These are operated by federal, state, and local authorities and exhibit significant differences in their results. This paper explores the differences in each and compares the variations over time and across databases. The federal government operates the Toxics Release Inventory (TRI) through the Environmental Protection Agency under the Emergency Planning and Community Right-to-Know Act of 1986 (EPA, 2004). This program applies to specific classes of facilities that manufacture or process any of the 609 listed chemicals in a quantity that exceeds a specified threshold. These facilities are required to report the amount of chemicals that are disposed, transferred off-site, or released. Although the TRI provides information about a vast number of stationary sources, it has notable limitations, which include frequent changes in reporting requirements since its inception in 1987, and failure to cover all toxic chemicals and industrial sectors (EPA, 2004). The State of California through the California Air Resources Board (ARB) operates a quadrennial inventory of stationary source emissions known as the Air Toxics “Hot Spots” Information and Assessment Act (AB 2588, 1987) (ARB, 2004). Under this act, stationary sources must report the quantity of certain substances that are routinely released to the air. A subsequent risk assessment is conducted, and public notification follows if a significant risk is found. Lead and lead compounds are reported individually, and a lead mass fraction is applied to emissions of typical lead compounds. Again there have been temporal changes in reporting requirements, which limits the ability to compare emissions over time. Additionally, since the database is updated once every four years, changes in annual emissions will go unnoticed for some time. The regional authority for the SOCAB is the Air Quality Management District, which requires facilities to file an Annual Emissions Report (AER) along with payment of applicable fees (AQMD, 2004). Lead emissions must be reported to the AER program if more than 0.5 pounds of lead or lead compounds are released to the air in one year. Like the ARB, a lead mass fraction is applied to typical lead compound emissions. AER data before 2001 is self-reported by facilities (AQMD, 2003). Furthermore, there are sometimes differences in the emissions reported to the AER and the AB 2588 databases by individual facilities in the same year. These discrepancies have yet to be resolved. Here we consider differences among these three databases. In particular, we address how temporal changes in reporting requirements give misimpressions of increased or decreased emissions over time. We also look at the sources of uncertainty in each database in search of inherent inconsistencies among the databases.

11C-1

PREDICTING SECONDARY ORGANIC AEROSOL FORMATIONS RATES IN SOUTHEAST TEXAS,

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Rates of secondary organic aerosol (SOA) formation, due to the reactions of aromatics and monoterpenes, were estimated for southeast Texas by incorporating a modified version of the Statewide Air Pollution Research Center's chemical mechanism (SAPRC99) into the Comprehensive Air Quality Model with extentions (CAMx version 3.10). The model included explicit representation of the reactions of α-pinene, β-pinene, sabinene, d-limonene and carene with O3, OH radical and NO3 radical. The model also included separate reactions for low and high-SOA yield aromatics. The form of the SOA yield model was based on a commonly used equilibrium phase partitioning model, and specific yield parameters were based on environmental chamber experiments. The reactions of monoterpenes (predominantly α-pinene and β-pinene) with ozone led to the most regional SOA formation, followed by monoterpenes with the nitrate radical. Aromatic-OH reactions led to less regional SOA-formation compared to monoterpenes; however, this formation occurs close to the urban and industrial areas of Houston. In contrast, SOA formation due to the reactions of monoterpenes occurred in the forested areas north of the urban area. The results of this study are in qualitative agreement with estimates of SOA formation based on ambient data from the same time period.

11C-2

THE NEXT GENERATION SECONDARY ORGANIC AEROSOL MODELS: DYNAMICS OF SOA IN SOUTHERN CALIFORNIA,

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Secondary organic aerosol (SOA) is an important component of atmospheric particulate matter (PM) and formed in situ in the atmosphere. Several of anthropogenic and biogenic emissions contain volatile organic compounds (VOCs), that undergo atmospheric oxidation to produce large number of organic compounds. These oxidation products possess variety of functional groups resulting into organic compounds that differ widely in their chemical and physical properties. Organic species with sufficiently low vapor pressure partition to ambient aerosol phase leading to the formation of SOA [1]. SOA has potential to contribute significantly to the total ambient particulate burden, especially during intense smog episodes. For instance, in Southern California, where air quality standards are not met over 100 days a year, SOA concentration levels constitute up to 70 percent of total PM. The understanding of dynamics of SOA formation is essential to design effective control strategies that would reduce ambient particulate matter. In this study, we incorporate the updated versions of Caltech Atmospheric Chemistry Mechanism (CACM) and Model to Predict Multi-phase Partitioning of Organics (MPMPO) [2] gas/particle partitioning module into the California Institute of Technology (CIT) three-dimensional air quality model to simulate secondary organics in the South Coast air basin of California. We conducted simulations to predict gas and aerosol phase concentrations of secondary organic constituents for 8-9 september, 1993 episode. We present temporally and spatially resolved SOA concentration profile and analyze diurnal variations. The nature of origin of SOA is identified in several areas of southern california. We also discuss the impact of NOx emissions on the dynamics of SOA formation. References [1] Pankow, J.F., An Absorption model of gas-particle partitioning of organic compounds in the atmosphere, Atmos. Environ, 28, 185-188, 1994 [2] Griffin, R.J., Dabdub, D., Seinfeld, J.H., Development and initial evaluation of dynamic species-resolved model for gas-phase chemistry and size-resolved gas/particle partitioning associated with secondary organic aerosol formation, submitted.

11C-3

SENSITIVITY ASSESSMENT OF PARTICULATE MATTER (PM 2.5) MODEL FOR THE EASTERN UNITED STATES, JIA-YEONG KU, Christian Hogrefe, Gopal Sistla, Kevin Civerolo, Winston Hao, New York State Department of Environmental Conservation, Albany, NY

The EPA Community Multiscale Air Quality (CMAQ) model is used to simulate the August 6 to 16, 2002 high PM2.5 episode. The meteorological and emission inputs to CMAQ were developed using the Penn State/NCAR Mesoscale Model version 5 (MM5) and the Sparse Matrix Operator Kernel Emissions (SMOKE) processor. The CMAQ PM2.5 total mass is an estimate based upon the contribution of several species: sulfate, nitrate, ammonia, organic carbon, elemental carbon, and crustal or soil. In this study, we will evaluate these total PM2.5 mass estimated from the CMAQ simulation against the hourly TEOM measurements. Furthermore, since the species contributing to the PM2.5 total mass exhibit different spatial and temporal patterns, we compare model predictions against measured species to asses CAMQ's capability to capture these patterns and the relative contributions of individual species to total PM2.5 concentrations during the episode considered here. We also present results from a series of sensitivity simulations aimed at assessing the response of simulated PM2.5 total mass to the reduction in species emissions.

11C-4

USING SULFUR PREDICTIONS FROM A GLOBAL-SCALE TRANSPORT MODEL TO SPECIFY BOUNDARY CONDITIONS IN A REGIONAL-SCALE AIR QUALITY MODEL, MICHAEL G. BARNA, National Park Service, Fort Collins, CO; Eladio M. Knipping, Electrical Power Research Institute, Palo Alto, CA

The influence of boundary conditions in regional air quality model simulations is receiving increasing attention, especially when the models are used to develop source/receptor relationships for air pollution. This presentation discusses the application of the GOCART (Georgia Tech/Goddard Global Ozone Chemistry Aerosol Radiation Transport) global transport model (Chin et al., 2000) to specify sulfur boundary conditions for the REMSAD (Regional Modeling System for Aerosols and Deposition) regional air-quality model (SAI, 2002). As part of the BRAVO (Big Bend Regional Aerosol and Visibility Observational) Study (Pitchford et al., 2004), the REMSAD regional air-quality model was employed to estimate particulate sulfate contributions from several geographical source regions to Big Bend National Park located in southwestern Texas. The simulation period was July – October 1999. Two "base case" simulations were developed. Both of these simulations used the best-available estimates of sulfur dioxide and primary particulate sulfate emissions, but differed in their treatment of sulfur mixing ratios specified at the model boundary. The first simulation used fixed values of 200 pptV and 280 pptV for sulfur dioxide and particulate sulfate, respectively; these concentrations decreased in the upper model layers, dropping to approximately 50 pptV and 70 pptV in the highest model layer specified at 50 mb. The REMSAD model boundary spanned both urban regions as well as rural and maritime regions, and the sulfur values listed above were specified as a compromise to SO2 and sulfate mixing ratios found within the various demographic regimes. The second simulation used spatially-varying mixing ratios for sulfur dioxide and particulate sulfate, which were calculated by the GOCART global transport model. Unfortunately, GOCART simulation results for 1999 were unavailable, and GOCART sulfur estimates for July – October 2000 were used instead. These 2000 data were used to develop a four-month average estimate of sulfur dioxide and particulate sulfate mixing ratios for the REMSAD domain boundary, with the assumption that, over a multi-month time span, the boundary conditions for the two years would be fairly consistent. The introduction of the spatially-varying GOCART sulfur mixing ratios had two favorable results: a reduction in the magnitude of sulfate predicted at Big Bend National Park attributed to sulfur mixing ratios specified at the model boundary (thus yielding results commensurate with attributions calculations based on several receptor-based methods), and an overall improvement in REMSAD's ability to simulate regional sulfate concentrations. The initial estimate of boundary-condition impact on simulated sulfate at Big Bend National Park was lowered from 20% (0.46 μg/m3) to 7% (0.14 μg/m3) for the spatially-fixed and spatially-varying cases, respectively. A model performance evaluation utilizing CASTNet (Clean Air Status and Trends Network) sulfate observations versus model predictions showed an improvement in estimated sulfate when the GOCART boundary concentrations were employed. For example, the normalized bias (all sites) was reduced from 32% to 21% and the normalized gross error (all sites) was reduced from 48% to 45%. These results suggest that future regional air-quality modeling simulations should incorporate boundary conditions estimated by global-scale transport models.

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12PA-1

THE INFLUENCE OF MINERAL DUST COMPONENTS ON THERMAL/OPTICAL ANALYSIS FOR CARBONACEOUS MATERIAL,

GUADALUPE PAREDES-MIRANDA, L.-W Antony Chen, John G. Watson, Judith C. Chow, Desert Research Institute, DRI/DAS, Reno, NV; K. Fung, AtmAA, Inc., Calabasas, CA

Thermal/optical methods have been widely used for analyzing the carbon content in ambient and source aerosol samples. Particles deposited either onto filter substrates (e.g., quartz, glass or aluminum) or onto inert receptacles are heated to designated temperatures in either inert or oxidizer environment, and carbon evolved is converted to CO2 or CH4 and quantified. The more volatile carbon fraction that evolves at a temperature of about 450oC is referred to as organic carbon (OC), in contrast to element carbon (EC) that is oxidized only at a higher temperature of approximately 800oC. However, atmospheric dust particles typically contain minerals that may cause the combustion of EC at a lower temperature. This implies that the dust material coexisting in the sample influences partitions between charred OC and EC fractions. To examine how the composition and quantity of dust particles influence the EC combustion in an inert atmosphere, a controlled experiment was performed with different types of EC reference materials (Kochy, 1990; Polyscience, Inc., Warrington, PA, etc.). Different quantities of EC were analyzed in a conventional carbon analyzer in contact with four different catalysts (MnO2, CuO, TiO2, Fe2O3). The oxidation rate of EC at different temperatures was quantified by measuring CO2 evolved per unit time. The dependence of reaction rate on the temperature shows a good Arrhenius curve, which indicates constant activation energy for each catalyst. It is concluded that the analysis of carbonaceous compound at a temperature greater than 800oC will be substantially influenced by the dust particles present in the sample.

12PA-2

PARTICULATE CARBON MEASUREMENTS IN CALIFORNIA'S SAN JOAQUIN VALLEY,

JUDITH C. CHOW, John G. Watson, Douglas H. Lowenthal, Desert Research Institute, Reno, NV; Karen Magliano, California Air Resources Board, Sacramento, CA

Aerosol carbon sampling methods and artifacts were evaluated at the Fresno Supersite and during the California Regional Particulate Air Quality Study (CRPAQS). PM2.5 sampling was conducted using Desert Research Institute (DRI) sequential filter samplers (SFS) from December 1999 through February 2001 at urban Fresno and Bakersfield, and at Angiola, a rural site in the San Joaquin Valley (SJV). Additional filter-based sampling was done in Fresno as part of the U.S. Environmental Protection Agency (EPA) Supersites program using an Andersen Instruments single-channel Federal Reference Method (FRM) sampler and a multiple channel RAAS (reference ambient air sampler). Continuous particle carbon measurements were made at Fresno and Angiola during CRPAQS with the R&P 5400 continuous carbon analyzer. Carbon sampling artifacts at the Fresno Supersite were evaluated with the RAAS sampler configured with carbon-denuded and undenuded channels with quartz-fiber backup filters preceded by Teflon and quartz-fiber filters. Organic carbon (OC) and elemental carbon (EC) concentrations were measured on quartz filters with the DRI thermal/optical reflectance (TOR) method. Carbon concentrations were higher during the colder months and the trend was most pronounced at Fresno and Bakersfield, attributable to increased residential wood combustion during winter and to wintertime inversions that trap urban air pollutants. OC and EC displayed similar diurnal trends at Fresno during winter (December–February) and summer (June–August) and at Angiola during winter. In Fresno during winter, OC and EC concentrations peaked at night due to residential wood combustion and the development of a nighttime inversion. There was also a suggestion of a morning rush-hour effect at 0700 PST. During summer, there were distinct morning and late afternoon rush hour peaks. The winter pattern at Angiola was different. Concentrations and their variations were smaller than at the urban sites. A midday peak may reflect transport to this remote site. Collocated measurements of OC and EC on undenuded quartz-fiber filters were made in Fresno with the SFS, FRM, and RAAS samplers. Average ratios of RAAS/SFS, FRM/SFS, and RAAS/FRM OC were 1.06 ± 0.18, 0.99 ± 0.13, and 1.07 ± 0.17, respectively. Average ratios of RAAS/SFS, FRM/SFS, and RAAS/FRM EC were 1.02 ± 0.30, 1.11 ± 0.25, and 0.92 ± 0.24, respectively. All average differences between samplers were less than their respective measurement uncertainties. Further, the average ratio of RAAS denuded to undenuded front quartz-fiber filter EC was 1.04 ± 0.59 and the average difference was less than its measurement uncertainty. On average, undenuded front quartz-fiber filter OC was 10% higher than denuded OC (front + backup). Quartz-behind-Teflon OC was significantly higher (70%) than quartz-behind-quartz OC, suggesting desorption from the Teflon filter. Differences between denuded OC and OC obtained by subtracting the quartz-behind-Teflon or quartz-behind-quartz OC were less than twice their measurement uncertainties in most cases. While OC and EC concentrations were 3 to 4 times higher in winter than summer, quartz backup [to Teflon and quartz filters] OC concentrations showed little seasonal variation. Volatile polycyclic aromatic hydrocarbons (PAH) and alkanes also showed large seasonal differences, suggesting that the amount of volatile organic compounds absorbed by front and backup quartz filters results from saturation of the filter rather than equilibrium with volatile compounds in the sample stream.

12PA-3

COMPARISON OF REAL TIME METHODS FOR MEASUREMENT OF BLACK CARBON, W. Patrick Arnott, Judith Chow, Dana Trimble, John Watson, Desert Research Institute, Reno NV

Real time measurements of black carbon mass concentration (BC) at the Fresno supersite will be presented. Measurement methods include photoacoustic aerosol light absorption accomplished with an instrument operating at 1047 nm, the aethalometer filter based method, and the new filter based instrument, multi-angle aerosol absorption photometer. Time series are available for 11 months, including the winter season 2003 to 2004. Photoacoustic instruments directly measure aerosol light absorption in-situ and BC is inferred from this measurement. In contrast, the filter-based methods have artifacts caused by a small fraction of aerosol light scattering affecting the light absorption measurement. Filter-based methods must also be calibrated to deal with the change of the filter multiple scattering enhancement factor as the filter darkens. Comparisons with the photoelectric aerosol sampler (PAS) instrument will also be presented. This instrument was designed to indicate particle bound PAH concentration with the use of a UV lamp to ionize particles containing PAH's, followed by subsequent measurement of particle charge. Direct source sampling measurements indicate that the PAS likely responds to BC itself.

12PA-4

SEASONAL CORRELATIONS BETWEEN OF NIOSH AND IMPROVE CARBON MEASUREMENTS, MIN-SUK BAE, James J. Schauer, Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, Wisconsin, Jay R. Turner, Chemical Engineering, Washington University, St. Louis, Missouri, Judith C. Chow, Desert Research Institute, Reno, Nevada, Philip K. Hopke, Chemical Engineering, Clarkson University, Potsdam, NY

Thermal/optical methods have been widely used for the determination of the source and ambient aerosol organic carbon (OC) and elemental carbon (EC) for many years. Traditionally, organic and elemental carbon measurements have been made by collecting particulate matter on quartz fiber filters that are subsequently analyzed by off-line thermal evolution and combustion techniques. Two commonly employed methods in the United States are the National Institute of Occupational Safety and Health (NIOSH) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) methods. Although both the NIOSH and IMPROVE analyses employ similar strategies for fractionating light absorbing and nonabsorbing carbonaceous particulate matter but their temperature and optical monitoring protocols are different. Two types of 24 hour integrated samplers were operated at the US EPA funded St. Louis Midwest Supersite. All samples used for each analyses were collected downstream of PM2.5 cyclones. Low volume samplers were used to collect for daily particulate matter samples that were analyzed for OC and EC by the NIOSH and IMPROVE methods. High volume sampler that operated at 92 lpm were used to collect particulate matter samples that were used for organic speciation and source attribution modeling. In this study, total 809 samples including blanks were analyzed by the NIOSH and IMPROVE methods. Although the total carbon (TC) measured by the two different analyses showed excellent agreement, there existed considerable differences in the split between the OC and EC measured by the two methods. EC levels measured by the IMPROVE method were higher than EC levels measured by the NIOSH methods. In addition, distinct seasonal trends were observed in the relationship between the IMPROVE EC and the NIOSH EC. Organic tracers, which were used to identify the sources of the carbonaceous aerosol was used to identify the carbonaceous aerosol sources that are the dominate contributors to the seasonal relationship between the NIOSH and IMPROVE EC analyses. These results and the associated implication will be presented.

12PA-5

ANALYSIS OF ATMOSPHERIC RELEVANT SUBSTITUTED PHENOLS IN AQUEOUS SOLUTION USING HPLC-APCI-MS,

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Oxygenated aromatic compounds such as phenols, cresols and nitrophenols have been identified both in the gaseous and aqueous phase of the atmosphere. Substituted phenols may be emitted directly (vehicle fuel exhaust, industrial processes and biomass burning) or they are formed by the atmospheric oxidation of aromatic hydrocarbons. Due to their toxicity and phytotoxicity, their chemical behaviour and concentration in the atmosphere is of note. Especially the phytotoxic nitrophenols stand in the suspicion as possible contributors to the forest decline. The predominant sink process for such compounds can be the reaction with free atmospheric radicals, such as OH- and NO3-radicals. In order to understand the behaviour of these compounds in the atmosphere, also the products of these reactions are important. For this reason, an analytical method is necessary for the analysis of several substituted phenols and their oxidation products in aqueous solutions. Analysis of environmental water samples has commonly been performed by HPLC-UV [1] or GC-MS. However, the introduction of atmospheric pressure ionization techniques (API) for HPLC-APCI-MS coupling, offers a new possibility for the analysis of aqueous samples. Numerous publications in the last years report the applicability and advantages of this analytical method. Especially the easy sample pre-treatment, the short analytical time and the high sensitivity make the LC-APCI-MS coupling to an interesting tool for the environmental analysis.[2] Therefore, an SPE-LC-APCI-MS method is developed for the routinely analysis and enrichment of substituted phenols in aqueous solution. This method can be used to analyse real atmospheric samples (biomass burning and cloud water) as well as samples from laboratory experiments (kinetic investigations and chamber studies). Accurate yet fast analytical methods are essential in order to obtain input parameters for tropospheric chemical models such as CAPRAM (Chemical Aqueous Phase Radical Mechanism) [3]. In turn, such analytical technique can be also used for model validation. We present first results from the analysis of substituted phenols especially nitrophenols using HPLC-APCI-MS from laboratory products studies of atmospheric relevant phenolic compounds with nitrate radicals in the aqueous phase and a source emission study of biomass burning aerosols.

[1] W. Schüssler, L. Nitschke, Chemosphere, 2001, 42, 277. [2] R. Wissiack, E. Rosenberg, J . Chromatogr. A, 2002, 963, 149. [3] B. Ervens, C. George, J. E. Williams, G. V. Buxton, G. A. Salmon, M. Bydder, F. Wilkinson, F. Dentener, P. Mirabel, R. Wolke and H. Herrmann, J. Geophys. Res., 2003, 108, 4426.

12PA-6

A NEW INSTRUMENT FOR THE HOURLY ORGANIC SPECIATION OF ATMOSPHERIC AEROSOLS,

Brent J. Williams, Allen H. Goldstein, University of California, Berkeley, CA ; Nathan M. Kreisberg and SUSANNE V. HERING, Aerosol Dynamics Inc., Berkeley, CA

Organic matter is a major constituent of airborne particles, comprising 20-50% of the mass of airborne particles below 2.5 μm in diameter. The composition is complex, with hundreds of compounds identified through chromatographic mass spectrometry techniques. While the identified compounds only comprise a fraction of the total organic mass, they can serve as valuable tracers for sources. For example, hopanes can serve as a unique tracer for fossil fuel combustion while levoglucosan is a unique tracer for wood combustion. A substantial limitation in the use of organic marker compounds for source identification is the difficulty, and cost of the analyses. Needed are time-resolved, cost-effective measurements of specific organic marker compounds. We present a new instrument- the Thermal desorption Aerosol GC-MS/FID (TAG) for the in-situ, time-resolved identification and quantitation of organic marker compounds in airborne particles over the size range from 0.1 to 2.5 μm. Atmospheric aerosol samples are collected into a thermal desorption cell by means of humidification and impaction. The sample is thermally desorbed onto a GC column for subsequent GC-MS/FID analysis. A Teflon filter can be alternatively switched in-line to remove all particles and provide a dynamic field blank. The collection and analysis steps are automated, yielding hourly speciation around the clock. Our approach offers the advantage of building on past research using filter-based GC/MS analyses to quantify organic material and identify the origins of organic aerosols. Initial results are presented for ambient measurements made in Berkeley, CA during the Spring of 2004 and at Chebogue Point, Nova Scotia, Canada from July-August 2004 during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT 2004) study. Data taken at both sites show clearly resolvable chromatographic peaks absent from the dynamic filter blanks that represent individually eluting aerosol compounds. In Berkeley, many compounds, including levoglucosan, are easily identified with a NIST quadrupole mass spectra database with high assurance. At Chebogue Point, compounds were equally resolvable in the chromatograms, but were poorly identified using the NIST database. Comparisons to other measurements indicate that the aerosol was highly oxygenated. Factor analysis showed several reoccurring groups of organic compounds associated with transport from different source regions.

12PA-7

CHARACTERIZATION OF PCBS IN GAS AND PARTICULATE PHASE IN AIR SAMPLES AT THE METROPOLITAN AREA OF SANTIAGO, CHILE,

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In order to characterize the profile concentration of 18 polychlorinated biphenyls (PCBs) congeners, as well as to evaluate the importance of these toxic organic pollutants in the urban atmosphere of Santiago de Chile, monitoring campaign was carried out in the winter period (June to October 2002). Sampling was carried out at the Pudahuel Monitoring Station, located in the occidental part of the city. Samples were collected using a novel aerosol sampler (Partisol 2300 Speciation Sampler from Rupprecht & Patashnick). The sampler, equipped with cartridges provided with PM2.5 impactors, 0.45 [mm] pore size teflon membrane filters (F) and a polyurethane foam filter (PUF). It allows the identification and quantification of PCBs present in gaseous phase as well as those associated to particulate matter (PM). Once in the laboratory, the samples were extracted, purified and quantified by GC-ECD, using Internal Standard Method. The mean concentration of PCBs observed at the occidental sector (Jun/Oct, 2002), was 251 pg/m3 in filter, 922 pg/m3 in the PUF and 1173 pg/m3 in (F + PUF). While in central area (Sept 2002), of Santiago, were 38 pg/m3 in filter, 119 pg/m3 in PUF and 158 pg/m3 in (F + PUF). In general, PCBs in air samples are mostly found associated to gas phase. In the literature, only 5 - 10 % are associated to the particulate matter. In present work, the distributions of PCBs in the gaseous and particulate phase show a different tendency in Santiago than cities in North America or Europe. Whereas in Santiago the proportion of volatile PCBs associated to gas phase is about 77% and, 23% to particulate matter, in other countries predominate the PCBs retained on PUF, associated to gas phase.

12PA-8

AN ION CHROMATOGRAPHIC METHOD FOR ANALYSIS OF WATER-SOLUBLE SHORT-CHAIN ORGANIC ACIDS IN AMBIENT PARTICULATE MATTER,

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An ion chromatographic method has been developed to separate and quantify water-soluble, short-chain organic acids present in ambient particulate matter. Samples collected at Potsdam and Stockton, NY from November 2002 through June 2004 have been used for this study. A Dionex IC-DX500 ion chromatography system was used to analyze the water leachate from quartz filters exposed in an Andersen RAAS speciation network sampler. The quartz filters were leached using 10 ml of water, ultrasonicated, subjected to mechanical shaking, centrifugation and filtration prior to the IC analysis. A Dionex EG-50 eleunt generator system with KOH cartridge capable of delivering high purity eluent and compatible with both gradient and isocratic applications was used. A standard aqueous solution containing acetic, propionic, formic, glutaric, adipic, succinic, malic, malonic, maleic, and oxalic acids was prepared from reagent grade chemicals and was used for method development and quantitation of the species in the analyzed samples. It will be shown that suitable resolution for the species of interest is achieved, even in the presence of common inorganic anions present in ambient particles. Acetic, propionic, formic, malonic and oxalic acids have been quantified using this method. It will also be shown that, where beneficial, better resolution can be achieved by altering the eluent concentrations, usually with an increase in the run time.

12PA-9

LIGHT SCATTERING BY FINE PARTICLES DURING PAQS: MEASUREMENTS AND MODELING,

Juan C. Cabada, Andrey Khlystov, Ann B. Wittig, SPYROS N. PANDIS, Carnegie Mellon University, Pittsburgh, PA; Christodoulos Pilinis, University of Aegean, Greece

Light scattering by fine particulate matter was measured during the Pittsburgh Air Quality Study (PAQS) as close to ambient conditions as possible. Several approaches are used for the theoretical calculation of scattering coefficient and the results are compared to the direct measurements. The first approach uses ambient high-time and daily resolved PM2.5 composition concentrations to estimate the scattering coefficient assuming that the aerosol is an external mixture. The second approach uses a thermodynamic model and Mie theory to predict the scattering coefficient of aerosols from daily size-composition distributions. The third approach introduces high-time and daily resolved ambient aerosol water concentrations and concentrations of sulfate, nitrate, organic material and soil with fixed scattering efficiencies. During the summer the first two approaches underestimate the measured scattering coefficient by around 20%. Agreement within experimental error is obtained between the measured scattering coefficient and the model incorporating measured water aerosol concentrations. During the winter the first two approaches tend to over-predict the measured scattering by around 15%. This over-prediction is weakly correlated to the organic mass. The modeling approaches suggest that sulfate and the associated water contributes 65-73% to the scattering coefficient during the summer with organic material contributing 25-30%. During the winter, sulfate accounts for 35-43%, nitrate 24-32% and organic material 30-40% of the scattering coefficient.

12PA-10

TOWARDS AN INTEGRATED SINGLE SCATTERING ALBEDO INSTRUMENT: DEVELOPMENT OF THE PHOTO-ACOUSTIC ABSORPTION COMPONENT,

Daniel Lack, Anders Pettersson, NOAA Aeronomy Laboratory, 325 Broadway, Boulder, CO 80305, United States AND Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder; Edward Lovejoy, A.R. Ravishankara, NOAA Aeronomy Laboratory, 325 Broadway, Boulder, CO

Single scattering albedo (ratio of aerosol scattering to total aerosol extinction) is one of the most important aerosol properties for determining their influence on climate. Direct measurement of the aerosol extinction at high sensitivity and time response using the Cavity Ring-Down (CRD) technique is now available while several methods for the scattering or absorption component of extinction exist. We have developed a laboratory instrument for the direct measurement of absorption by aerosol based on photo-acoustic absorption spectroscopy. The system uses multiple noise reduction and signal enhancement techniques and provides excellent sensitivity and time response at 532nm. Instrument calibration is achieved using total extinction of ozone measured by Cavity Ring-Down (CRD) extinction technique and a software controlled phase lock for the resonator calibration. We will present the instrument development, calibration tools and experimental trials with absorbing test aerosol. The systems applicability to field deployment will also be discussed.

12PA-11

DECONVOLUTION AND QUANTIFICATION OF PRIMARY AND OXYGENATED ORGANIC AEROSOLS BASED ON AEROSOL MASS SPECTROMETRY,

QI ZHANG, Jose-Luis Jimenez, CIRES, University of Colorado, Boulder, CO; M. Rami Alfarra, James Allan, Hugh Coe, School of Earth, Atmospheric and Environmental Science, The University of Manchester, Manchester, UK, Douglas R. Worsnop, Manjula Canagaratna, Aerodyne Research Inc, Billerica, MA

A new technique has been developed to deconvolve and quantify the mass concentrations and size distributions of primary and oxygenated organic aerosols (POA and OOA) using high time resolution organic mass spectral data obtained with an Aerodyne Aerosol Mass Spectrometer (AMS) and a custom principal component analysis (PCA) method. Two mass-to-charge ratios (m/z's) 57 (mostly C4H9+) and 44 (mostly CO2+)—the identified AMS mass spectral tracers for POA and OOA, respectively—are used as the initial principal components. This technique was applied to the AMS organic aerosol data acquired at the EPA Pittsburgh Supersite during September 2002. The parameterized organic concentrations (= POA + OOA) agree very well with the measured values (r2 = 0.997, slope = 0.998) and the reconstructed organic data matrix (3199 time steps × 300 m/z's) explains 99% of the variance in the measured time series. In addition, the extracted mass spectrum of POA shows high similarity to those of directly sampled diesel exhaust, lab-generated lubricating oil aerosol, and freshly emitted traffic aerosols observed in urban areas, while the spectrum of OOA closely resembles those of aged organic aerosols sampled in rural areas and also shows similarity with the spectrum of fulvic acid (from Suwanee River)—a humic-like substance that has previously been found to replicate the functional behavior of the polyacid components found in highly processed and oxidized atmospheric organic aerosols, when subjected to other analytical procedures. The major findings arising from the concentrations and size distributions of POA and OOA in Pittsburgh will be reported. The changes in the chemistry of POA and OOA during nucleation events and during periods when acidic particles were observed will also be discussed.

12PA-12

THE USE OF DATA MINING TOOLS FOR THE ANALYSIS OF SINGLE PARTICLE MASS SPEC DATA,

LEI CHEN, Zheng Huang, Raghu Ramakrishnan, University of Wisconsin; David R. Musicant, Deborah S. Gross, Carleton College and James J. Schauer, University of Wisconsin

Over the past decade, several single particle mass spectrometry based instruments have been developed that allow real time chemical analysis of aerosols. These instruments provide very rich data streams that cannot be fully exploited with traditional data analysis tools, which have been widely applied to air quality data in the past. Several of the key challenges associated with the analysis of single particle mass spectrometry data include quantification, ambiguity of the mass spectra, and the enormity of the data sets. These arise from the real time nature of single particle mass spectrometry data due to the insufficient time for sample clean up/separation and full instrument calibration. As a result, preprocessing has been widely use to filter single particle data to allow the isolation of simple data streams that are amenable to traditional aerosol data analysis tools. This approach, however, does not fully utilize the richness of single particle mass spectrometry data. Through a collaborative effort of computer scientists and atmospheric chemists at the University of Wisconsin-Madison and Carleton College, advanced data mining tools are being applied to the analysis of Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) data. These efforts provide a foundation to better understand and interpret ATOFMS data, as well as provide a mechanism to better interface ATOFMS data with other real time aerosol measurements. Examples of the application of data mining tools for the analysis of ATOFMS data will be presented.

12PD-13

AMBIENT AEROSOL SIZE DISTRIBUTIONS AND NUMBER CONCENTRATIONS MEASURED DURING THE PITTSBURGH AIR QUALITY STUDY, CHARLES STANIER, University of Iowa, Iowa City, IA; Andrey Khlystov, Duke University, Durham, NC; Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA and University of Patras, Patra, Greece

Twelve months of aerosol size distributions from 3 nm – 560 nm, measured using Scanning Mobility Particle Sizers (SMPS) are presented with an emphasis on average number, surface, and volume distributions, and seasonal and diurnal variation. The measurements were made at the main sampling site of the Pittsburgh Air Quality Study from July 2001 – June 2002. These are supplemented with 5 months of size distribution data from 0.5-2.5 µm measured with a TSI Aerosol Particle Sizer (APS) and 2 months of size distributions measured at an upwind rural sampling site. Measurements at the main site were made continuously under both low and ambient relative humidity. The average Pittsburgh number concentration (3-500 nm) is 22,000 cm-3 with an average mode size of 40 nm. Strong diurnal patterns in number concentrations are evident as a direct effect of the sources of particles (atmospheric nucleation, traffic, and other combustion sources). New particle formation from homogeneous nucleation is significant on 30-50% of study days and over a wide area (at least a hundred kilometers). Rural number concentrations are a factor of 2-3 lower (on average) than the urban values. Average measured distributions are different than model literature urban and rural size distributions.

12PD-14

A METHOD FOR THE IN SITU MEASUREMEN TOF FINE AEROSOL WATER CONTENT OF AMBIENT AEROSOLS: THE DRY-AMBIENT AEROSOL SIZE SPECTROMETER (DAASS), CHARLES STANIER, University of Iowa, Iowa City, IA; Andrey Khlystov, Duke University, Durham, NC; Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA and University of Patras, Patra, Greece

Hygroscopic growth of atmospheric particles affects a number of environmentally important aerosol properties. Due to the hysteresis exhibited by the aerosol hygroscopic growth, the physical state of particles and the amount of aerosol water is uncertain within a wide range of relative humidities found in the troposphere, leading to uncertainties in optical and chemical properties of the aerosol. Here we report the design and tests of an automated system that was built to assess the amount of aerosol water at atmospheric conditions. The system consists of two Scanning Mobility Particle Sizers (SMPS) and an Aerodynamic Particle Sizer (APS) that measure the aerosol size distribution between 3 nm and 10 micron in diameter. The inlets of the instruments and their sheath air lines are equipped with computer controlled valves that direct air through Nafion dryers or bypass them. The Nafion dryers dehydrate the air streams to below 30% RH at which point ambient particles are expected to lose most or all water. The switch between the dried and the ambient conditions occurs every 7 minutes and is synchronized with the scan times of the aerosol spectrometers. In this way the system measures alternatively dried (below 30% RH) and ambient aerosol size distributions. A comparison of the ambient RH and the dried RH size distributions and the corresponding integrated volume concentrations provides a measure of the physical state of particles and the amount of aerosol water. The aerosol water content can be treated as a growth factor or as an absolute quantity, and can be calculated as a time series or as a function of relative humidity (humidigram). When combined with aerosol composition measurements, the DAASS can be used to compare hygroscopic growth models and measurements.

12PD-15

PENETRATION OF THE AMBIENT ULTRAFINE AEROSOL INTO A CARDIAC REHABILITATION FACILITY IN ROCHESTER, NY,

DAVID OGULEI, Philip Hopke, Clarkson University, Potsdam, NY; David Chalupa, Mark Utell, University of Rochester Medical Center

Epidemiological studies have suggested a link between increases in ambient particulate matter (PM), essentially particle numbers, and an accelerated onset of cardiorespiratory mortality and mobidity. Such studies imply that vigorous studies be conducted to establish relationships between PM concentrations in the indoor environment and those measured in the outdoors. The indoor environment plays an important role in the exposure of an individual to air pollutants since people spend the vast majority of their time inside buildings. In this study, the relationship between indoor and outdoor levels of particulate matter was examined for a functional cardiac rehabilitation facility located in a commercial building in Rochester, NY. The facility offers both preventive and rehabilitative care for individuals recovering from or at risk for heart disease and is located approximately two miles from the University of Rochester Medical Center. Continuous size-fractionated particulate matter samples were simultaneously measured from indoor and outdoor air of the facility using an MSP Wide-range Particle Sizer (WPS). The initial sampling period was July 2004 and a second set of measurements were made in November 2004. The rehabilitation facility data were compared with concurrently-measured SMPS data from the New York State Department of Environmental Conservation (DEC) site located a few miles from the facility site. A quantitative comparison was made between the measured number concentrations at each location by computing the spatial correlation index (r) for the time-size plots for each of the days of the study. All of the calculated r-values were very large compared to the cut-off value of 1.6 meaning that there were highly significant correlations among these data. The relationship was observed to be stronger between the indoor and outdoor values at the Rehabilitation Center (r ≥200) than between the outdoor and DEC (r ≥130) or between the indoor and DEC values (r ≥65). The results also showed a high level of penetration for this building especially for particles in the size bins 0.01- 0.05 µm and 0.1 - 0.5 µm for which the penetration fractions (I/O) were approximately 0.8 and 0.7, respectively.

12PD-16

PARTICLE DENSITY AND SHAPE FACTORS ESTIMATED FROM MERGING AERODYNAMIC AND MOBILITY SIZE DISTRIBUTIONS,

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Different particle sizing techniques, depending on their principle of operation, provide different measures of aerosol size. For example, cascade impactors and Aerodynamic Particle Sizer (APS, TSI Inc.) provide measurements of the aerodynamic–equivalent size. The Scanning Mobility Particle Sizer (SMPS, TSI Inc) measures mobility-equivalent size, while Aerodyne Mass Spectrometer (AMS, Aerodyne Research Inc) measures vacuum-aerodynamic-equivalent size. Combining measurements of aerosol size distribution from these instruments into a single spectrum presents a challenge, but also provides an insight into other aerosol characteristics, such as particle shape and density. A simple algorithm was developed to combine electrical mobility and aerodynamic size distribution data into a single size distribution, providing particle density and the shape factor. Combining the SMPS spectra with the size distributions measured with the AMS also provides information on particle density and the shape factor, but at smaller sizes. These algorithms were tested by comparing size distributions measured with SMPS-APS and SMPS-AMS combinations to collocated measurements using other instruments. The integrated aerosol volume was compared to the PM2.5 mass concentration measurements using TEOM, providing a measure of the average bulk aerosol density. The aerosol density estimated from the TEOM comparison was compared to the densities obtained from the merging of SMPS, APS and AMS size distributions.

12PD-17

ACCESSING EPA PM SUPERSITES DATA IN THE NARSTO DATA ARCHIVE, LES A. HOOK, Sigurd W. Christensen, Tammy W. Beaty, Oak Ridge National Laboratory, Oak Ridge, TN; Kathleen L. Morris, NASA Langley Research Center, Hampton, VA

The invaluable atmospheric measurements data collected by the participants of the U.S. EPA Particulate Matter (PM) Supersites Program are being archived and are publicly accessible at the NARSTO Permanent Data Archive (PDA) located at the NASA Langley Research Center Atmospheric Sciences Data Center (LaRC ASDC). Data from each of the eight Phase 1 and 2 Supersites projects were organized into project data sets by either individual measurement type or by sampling site (e.g., all measurements made at Queens College). General data types include: filter and continuous PM mass and chemistry; particle number, size, and optical properties; meteorological measurements; canister VOC analyses; single particle size and chemical composition; continuous gaseous measurements; and LIDAR data, among others for a particular project. Documentation accompanies each data set in the archive. Overview documents are intended to inform potential data users and include data set summaries, points of contact, readme files, and sample plots and images. More detailed information may include Project sampling plans, QA plans, final QA reports, and research procedures as provided by the project. The data files are in the NARSTO Data Exchange Standard (DES) format. The files have a tabular layout and are stored as ASCII comma-separated values files (.csv). The DES is a self-documenting format with three main sections: a header that contains information about the contents of the file and the data originator; a middle section that contains metadata tables that define sampling sites, quality flags, and other codified fields; and the data section that contains key variable, sampling and analysis information, and the data values with quality flags. The DES has a standardized set of metadata fields with defined consistent values that are applied across all projects and data types. Before a data file was archived, the NARSTO Quality Systems Science Center (QSSC) verified the format and metadata values, checked sampling locations, times, and flags for internal consistency, and reviewed a time-series plot for each variable. The DES and metadata are described in detail on the QSSC web site [http://cdiac.esd.ornl.gov/programs/NARSTO/]. To access the data at the ASDC, link to NARSTO Data Sets page on their web site [http://eosweb.larc.nasa.gov/PRODOCS/narsto/table_narsto.html]. Users can search for data and review documentation without registering, but the ASDC requires that data users register before ordering and downloading data from their FTP site. The flexible ordering system allows a user to obtain, for example, one or all of the data files in a given data set, all of the data files for a Supersite or all data files for a certain data type across several Supersites. One advantage of user registration is change notification. If a data file that you have downloaded is updated, you will be notified by the ASDC and advised to download the latest version. Assistance with obtaining and using Supersites data may be requested from the ASDC or the NARSTO QSSC. ORNL research was sponsored by U.S. Environmental Protection Agency and U.S. Department of Energy and performed at Oak Ridge National Laboratory (ORNL). ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725

12PD-18

SPATIAL ANALYSIS USING HIGH TIME RESOLUTION BC (AETHALOMETER) AND PM2.5 (THERMO ELECTRON SHARP MONITOR) MEASUREMENTS AT STILES STREET IN NEW HAVEN, CT, PETER BABICH, Randall Semagin, Michael Geigert, CT Department of Environmental Conservation; Kevin Goohs, Thermo Electron

The Stiles Street monitoring site in New Haven, CT is the only site in CT to have exceeded the annual PM2.5 National Ambient Air Quality Standard (NAAQS) of 15 □g/m3. The three-year average from 2000-2002 at Stiles Street was 16.6 □ g/m3. A PM2.5 attainment/non-attainment designation decision is scheduled to be made by the end of 2004. The Stiles Street site is situated 70 ft. from a major interstate (I-95) and 30 ft. from an on-ramp with heavy diesel truck traffic, and therefore is significantly influenced by these micro-scale sources. The CT Department of Environmental Protection (CT DEP) deployed several special purpose monitors to evaluate the elevated PM2.5 levels observed at Stiles Street. Along with six New Haven FRM sites (three existing and three new), an Aethalometer configured to gather 1-min. BC measurements was deployed at Stiles Street. This data, along with BC measurements obtained at the Criscuolo Park site located approximately one-half mile away, was used to determine micro-, middle-, and neighborhood-/urban-scale contributions by spatial analysis using a moving-average subtraction method. In response to EPA’s 9-point analysis issued July 29, 2004, which stated that Stiles Street should be considered for PM2.5 non-attainment designation, CT DEP submitted a rebuttal package that included results of a BC spatial analysis for the 2nd quarter, 2004. This analysis indicated that micro-scale sources contributed approximately 2 to 4 µg/m3 of PM2.5, which was consistent with the differences between Stiles Street and the other New Haven monitoring sites. Subsequent to this analysis and submittal of the rebuttal to EPA’s 9-point analysis, the CT DEP continued the high time resolution BC measurements and added high time resolved PM2.5 measurements using a Thermo Electron Model 5030 SHARP Monitor. The SHARP Monitor combines both light scattering photometry and beta radiation attenuation for continuous PM2.5 measurements. The 1-min. PM2.5 measurements obtained from the SHARP Monitor allows for spatial analysis to be performed similar to what was done for BC, to more directly determine PM2.5 contributions from local sources. With every day FRM sampling at Stiles Street as well, this also provides a platform to evaluate the performance of the Thermo Electron SHARP Monitor. The most current data will be analyzed and reported on in this presentation.

12PD-19

SYNOPTIC SCALE WEATHER PATTERNS IMPACTING THE ST. LOUIS AEROSOL,

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Synoptic scale air mass behavior can exert a strong influence on ambient particulate matter burdens. Following the method of Dorling, et al. (Atmos. Environ., 26A: 2575-2581 (1992)) we have implemented an iterative air mass back trajectory clustering algorithm to classify regional air mass flows impacting the St. Louis area towards supporting an interpretation of aerosol data collected at the St. Louis – Midwest Supersite. A variety of diagnostic tests have been incorporated to quantify the robustness of the individual trajectories, including but not limited to launching forward trajectories at various points along each backward trajectory and quantifying the extent to which the air mass path is retraced. Clustering has been repeated using a range of air mass arrival heights and also temporal durations to assess the intrinsic stability of the identified clusters. A scheme has been implemented to declassify trajectories which do not adequately follow the behavior of the cluster to which they are initially assigned. The clustering results are used to determine seasonal and year-to-year differences in regional air mass flows. Finally, seasonal and year-to-year differences in aerosol chemical and physical properties are interpreted in light of the differences in synoptic scale weather patterns. This presentation summarizes the clustering methodology, robustness tests and identified caveats, distributions of observed regional air mass flows, and implications to observed temporal patterns in aerosol concentrations.

12PD-20

CHARACTERIZATION OF POSITIONAL ISOMERS OF NITRO-PAHS AND OTHER SELECTED SPECIATED ORGANIC COMPOUNDS ASSOCIATED WITH PARTICULATE MATTER. THEIR RELATIONSHIP WITH REGULATED POLLUTANTS,

PATRIZIA DI FILIPPO, Federica Incoronato, Donatella Pomata, Carmela Riccardi, Sergio Spicaglia, National Institute of Occupational Safety and Prevention, Rome, Italy. Angelo Cecinato IIA-CNR, Monterotondo Scalo, Rome, Italy

Regulated and unregulated air pollutants were determined during intensive seasonal sampling campaigns in a mixed industrial/semi-rural area in the outskirts of Rome, Italy. Characterization of positional isomers of nitro-PAHs and other organic compounds associated with particulate matter was investigated in two sites located opposite with respect to a hospital waste incinerator, and upwind and downwind according to the direction of the prevailing local winds. The identification of unregulated pollutants and their relationship with CO, NOx, SO2, O3, and PM10 permitted to study the contribution of the air pollution sources to air quality. Unregulated pollutant concentrations were significantly lower than in an urban atmosphere; VOCs peaked during night, according to a strong atmospheric stability and a surface based inversion layer. The predominance of heavy odd-carbon n-alkanes, with peaks in correspondence of C29, indicated a stronger biogenic influence. No significant correlation of PAHs and nitro-PAHs versus CO, NOx, SO2, O3, and PM10 was observed, showing different source contributions. The ratio 2-NF/1-NP suggested that the prevalent source of nitro-PAHs was the primary emission, while 2-NF/2-NP ratio indicated that the daytime OH-initiated reaction was the dominant gas-phase formation pathway.

12PD-21

AMBIENT MERCURY MONITORING IN THE GREATER PITTSBURGH REGION,

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Given the United States' reliance on coal fired power plants (CFPP) for electricity production, concerns have been raised about the amount of mercury released into the environment from power generation. However, the relationship between coal fired power plant emissions and ambient mercury levels is not well understood. To improve the general understanding in this area, a mobile ambient air quality monitoring station was deployed in the vicinity of a local power plant in southwestern Pennsylvania. The ambient air quality was measured at this site from late May through late September of 2004. The goal of this work was to sample intermittent plume hits from the power plant, and to compare mercury levels in the plume to ambient levels at the same site. The mobile trailer monitoring site is located on a ridge approximately 3 km due north (N40.281, W79.917) of the nearest power plant, a 510 MW plant constructed during the 1950s that burns bituminous coal. The plant is located in northern Washington County along the Monongahela River (N40.250, W79.917). A smaller CFPP is located nearby to its southwest. Other CFPPs in western Pennsylvania and additional mercury sources located in Ohio are thought to be far enough away from the monitoring site to have minimal impacts on ambient measurements. The mobile trailer is equipped to monitor the following species: gas phase SO2 and NOx, particulate matter, elemental mercury (Hg0), oxidized or reactive gaseous mercury (HgR), and particulate mercury (HgP). The mobile trailer is also equipped with a weather station. Comparison of monitored species at the mobile site to the ambient air quality monitoring site at the nearby National Energy Technology Laboratory (NETL) can provide additional evidence that trends observed at the mobile site are due to the plume of interest and not to elevated ambient levels. Plume hits potentially due to the CFPP were identified by a combination of elevated SO2 and HgR concentrations and southerly wind directions. The monitoring during the summer of 2004 indicates that only on a few occasions do the local power plants contribute significantly over the background levels to the ambient mercury in the greater Pittsburgh region.

12PD-22

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY OF SECONDARY ORGANIX AEROSOLS WITHIN AND ABOVE A FOREST CANOPY,

WILLIAM VIZUETE

Biogenic volatile organic compounds undergo atmospheric reactions yielding more oxygenated and less volatile species. Some of these less volatile species condense onto particles in the atmosphere forming secondary organic aerosol (SOA). The high yield of SOA from sesquiterpenes (C15H24) and some monoterpenes (C10H16) cause these biogenic hydrocarbons to play a significant role in SOA formation. Results from recent studies have shown that reactions with ozone limit the lifetimes of certain sesquiterpenes to several minutes. These short lifetimes may mean that much of the SOA conversion occurs within the vegetation canopy. The work presented here will attempt to quantify the compositional changes to aerosols resulting from chemistry within the forest canopy. Aerosol measurements were taken during a three week field campaign sponsored by the Environmental Protection Agency (EPA) and National Science Foundation (NSF) in a North Carolina Loblolly pine plantation during the summer of 2003. The loblolly pine plantation is a Free-Air CO2 Enrichment Site (FACTS-1) operated by Duke University. The research site consists of six free-air CO2 enrichment rings. Three of the rings provide elevated atmospheric CO2 concentrations and three are ambient control rings. These structures reach well above the forest canopy and form an ideal location to take measurements. Aerosol samples were collected within and above the forest canopy using a Hering Low Pressure Impactor. Chemical functional groups present in the aerosols collected by the impactors were identified using Fourier Transform Infrared (FTIR) spectroscopy. Shifts in the ratios of aliphatic to carbonyl functional groups were used to assess the degree of oxidation of the aerosol species above the canopy, within the canopy, and at ground level. This presentation will describe the variation of aerosol chemical composition at these sampling locations.

12PD-23

CHARACTERIZATION OF PAHS IN GAS AND PARTICULATE PHASE IN AIR SAMPLES AT THE METROPOLITAN AREA OF SANTIAGO, CHILE 2002,

FRANCISCO CERECEDA, Universidad Técnica Federico Santa María; Avenida España 1680; Valparaíso; V Región; Chile

A monitoring campaign of PM2.5 was carried out in the winter period, from June to October 2002 in the urban atmosphere of Santiago de Chile. The purpose of the study was to characterize the concentration profile of 16 EPA polycyclic aromatic hydrocarbons (PAHs), as well as to evaluate their possible sources of these toxic organic pollutants. Sampling was carried out at the Pudahuel Monitoring Station, located in the occidental part of the city. Samples were collected using a novel aerosol sampler (Partisol 2300 Speciation Sampler from R&P). PAHs in gaseous phase as well as associated to particulate matter (PM) were detected and quantified using gas chromatography/FID analysis. The mean concentrations of total PAHs (TPAH), observed in Pudahuel between Jun-Oct. 2002, considering the sum of those retained on polyurethane foam filter (PUF) and on filter (F), were 1370 ng/m3, whereas in downtown Santiago (Jun/Oct 2001), were found only 84 ng/m3. In Pudahuel, a high and sustained mean concentration in (F +PUF) of PHEN (38-217 ng/m3) and (BBF+BKF) (13-2217 ng/m3) was observed. Those high concentrations can be associated to biomass burn. The distribution of PAHs in the gaseous and particulate phase shows an opposite tendency in Santiago than cities in North America or Europe. Whereas in Santiago the proportion of volatile PAHs in the PUF was larger than in the filter, even for the less volatile PAHs, while in the northern countries the PAHs retained on filters predominated. Mean values of the *CPAH/TPAH ratio are indicative of emissions from non-catalyst and catalyst equipped automobiles and heavy-duty diesel trucks. These ratio calculated for Pudahuel 2002 was 0,73, that is not indicative of these emission sources. This ratio is very different from that observed in downtown in 2001 (0,53), which is associated mainly to mobile source emission. These conclusions are further supported by the molecular diagnostic ratios of other PAHs, such as [BAA/(BAA+CHR)] ratio that in Pudahuel was 0,59, indicating a considerable contribution of PAHs generated by biomass burning. The [IND-PYR/(IND-PYR+BGHIP] ratio found in Pudahuel (0,61) is smaller than the value found in downtown 2001 (0,66), indicating that diesel fuel is a source of PAHs in both part of the city, but a minor source in Pudahuel.

12PD-24

BLACK CARBON MEASUREMENTS IN CHICAGO, ILLINOIS,

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Black carbon (BC) is the most strongly absorbing constituent in fine aerosol fractions. Aerosol radiative forcing is important in regional and global-scale radiative balance, as aerosols can scatter and absorb incoming radiation. BC is a primary aerosol emitted through incomplete combustion of fossil fuels, mostly by diesel engines. Diesel traffic is significant in urban areas, and BC moves out into surrounding regions. To obtain BC data, we operated a seven-channel aethalometer at the Hinds Laboratory's Urban Atmosphere Observatory at the University of Chicago. The results of the initial measurements indicate that significant loadings of BC are released from the Chicago area during the rush hour, as anticipated. Daily emissions of BC are typically in the range of 4-10 micrograms per cubic meter. Weekend and holiday BC levels are typically lower than weekday levels by a factor of approximately five. Daily BC averages of 1 microgram per cubic meter were observed in sampling from June 2004 to October 2004. Results of sampling in the Mexico City megacity complex in April 2003 also showed a fivefold decrease in BC during periods with reduced diesel traffic. The Chicago BC measurements are continuing. Plans are under way to add a second sampling site closer to downtown Chicago, at the University of Illinois at Chicago, for further comparison. We also hope to compare data before and during construction on major highways in Chicago, when heavy diesel engine usage is anticipated. This work was supported by the U.S. Environmental Protection Agency through a grant for the Center for Environmental Science. The submitted manuscript has been created by the University of Chicago as operator of Argonne National Laboratory under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the government. Argonne National Laboratory is operated by the University of Chicago for the U.S. Department of Energy, Office of Science, under contract W-31-109-Eng-38. The Center for Environmental Science is supported through a grant from the U.S. Environmental Protection Agency.

12PD-25

PARTICULATE ORGANIC MATTER IN THE ATMOSPHERE OF ROME, ITALY: ITS COMPOSITION AT THE REFERENCE BACKGROUND URBAN SITE,

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Airborne particulate matter (both total and pulmonary fraction PM10) was collected for chemical investigations inside the largest green park in the city (Villa Ada), sited in downtown Rome. A monitoring station for regulated atmospheric pollutants is currently running there, as this site has been identified as representative of the urban "background pollution". Indeed, that site lies quite far from any major anthropic emission source including vehicles, domestic heating, cooking, house cleaning, handicraft and commerce activities. For this study, the station was implemented with the measurement of unregulated organic pollutants (n-alkanes, PAHs, nitro-PAHs and fatty acids), conducted over one year starting from May 2003. A pair of sequential samplers aspirating air at 1.0 m3 min-1 were used, one of which was equipped with an inertial impactor cutting off particles with aerodynamic diameters larger than 10 µm. Aerosols were collected day per day, beginning at 00:00 local time, onto 47 mm o.d. quartz filter membranes, then were pooled in four groups per month [1~7; 8~15; 16~22; 23~end], solvent extracted and analysed by applying gas chromatographic and mass spectrometric methods. Briefly, the results obtained indicate that: - fatty acids, and in some cases n-alkanes, represent the major group of components identified, in terms of relative abundance; - depending upon the year time, bacterial activity or high vegetation seems to be the main source of long-chain fatty acids, whilst the predominance of A16 and A18 indicates the role played by vehicle traffic on pollution of Rome atmosphere; - n-alkanes present the monomodal distribution centred at C19~C24, typical of anthropogenic (petrogenic) emission, while the contribution of high vegetation (C27~C35 odd carbon homologues) is strongly dependent on seasonality; - PAHs reach quite high concentration in cold months, whilst in spring and summer the meteo-climatic regime seems to promote their dispersion and decomposition; - nitro-PAHs present in the air originate from both direct emission and in-situ generation, with the former source prevailing during winter time; - although vehicles seem to be the major source of pollution in Rome, however other year time modulated emitters contribute to the presence of organic particulates, reducing the quality of the atmosphere of that city.

12PD-26

FINE PARTICULATE ABRASION PRODUCTS FROM LEAF SURFACES OF URBAN PLANTS: COMPARISON BETWEEN LOS ANGELES AND PITTSBURGH,

ORHAN SEVIMOGLU, Wolfgang F. Rogge, Anna Bernardo-Bricker, Florida International University, Miami, FL; Allen Robinson, R. Subramanian, Carnegie Mellon University, Pittsburgh, PA

Up to now, only one source profile for organic PM2.5 was available for samples collected during a leaf surface abrasion study conducted for Los Angeles (Rogge et al., ES&T, 27, 2700-2711, 1993). These PM2.5 source profiles for "green" and "dead" leaf surface abrasion products are widely used throughout the USA for source apportionment studies, despite the different distribution of plants and trees from location to location. Here, an additional source profile for organic constituents associated with fine particulate leaf surface abrasion products from the Pittsburgh area has been generated. Green leaves from 11 common tree species that are characteristic for the Pittsburgh area were harvested and composited according to a tree survey for that area. To simulate leaf surface abrasion by the wind, the leaf composite was agitated in a clean Teflon bag while a purified airstream flowed through, similar to the procedure used for the Los Angeles samples. Fine particles (d ≤ 2.5 pm) shed from the leaf surfaces were extracted and analyzed using gas chromatography/mass spectrometry. Organic constituents including n-alkanes, n-alkanoic acid, n-alkenoic acids, resin acids, phenolic type compounds, and others. Trace amounts of PAH and oxy-PAH were identified and quantified as well. The Los Angeles and Pittsburgh profiles for leaf surface abrasion products from leaves are compared. Overall, the organics profiles for both sites are similar, with differences mainly for the concentration levels of most compound classes. Waxy n-alkanes levels are lower than that found for Los Angeles, possibly a result of the different plant composition as well as differences in climate. Instead, leaf surface n-alkanoic acids for green leaves from Pittsburgh show higher concentrations than the respective Los Angeles green leaf sample, closer to that observed for dead leaves. Individual PAH levels for the Pittsburgh leaf surface abrasions are up to 10 times higher than what was found for the Los Angeles set of green and dead leaf samples.

12PD-27

SOURCE PROFILES FOR ORGANIC PM2.5 FOR DIESEL TRUCKS AND GASOLINE VEHICLES DETERMINED FOR THE SQUIRREL HILL TUNNEL IN PITTSBURGH, PA,

ANNA BERNARDO-BRICKER, Wolfgang F. Rogge, Orhan Sevimoglu, Florida International University, Miami, FL; Allen Robinson, Eric Lipsky, Andrew Grieshop, Carnegie Mellon University, Pittsburgh, PA

The Squirrel Hill Tunnel is a 4-lane highway tunnel on Interstate 376 on the eastern edge of the City of Pittsburgh. It is 4,225 feet long, has a 2.5% up-grade in the westerly direction and carries both commercial and non-commercial traffic. Sampling was conducted in the tunnel's west-bound tube during November of 2002. Furthermore, ambient background samples were collected as well to correct for intrusion of ambient air pollution into the tunnel. All together more than twenty PM2.5/PUF sample pairs were collected. These samples were analyzed for: n-alkanes, iso- and anteiso-alkanes, n-alkanoic acids, n-alkenoic acids, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, alkylcyclohexanes, resin acids, levoglucosan, phenolic type compounds, sterols, thiazoles, hopanes, steranes, PAHs, oxy-PAHs, N-Hetero-PAHs, S-Hetero-PAHs, and others. Here, the tunnel samples will be discussed in reference to measured ambient organic compound concentrations. Further, using information about the type of vehicles entering the tunnel, we will attempt to categorize tunnel sample according: mainly gasoline powered vehicles versus mainly diesel trucks and therefore, provide source profiles for the Eastern US that will be helpful in source/receptor apportionment studies.

12PF-28

IDENTIFICATION OF GASOLINE AND DIESEL EMISSIONS IN THE PM2.5 OF A MIDWESTERN U.S. AREA,

EUGENE KIM, Philip Hopke, Clarkson University, Potsdam, NY

In recent studies, positive matrix factorization (PMF) was applied to ambient PM2.5 (particulate matter less than 2.5 micrometer in aerodynamic diameter) compositional data sets of daily integrated samples including eight individual carbon fractions collected at four monitoring sites across U.S.: Atlanta, GA, Washington, DC, Brigantine, NJ, and Seattle, WA. PM2.5 carbon was analyzed using the Interagency Monitoring of Protected Visual Environments/Thermal Optical Reflectance (IMPROVE/TOR) method that divides carbon into four organic carbon (OC), pyrolyzed organic carbon (OP), and three elemental carbon (EC) fractions. In these studies, gasoline emissions could be distinguished from diesel emissions based on the differences in the abundances of the carbon fractions between the two sources. The objectives of this study are to examine the use of carbon fractions to identify PM2.5 sources in Midwestern U.S. area and estimate their contributions to the PM2.5 concentrations. In the present study, PMF was applied to an ambient PM2.5 compositional data set of 24-hour integrated samples including eight individual carbon fractions collected at the IMPROVE monitoring site in Bondville, IL. PMF identified eight sources including gasoline and diesel emissions. The compositional profiles for gasoline and diesel emissions are similar to those resolved in previous studies. Also, using the temperature resolved carbon fractions enhanced the separation of carbon-rich secondary sulfate aerosols.

12PF-29

LABORATORY EXPERIMENTS EXAMINING ULTRAFINE PARTICLE PRODUCTION BY RE-BREATHING OF ROAD DUST THROUGH A DIESEL ENGINE,

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Re-breathing involves the uptake and internal processing of ambient road dust particles by vehicular engines. The effect of re-breathing will be to transfer road dust constituents from the coarse mode into the fine and ultrafine modes. This has serious implications since small transfers of coarse mode mass can produce large numbers of fine and ultrafine particles, potentially increasing the risk of respiratory health effects. An essential step in validating the significance of this process is identifying the presence of road dust constituents in the fine and ultrafine particles of an engine's exhaust. These particles should contain mixtures of EC/OC and road dust elements. A series of experiments have been performed to examine the feasibility of re-breathing. Road dust was re-suspended in the intake air of a diesel engine and the exhaust monitored for single particle size and composition using RSMS-2, a single particle mass spectrometer, as well as bulk properties using a MOUDI sampler with subsequent analysis by ICP-MS. All single particle spectra have been individually calibrated, inspected and separated into two categories: those containing EC/OC mass peaks only and those containing both EC/OC and Ca/CaO/Fe mass peaks. To distinguish between road dust re-breathing and the engine's oil as possible sources of ultrafine calcium, identical experiments and analyses were performed with particle free air. Results indicate that the fraction of single particles containing calcium for the case of road dust intake, as compared to clean air intake, increases by factors ranging from 2 to 9, depending on the operational parameters of the experiment. Data from the MOUDI analysis is in good agreement with single particle results; showing total Fe mass concentration increasing by a factor of 65 and total Ca mass concentration by a factor of 6. To validate the existence of these constituents in road dust particles, the road dust samples used in these experiments were also directly analyzed. Again, both techniques were in very good agreement in terms of particle size and composition. Comparison of these results with those described previously not only supports the feasibility of re-breathing, but clearly elucidates the shift in Ca/Fe mass from the coarse mode to the fine and ultrafine modes during the process of re-breathing.

12PF-30

ESTIMATING AND UNDERSTANDING THE IMPACTS OF FIRE ON REGIONAL PARTICULATE MATTER CONCENTRATIONS,

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The terrestrial biosphere plays a significant role in the processes that control air quality. Direct aerosol emissions from vegetation and wildfires and secondary aerosols formed from biogenic volatile organic compounds (VOC) can impact public health, reduce visibility, change cloud properties, and control climate processes. Understanding these emissions and including these processes in regional air quality model simulations is essential for evaluating air pollution and visibility deterioration, and for creating effective policies to reduce such problems. This paper reviews a new modeling approach that can be used to estimate the emissions from fires. Fires emit a variety of gases and aerosol to the atmosphere, including VOC, particulate matter (PM), ammonia (NH3), and sulfur dioxide (SO2). We present here a methodology for creating fire emission inventories for these and other emissions for input to regional air quality models. This model framework utilizes existing data, including satellite data, such as the MODIS Thermal Anomalies product. Emissions from fires in all of North America are included in the emissions inventory since fires in Canada and Central America often impact air quality in the United States. The output from this model will enable regional photochemical modelers to easily include relevant fire emissions into their model simulations and to determine if those emissions impact the predicted air quality. If fire emissions are shown to have an effect on the modeled air quality, and further, on the conclusions made from the model simulations, more detailed fire emissions inventories can be created. Examples of the fire emission estimates for 2002 through 2004 developed from this model framework will be provided. Estimated PM2.5 emissions from North American fires will be compared to those emissions from anthropogenic sources, and the magnitude of the emissions from fires, both in forested regions and in agricultural land uses, will be assessed. The importance of biogenically-derived and anthropogenic organic carbon particulate matter will be addressed using the results from this model, the National Emissions Inventory, and estimates of organic aerosol created from the oxidation of certain biogenic VOC [see Milford et al., this conference]. Regional air quality impacts of those emissions will be evaluated with the Community Multiscale Air Quality Model (CMAQ). The implications of the emissions on the model results, and further, on potential policy decisions guided by model results will be addressed.

12PF-31

AEROSOL COMPOSITION DISPARITY BETWEEN NORTHERN AND SOUTHERN STATES IN THE SOUTHEAST,

Wei Liu, Yuhang Wang, Armistead Russell and Eric S. Edgerton

SEARCH observations of aerosol compositions in Georgia and Alabama are compared to Mississippi and Florida using the Positive matrix factorization (PMF) method. One pair of urban and rural sites in each state is used to examine the regional and urban influence on PM2.5 concentrations in the Southeast. Spatial correlations of factors were investigated using the square of correlation coefficient (R2) calculated from the resolved G factors. Factors were normalized by using aerosol fine mass concentration data through multiple linear regression to obtain the quantitative factor contributions for each resolved factor. The aerosol composition characteristics are contrasted between urban and rural sites and between northern and southern sites. Besides PMF analysis, potential source contribution function (PSCF) analysis, which combines the aerosol data with the air parcel backward trajectories, is applied to identify possible source areas and pathways from these factors at the four sites. The combination of the two receptor modeling methods, PMF and PSCF, provides an effective way in identifying atmospheric aerosol sources and their likely locations. Emissions from different anthropogenic activities as well as secondary aerosol production are the main source measured in these sites.

12PF-32

SOURCE APPORTIONMENT OF PM10 IN THE SAN JOAQUIN VALLEY THROUGH INDIVIDUAL PARTICLE ANALYSIS USING SCANNING ELECTRON MICROSCOPY TECHNIQUES,

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Annual and 24-hour PM10 standards have been exceeded at most measurement locations in the San Joaquin Valley designating the area as nonattainment for PM10. Studies conducted by the California Air Resources Board (CARB) indicate that approximately 80 to 90 percent of the non-winter concentrations consist primarily of geological and carbonaceous material. Attempts to apportion the geological and carbonaceous particles using receptor models based on bulk chemical data have proved unsuccessful. Scanning electron microscopy (SEM) methods were explored to characterize PM10 in the Corcoran area of the San Joaquin Valley in an effort to determine whether the SEM data could distinguish among sources that have similar bulk chemical characteristics. Of particular interest was determining the impact from neighborhood, urban, and regional sources. During an intensive sampling program conducted in the Corcoran area over a period of thirty-seven days from October 9, 2000 until November 14, 2000, 227 PM10 samples were collected on polycarbonate (PC) filters. The samples were collected at five locations within Corcoran. Samples were also collected at a remote location to estimate regional influence on ambient air. Seventy of the samples were selected for analysis using computer controlled scanning electron microscopy (CCSEM) techniques. Approximately 1000 particles were characterized on each sample using CCSEM. Information on size and elemental composition for each particle was obtained along with a digital image. Individual particles characterized during the analysis were grouped into classes (particle species) based on their elemental composition. Images were reviewed off-line to assist in classifying the various species. Source samples of geological material were obtained from soil samples collected near the site of each ambient monitor. The source samples were analyzed using CCSEM following procedures established for the ambient samples. The CCSEM data obtained from the source and ambient samples was used as input to the Chemical Mass Balance (CMB) receptor model to apportion the crustal component. The CCSEM data obtained from the analysis of the remote ambient monitor site was used a source sample to estimate regional impact. Results indicate that regional dust was the dominant crustal source at most locations. One of the monitoring sites had a significant impacted from local crustal sources. A detailed review of the images associated with the carbon species indicated that the organic carbon fraction was composed mainly of vegetative material.

12PF-33

CHARACTERIZATION OF SHORT-TERM PARTICLE EVENTS BY REAL-TIME SINGLE PARTICLE MASS SPECTROMETRY,

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Single particle measurements were made in Baltimore, Maryland from March to December 2002 using the Real-Time Single Particle Mass Spectrometer RSMS-3. Single particle mass spectra were simultaneously collected in positive and negative ion modes over a size range of 50 to 770 nm in diameter. At the same time, a variety of continuous monitors were operating at the site including PM2.5, particulate sulfate and nitrate, organic and elemental carbon, criteria gaseous pollutants (NOx, SO2, and ozone) and meteorological parameters. Examination of these data revealed several types of short-term particle events. Each event was characterized by a rapid increase in particle mass and/or number that was also associated with a rapid change in one or more chemical components such as nitrate, sulfate and/or organic carbon. Two types of ultrafine nitrate particle events were observed: a large burst of nominally “pure” nitrate particles in the 50-90 nm size range, and a smaller (and less frequent) burst of “pure” particles in the 50-90 nm size range that grew to 110 -220 nm with time. Coincident with both of these events was an increase in the number of mixed composition particles containing nitrate, suggesting that they were formed by condensation of ammonium nitrate onto pre-existing particles. Meteorological variables, particle number concentrations and continuous nitrate mass measurements were compared to the single particle data. Number and mass concentrations estimated from RSMS-3 correlated well with similar measurements using other techniques. Ultrafine nitrate particle events were observed primarily in the spring and fall during periods of lower temperature and higher relative humidity as expected from ammonium nitrate equilibrium considerations. A few carbon particle events were observed in which total PM2.5 mass concentrations were elevated. These phenomena were characterized by the percentage of the particle mass that contained carbon. In these cases, over half the aerosol mass was carbon. Not only were mass concentrations high during this time, but RSMS-3 data showed high number concentrations of carbon particles at these times as well. Secondary aerosol events were also observed in which high overall particle mass concentrations were high. It was found that a majority of the particle mass was comprised of sulfate. Unfortunately, a significant bias exists for the detection of sulfate by RSMS-3 in that small particles are more likely to yield electrons than negatively charged atomic and molecular ions. Since sulfate is detected almost exclusively in negative ion spectra, small particles are less likely to show the presence of sulfate. Therefore, RSMS-3 data cannot be used for direct estimates of ambient mass or number concentrations of particulate sulfate. Nonetheless, these events can be potentially followed by RSMS through the detection of internally mixed particles that are consistent with aerosol processing in the atmosphere. The results of this analysis will be presented.

12PF-34

DETECTION OF A CONTAMINATING PLUME DURING A ROADWAY TUNNEL SOURCE SAMPLING EXPERIMENT USING A SINGLE PARTICLE MASS SPECTROMETER,

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Experiments were performed on five separate days in which the air from an exhaust duct in the ventilation shaft of a roadway tunnel was sampled and characterized by a single particle mass spectrometer (RSMS-2) and an SMPS. The single particle mass spectra from each experiment have been independently clustered into particle classes. Results indicate that the particle classes from the last four experiments are highly correlated, containing very similar chemical compositions; predominantly combinations of EC/OC, sodium and potassium salts, and road dust. Particle classes identified during the first experiment, however, are very different than the subsequent experiments; with ~ 92% of the spectra collected containing signature mass peaks for aliphatic amines. Other source sampling experiments have shown that this group of compounds is the dominant particle class in the emissions of a coke processing plant. In fact, the three largest particle classes identified during the first tunnel experiment (~ 96% of the spectra collected) are identical to three of the four largest classes identified during the coke plant sampling (~ 86% of the spectra collected). The nearest coke plant to the tunnel is situated ~ 15 km to the northeast. Meteorological data, collected at the Schenley Park site (~ 2.2 km northeast of the tunnel), shows that the wind blew from the direction of the coke plant for five hours previous to the collection of the tunnel sample, allowing plenty of time for the transport of the plume from the plant to the tunnel. Examination of the local topography reveals a major river channel running directly from the plant to the tunnel, limiting dilution between the two. Together, this evidence supports the hypothesis that the sample collected from the tunnel during the first experiment was highly contaminated by a plume from the coke plant.

13A-1

WILDFIRES IN EASTERN TEXAS IN AUGUST AND SEPTEMBER 2000: EMISSIONS, AIRCRAFT MEASUREMENTS AND IMPACT ON CHEMICAL AND PHYSICAL PROCESSES,

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The impact of wildfires on air pollutant concentrations in southeast Texas during August and September of 2000 was assessed through emission inventory development, emission inventory performance evaluation and air quality modeling. Fire emissions were estimated from acreage burned, fuel loading information and fuel emission factor models. A total of 389 km2 (96,100 acres) burned in wildfires in the domain encompassing the Houston/Galveston-Beaumont/Port Arthur (HGBPA) area during August and September 2000. The amount of acreage burned during these two months in 2000 was approximately an order of magnitude greater than the amount of acreage burned in wildfires during previous years for which detailed emission inventory data are available (1996, 3960 acres; 1997, 14,600 acres). On the days of highest wildfire activity in 2000, the fires resulted in an estimated 3700 tons of CO emissions, 250 tons of VOC emissions, 340 tons of PM2.5, and 50 tons of NOX emissions; estimated CO and VOC emissions from the fires exceeded light duty gasoline vehicle emissions in the Houston area on those days. When the appropriate aircraft data were available, aloft measurements of CO, mixing heights and wind speeds in the fire plumes were used to estimate emission rates. Emission rates based on emission factors were in excellent agreement with the emission rates based on observations, however, both the emission estimates and the observations had uncertainty bounds of a factor of 2. The estimated emissions from fires were used, together with a gridded photochemical model (the Comprehensive Air Quality Model with extensions, CAMx), to characterize the extent of dispersion of the fire emissions during the summer of 2000. Although the dispersion and photochemical impacts varied from fire to fire, air quality impacts extended over large areas (hundreds of square kilometers) and localized PM2.5 concentrations of >100 micrograms/m3 were observed.

13A-2

THE EFFECT OF A WOOD SMOKE EPISODE IN TEXAS ON FINE PARTICULATE MATTER CONCENTRATIONS AND COMPOSITION,

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To evaluate the impact of regional wildfires in East Texas on fine particulate matter concentrations and composition, source apportionment calculations were performed on a set of samples collected on days during a wood smoke episode, when particulate matter concentrations in Houston were greatly influenced by forest fires, and separately on other days not influenced by wood smoke at three sites in Houston. Analysis of the data collected on non-wood smoke-episode days indicated that the major contributors to PM2.5 mass were secondary sulfate, diesel and gasoline powered vehicles, other organics, wood combustion and meat cooking. Secondary sulfate represented almost 100% of the sulfate measured whereas primary sources were found to account for the majority of the measured organic carbon at three sites. On the wood smoke episode days, the same major sources were found to be contributing to PM2.5 levels at each site except that the contribution of meat cooking source was insignificant on these days, which was supported by the considerable decrease in octadecenoic acid levels during the episode. The contribution of the wood combustion source showed an increase by an average of 66% at all sites whereas the contributions of other primary sources did not increase significantly during the wood smoke episode. This result is consistent with the measurements of the concentrations of levoglucosan, which showed an increase of 63% during the wood smoke episode at each site, while the concentrations of other marker species were not dramatically higher on the wood smoke episode days. PM2.5 mass almost doubled on the wood smoke episode days, and the contributions of the secondary sources, namely secondary sulfate and other organics increased 42% and 72% at each site, respectively. The examination of the contribution of each source to the mass balance species confirmed the results obtained by other studies and justified the use of the correct molecular markers that represent fine particle mass.

13A-3

AIR QUALITY IMPACTS OF PRESCRIBED BURNING IN GEORGIA, SANGIL LEE, Karsten Baumann, Mei Zheng, Armistead Russell, Georgia Institute of Technology, Atlanta, GA, James Schauer, Rebecca Sheesley, University of Wisconsin, Madison, WI, Luke Naeher, University of Georgia, Athens, GA, Mark Clements, Southeast Regional Office, Installation Management Agency, U.S. Army, Fort McPherson, GA

Wildland fires are important sources of air pollutant emissions resulting in large amounts of fine PM and gaseous pollutants being released into the atmosphere. According to EPA, forest fires (wildfires and prescribed burning) contribute 18 % of the ambient primary fine particulate matter (PM2.5) emissions in Georgia. A major factor is that prescribed burning is the preferred method of choice to manage forested land in the southeastern U.S. For example, the three largest military installations in Georgia, Forts Stewart, Benning, and Gordon, actively burn. It is mandated by the Endangered Species Act for areas that provide natural habitat of endangered species, as is the case for most of the long leaf pine forests in the southeast. Hence, private land owners and land managers on military installations both use prescribed burning, however, at different intensities. While on a single day, up to 5,000 acres can be burned in a relatively concentrated fashion at the military bases, prescribed burns on private land are more scattered over Georgia, leading to more than 1 million acres annually (GFC, 2003). However, these fires are not well characterized in terms of chemical composition of their primary emissions of Particulate Organic Compounds (POC) in PM2.5 and also their impacts on air quality. PM2.5 emissions of prescribed burning were measured directly at the source during prescribed burns on large military installations near Augusta and Columbus, GA in the spring 2004. In addition to monitoring directly at the burns, ambient measurements also were made using hi-volume samplers and Particle Composition Monitors (PCM) at the State's regulatory monitoring sites in Augusta and Columbus before, during, and after the actual prescribed fires. Emission measurements made in the field provided a unique and realistic profile of the chemical composition of this type of biomass burning. In the past, Chemical Mass Balance (CMB) modeling approaches have made little to no distinction between wild fires, prescribed fires and residential wood burning for estimating source contributions from biomass burning. Most emission factors for open burning were determined in laboratory experiments that insufficiently represent the overall emissions of such large burns by not considering the significant emissions from the underlying soils and neighboring (or overhead) vegetation. The newly generated source profiles were applied in a CMB model to apportion the source contributions at the ambient receptor sites, and these results will be compared with estimated contributions using previous literature profiles.

13B-1

AGRICULTURAL AMMONIA EMISSIONS AND AMMONIUM DEPOSITION ASSOCIATED WITH PRECIPITATION IN THE SOUTHEAST UNITED STATES, VINEY P. ANEJA, Dena R. Nelson, and Paul A. Roelle. Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, NC; John T. Walker (now at U.S. Environmental Protection Agency, MC-E305-02, Research Triangle Park, NC); William Battye EC/R Inc., 6330 Quadrangle Drive, Chapel Hill, NC

Agricultural ammonia emissions and ammonium deposition associated with precipitation in the southeast United States Viney P. Aneja*, Dena R. Nelson, and Paul A. Roelle Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, North Carolina, USA John T. Walker Now at: U.S. Environmental Protection Agency, MC-E305-02, Research Triangle Park, NC 27711, USA William Battye EC/R Inc., 6330 Quadrangle Drive Chapel Hill, North Carolina 27517, USA * Corresponding Author Abstract Temporal and spatial variations in ammonia (NH3) emissions and ammonium (NH4+) concentrations and deposition associated with volume-weighted NH4+ concentration in precipitation are investigated over the period 1990–1998 in the southeast United States (Alabama, Florida, Georgia, Kentucky, North Carolina, South Carolina, Mississippi, and Tennessee). These variations were analyzed using an NH3 emissions inventory developed for the southeast United States and the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Results show that natural log-transformed annual volume-weighted average NH4+ concentration in precipitation shows only a very weak positive correlation with natural log-transformed annual NH3 emission densities within the corresponding county ($R2 = 0.12$, $p = 0.04$, $N = 29$). Investigation into wet NH4+ concentration in precipitation consistently yielded temperature as a statistically significant ($p < 0.05$) parameter at individual sites. Positive trends in NH4+ concentration in precipitation were evident at NADP sites NC35, Sampson County, North Carolina (0.2–0.48 mg L-1) and KY35, Rowan County, Kentucky (0.2–0.35 mg L-1) over the period 1990–1998. For presentation at 2005 AAAR PM Supersites Conference, Atlanta, GA February 2005.

13B-2

AMMONIA EMISSIONS FROM NORTH CAROLINA HOG FARMS: LAGOON AND SPRAY TECHNOLOGY AND POTENTIAL ENVIRONMENTALLY SUPERIOR TECHNOLOGIES,

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Ammonia Emissions from North Carolina Hog Farms: Lagoon and Spray Technology and Potential Environmentally Superior Technologies Ian C. Rumsey*, Viney P. Aneja and S.Pal Arya Department of Marine, Earth and Atmospheric Sciences North Carolina State University Raleigh, NC 27695 -8208, U.S.A Globally, the largest source of atmospheric NH3 is domestic animal waste contributing 20-35 Tg of nitrogen per year. In North Carolina, hog waste accounts for 47% (~0.15 Tg N yr-1) of all ammonia emissions. This is the result of an increase in hog population since the 1980's from ~3 million to ~10 million hogs. Currently swine waste is managed using Lagoon and Spray Technology (LST) also known as 'conventional' technology. A LST uses anaerobic lagoons to store the hog waste, and the effluent from lagoons is sprayed on surrounding crops as a source of nutrients. This technology leads to a number of sources of ammonia emissions. Alternatives to the LST have been developed and are called environmentally superior technologies (EST's).Two potential EST's were examined in this study, (1) EKOKAN: Up-flow Bio-filtration system, (2) BEST: Solids separation/ gasification for energy and ash recovery centralized system. The BEST technology used two different solid/separation techniques. Ammonia emissions were measured from water-holding structures at the EST's. In order to compare and contrast the LST and EST's, measurements for ammonia emissions were made at water-holding structures at two LST farms, Stokes Farm and Moore Farm, respectively. Measurements of NH3 flux were performed during two, two-week long periods, representing warm and cold seasons. Flux measurements were obtained by using a dynamic flow-through chamber system interfaced to a mobile laboratory containing the ammonia analyzer and the data acquisition system. During the sampling period, environmental parameters such as lagoon temperature, lagoon pH, and TAN were measured, as well as meteorological parameters such as wind speed, wind direction, air temperature, relative humidity, and solar radiation. Ammonia emissions were normalized to nitrogen excretion. For the LST's we have estimated an average emission from water-holding structures of 2.8 kg NH3/yr/head for Stokes farm and 2.7 kg NH3/yr/head for Moore farm. Averages of emissions were found to be significantly lower from the EST's than the LST's. The Ekokan EST yielded average emissions of 1.5 kg NH3/yr/ head. The BEST EST produced lower emissions of 1.1 kg NH3/yr/head for both solid/separation techniques. * Corresponding author Email:icrumsey@ncsu.edu For oral presentation at: Particulate Matter Supersites Program and Related Studies, An AAAR International Specialty Conference, Atlanta, GA February 7-11, 2005

13B-3

A PASSIVE FLUX DENUDER FOR EVALUATING FUGITIVE AMMONIA EMISSIONS,

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There is significant interest in developing economical methods to quantify ambient concentrations of gaseous pollutants. Passive samplers can provide an inexpensive alternative to direct sampling for these types of measurements. Conventional denuder technology has been developed to make measurements of semi-volatile pollutants, however active sampling of this type inherently requires electrical power and pumps. . Our passive flux sampler design is based on the approach that used a denuder tube, but the design was modified to use 47mm fabric denuders. Fabric denuders were originally developed to measure nitric acid in an active sampling mode. Cotton fabric with size of 100 µm spaced on centers of 250 µm has been shown to efficiently remove gaseous species when coated with a suitable adsorbent. Like filter types of active samplers, an open-face Teflon filter holder was used to locate a pair of fabric denuders. However, instead of an outlet to a pumping system, an open outlet is used. This open outlet was made from a section of machined 50mm PVC pipe. The other end of the PVC pipe is fitted with a similar pair of denuders, so there is symmetry on both sides of the center axis through the PVC pipe. No flow restriction device was necessary. Sample collection depended on the wind flowing through the assembly. The amount of ammonia collected, was therefore proportional to the wind speed, direction, and ammonia concentration. To measure the flux at a point, two such samplers were needed: one on an east-west axis, the other on a north-south axis. A variable speed blower was used to simulate wind speeds from 2 to 7 m sec-1. Measurements were then made of the pressure drop inside the denuder assembly for various air speeds generated by the blower. The pressure drop was calibrated for the flow rate through the denuder. The experimental results showed that the flow through the denuder is linearly reduced by approximately a factor of 11. Initial investigations were carried out at a dairy farm located on the California State University, Fresno, Agricultural Research Facility. Dairy farms and their practices of using lagoon effluent for fertilization of nearby agricultural fields have been known to be an important source of ammonia. The data reported here are from a dairy lagoon that underwent acidification and from the primary source, the dairy farm as a whole. Comparisons were made of the flux measurements obtained directly from the passive flux denuder and those calculated from an active filter pack sampler and wind velocity. The results show significant correlation between the two methods and invite further investigation into characterization of the passive flux denuder response. With further evaluation of this technique, it is possible that a larger inventory base for ambient ammonia emissions, can be developed more economically than by using active samplers.

13B-4

ESTIMATING AMMONIA EMISSIONS FROM LAGOON-ATMOSPHERE INTERFACE BY COUPLED MASS TRANSFER AND CHEMICAL REACTION MODEL AND WATER9 MODEL,

KANWARDEEP S BAJWA, Viney P. Aneja, North Carolina State University, Raleigh, NC; Clark Allen, RTI International, Research Triangle Park, NC

Ammonia has recently gained importance for its increasing atmospheric concentrations and its role in the formation of aerosols. Anaerobic lagoon and spray method, commonly used for waste storage and treatment in confined animal feeding operations (CAFOs), is a significant source of ammonia emissions. An emission model for ammonia from aqueous surface can help in the development of emission factors. Data collected from field measurements made at hog farm lagoons in south eastern North Carolina, using emission flux chamber, was used to validate the Coupled mass transfer and chemical reaction model and Equilibrium model developed by Aneja et al., (2001). Sensitivity analysis shows that ammonia flux increases exponentially with lagoon temperature and pH, but linear increase was observed with increase in total ammoniacal nitrogen (TAN). Ammonia flux shows a second degree increase with increasing wind speed. Model results of emissions based on the coupled mass transfer with chemical reaction model agreed well with the measurements. However, the US EPA’s WATER9 emissions model seems to predict greater ammonia emissions, especially at the higher wind speeds. WATER9 calculations were used to analyze mass transfer in the flux chamber. Aneja , V. P., Malik, B. P., Tong, Q., Kang, D., and Overton, J. H., “Measurement and modeling of ammonia emissions at waste treatment lagoon-atmospheric interface”, Water, Air and Soil pollution: Focus 1, 177-188, 2001.

13C-1

A QUANTITATIVE COMPARISON STUDY OF THERMODYNAMIC EQUILIBRIUM MODELS FOR MULTIPHASE MULTICOMPONENT INORGANIC AEROSOLS:EQUSOLV II AND ISORROPIA,

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A quantitative comparison study of two published thermodynamic equilibrium models, EQUISOLV II and ISORROPIA, were conducted under various atmospheric gas phase ammonia, acid gases, and fine particles concentrations, relative humidity (RH), and temperature. EQUISOLV II has been considered as the most comprehensive aerosol chemistry and thermodynamic model providing detailed particulate matter predictions including crustal elements, while ISORROPIA simplifies assumptions in an effort to increase computational flexibility. Model performances are evaluated for representative atmospheric environments over various particle compositions depending on various moral ratios, relative humidity, and temperature due to the fact that the compositions of particles in the atmosphere are highly sensitive to molar ratio changes, ambient temperature as well as RH. For the purpose of this comparison, we defined the four dimensionless ratios according to the chemical concentrations in the atmosphere: the molar ratio of total ammonium (TNH4) (i.e., sum of gaseous ammonia, NH3(g), and particulate ammonium, NH4+ (p)) to total sulfate (TSO4) : referred to as TNH4/TSO4, the molar ratio of total nitrate (TNO3) (i.e., sum of gaseous nitric acid, HNO3(g), and particulate nitrate, NO3-) to total sulfate (TSO4) : referred to as TNO3/TSO4, the molar ratio of total sodium chloride to total sulfate : referred to as TNaCl/TSO4, and the molar ratio of total cation species (TCAT) (i.e., sum of total ammonium, TNH4, and total sodium, TNa) to total sulfate : referred to as TCAT/TSO4. The relative strengths and weaknesses of each thermodynamic equilibrium model are analyzed by comparing the model simulation results under a variety of thermodynamic equilibrium regimes, and the causes for these discrepancies are discussed in detailed. The recommendations for the selection of such models for application in future 3-D air quality PM modeling studies are provided. In most atmospheric conditions, these two model predictions are generally comparable and agreeable under alkaline conditions (TCAT/TSO4 > 2.0). However, differences exist under certain conditions around or greater than 70% RH, and under acidic conditions (TNH4/TSO4 < 2.0 ; TCAT/TSO4 < 2.0). Especially, under acidic conditions, the nitrate concentrations in ISORROPIA are under-predicted due primarily to the different treatments of equilibrium chemical reactions and equilibrium constants. ISORROPIA predicted higher [H2O] for RH = 70% than EQUISOLV II due mainly to the consideration of Mutual Deliquescence Relative Humidity (MDRH) for mixed aerosol salts in ISORROPIA. The overall differences between these models are from due primarily to the different treatments of chemical species, equilibrium reactions, and the values of equilibrium constant, the calculation solution methods, i.e., the convergence iterations, binary activity method, multi-component activity coefficient method, and water activity method.

13C-2

EVALUATION OF THE CMAQ-AIM MODEL AGAINST SIZE- AND CHEMICALLY-RESOLVED IMPACTOR DATA AT A COASTAL URBAN SITE,

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In coastal environments, sea-salt particles may have a substantial influence on the atmospheric nitrate budget via their impacts on gas/aerosol partitioning and dry deposition. In many regional air quality models developed to date, the treatment of sea-salt chemistry has been excluded. Recently, a sectional aerosol model with thermodynamics derived from the Aerosol Inorganic Module (AIM) has been coupled to the Community Multiscale Air Quality model (CMAQ). The resultant CMAQ-AIM model includes treatment of sea-salt thermodynamics with dynamic mass transfer between the gas-phase and all size sections. The model is applied to simulate pollutant concentrations in the metropolitan area surrounding Tampa, Florida, in August 2001 and May 2002. As part of the Tampa Bay Regional Aerosol Characterization Experiment (BRACE), size-segregated impactor samples spanning the 0.1 – ~12 um aerodynamic diameter range were analyzed for inorganic ions including Na, NH4, Cl, NO3, and SO4 [1-2]. Model calculations from CMAQ-AIM, with nine size sections spanning the 0.039 – 20 um particle diameter range, are evaluated against these impactor data. This is the first evaluation of the CMAQ-AIM model against size-segregated aerosol measurements. In addition, a quantitative assessment of the effects of sea-salt aerosol on fine-particle mass and chemical composition will be presented. [1] S.W. Campbell, M.C. Evans, N.D. Poor, Atmos. Environ., 36: 4299-4307 (2002). [2] M.C. Evans, S.W. Campbell, V. Bhethanabotla, N. D. Poor, Atmos. Environ., 38: 4847-4858 (2004). Disclaimer: The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) and under agreement number DW13921548. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

13C-3

INVESTIGATION OF THE UNCERTAINTY IN THE INORGANIC SYSTEM RESPONSE TO CHANGES IN EMISSIONS USING THE GAS RATIO AS AN INDICATOR,

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A critical use of regional models of fine particulate matter is to predict changes in mass associated with changes in emissions. It would be very useful if a diagnostic indicator for 3-D air quality models could be identified that would illuminate the sensitivity of the inorganic system to change. The Gas Ratio (GR) of Ansari and Pandis may be such an indicator. The uncertainty in the nitrate replacement associated with a sulfate reduction is investigated for conditions at two supersites, Pittsburgh and St. Louis. The investigation uses a series of model sensitivity analyses with the Community Multi-scale Air Quality model, CMAQ. The uncertainty analyses examine the ability of the Gas Ratio to quantify differences in the nonlinear system response of nitrate replacing sulfate in the face of uncertainty in either total-nitrate or NHx. Since the GR is a ratio, the question whether the system would respond similarly if the GR were the same but the concentration levels of the components were different is also examined. The analysis developed GR’s on the basis of 24-hour averages of the gas and fine particle concentrations. In general, the GR is found to be a useful qualitative construct to guide inquiry about the system. It is found that the relative reduction factors (rrf) describing the nitrate increase for a sulfate decrease are insensitive to uncertainty in the total-nitrate in the system. On the other hand, the rrf’s for nitrate are sensitive to uncertainty in NHx. A positive bias in NHx results in a smaller nitrate rrf and vice versa. Also, the same GR’s produced by different conditions do not give the same rrf’s for nitrate replacement. Ammonia plays a significant role here. Thus, uncertainty in ammonia emissions is very important and appears to lead to uncertainty regarding simulation of the nitrate replacement of sulfate, that is, the estimated control strategy response. Disclaimer: The research presented here was performed under the Memorandum of Understanding between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Commerce’s National Oceanic and Atmospheric Administration (NOAA) under agreement number DW13921548. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

13C-4

AN EVALUATION OF A DETERMINISTIC MODELLING SYSTEM AND A NEURAL NETWORK MODEL FOR FORECASTING THE CONCENTRATIONS OF PM2.5 IN AN URBAN AREA,

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This study evaluates two fundamentally different methods of forecasting PM2.5 concentrations in time, by comparing the model predictions with observations. The methods considered are a neural network model based on a fully connected multi-layer perceptron (MLP) (Niska et al. 2004), and a deterministic urban dispersion modelling system developed at the Finnish Meteorological Institute (UDM-FMI). MLP has been shown to be suitable for atmospheric sciences and especially for predicting complex relationships between multiple variables. The urban dispersion modelling system UDM-FMI contains various models for atmospheric boundary layer scaling, evaluating the emissions, the dispersion of traffic-originated pollution (using the CAR-FMI model), the dispersion of pollution from stationary sources, and population exposure (Karppinen et al. 2000). The Numerical Weather Prediction (NWP) model used in this study is the Finnish variant of the HIRLAM model, version 4.6.2 that was in operative use at the FMI from 1999 to 2003. This model computes forecasts of various meteorological parameters with a spatial resolution of 22 km, in 31 vertical levels. In this study, we used a single grid point nearest to the air quality monitoring stations as input for the air pollution models. The reference air pollutant concentrations were obtained from the Helsinki Metropolitan Area Council (YTV). The innovative aspect of this study was to use the forecasts of a NWP model as meteorological input data for dispersion and neural network models. We have utilised the daily forecasts (+ 24 h), as these are the most relevant from a regulatory point of view. Generally, the neural network model forecasts the urban fine particle matter (PM2.5) concentrations fairly well. However, the model performance tends to deteriorate for the highest measured concentrations. This is partly due to the scarcity of suitable training data for the high-concentration episodic situations. The performance of the deterministic model was fairly good in forecasting the daily average values of concentrations, but moderate for forecasting the hourly time series of concentrations of PM2.5. However, both modelling systems are shown to be useful tools of assessment for regulatory purposes. The model applications are partly complementary, as the MLP performs reasonably well for predicting the concentrations at a fixed location, while the deterministic modelling system can produce better the forecasts of the spatial distributions of concentrations and population exposure.

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14A-1

AEROSOL SIZE DISTRIBUTIONS: A COMPARISON OF MEASUREMENTS FROM SUMMER AND WINTER FIELD CAMPAIGNS IN QUEENS, NY,

G. Garland Lala, Olga Hogrefe, Kenneth Demerjian, Atmospheric Sciences Research Center, Albany, NY

Aerosol Size Distributions: A comparison of measurements from summer and winter field campaigns in Queens, NY. G. Garland Lala, Olga Hogrefe, Kenneth Demerjian Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY 12203 Albany, NY Aerosol size distributions were measured during the summer of 2001 and the winter of 2004 at Queens, NY as part of the Supersite program. Several instruments (Nano SMPS, Long SMPS, and APS) were used to characterize the aerosol size distributions over a range from 10 nm to 10 µm. These measurements illustrate the differences in aerosol processes due to seasonal differences in meteorological conditions and sources. Size distributions from both programs exhibit a persistent mode at around 85 nm. The distributions also show small aerosol events characterized by the appearance of a second mode or a shift in the dominant mode to near 25 nm. The amplitude of these modes in the summer 2001 data is close to the size of the persistent mode but in the winter measurements, the amplitudes are commonly larger than the size of the persistent mode. These characteristics are probably related to the differences in aerosol sources as well as the rate of coagulation of small aerosols. During both seasons, departures of the size distribution from the average tend to occur during events that may be related to advection or local sources. In some cases these changes are clearly related to air mass changes. Diurnal changes are not clearly recognizable because they are masked by longer period changes. Future analysis will concentrate on the incorporation of other data that may provide information on aerosol sources and formation processes.

14A-2

SIZE DISTRIBUTION OF FINE PARTICULATE IN THE URBAN AREA OF MILAN (ITALY),

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Fine particulate presence at urban sites in the city of Milan (Italy) is characterised in terms of particles' size distribution and PM10, PM2.5, PM1 mass concentration for the cold (October to March) and warm (April to September) season. Workdays' and weekends' data from a low-volume particle size laser analyser (Grimm model 1108) are analysed for assessing the effect of the reduced traffic circulation on Sundays, when concentration levels are about 25% lower than on working days. Simultaneous monitoring of fine particles' presence (from 0.3 µm up to 20 µm of diameter) has been performed between August 2002 and December 2004 at sites characterised by a different exposure to the traffic source: a urban background site, not directly exposed to traffic emission; a tunnel site, directly exposed to the traffic emissions, where the monitor was located in the kerbside position in the middle of a 250 m-long tunnel of the city centre; a site in a residential area of the city. Daily behaviours of particles' size (number, surface, volume) and mass distributions (PM10, PM2.5 and PM1) are analysed, based on 1-hour averaged particles' counts. At open-air sites, particles' size distributions present similar shape in both seasons, with 99.8% of the total number of particles characterised by a diameter smaller than 1 µm. In the cold season, however, the total number of particles is 40% greater than in the warm period: the increase in the total number of particles mostly derives from a larger presence of the smallest particles (below 0.65 µm), as a consequence of the enhanced strength of the processes leading to the formation of the secondary component of atmospheric particulate, while for the coarse fractions comparable counts are observed. Sundays' distributions are shifted towards lower values compared to Wednesdays': whereas for particles below 0.4 µm the distributions tend are quite close, the difference between the distributions is more relevant for the larger granulometric cuts, for the lower emissions and resuspension associated to the Sundays' traffic flows. Compared to ambient air observation at the tunnel site, a huge increase in particles' counts is observed, especially in the size range between 0.5 and 5 µm, as a consequence of the primary particulate traffic emissions and of the resuspension of soil dust deriving from traffic flow in the confined volume of the tunnel, whereas below 0.5 µm the particle counts are similar to those measured in the ambient air. According to all these findings, the reduced traffic circulation on Sundays mainly affects the presence of particles exceeding 0.5 µm of diameter, while it has only a limited influence on the finest size fractions, characterised by a large and diffused background presence, deriving from secondary formation processes in the atmosphere. Thus, short-term interventions (as occasional traffic restrictions) aimed to control acute episodes of fine particulate pollution appear poorly effective, while long-term actions, suitable for controlling also the precursors of the secondary components of the fine atmospheric particulate, as primary pollutants NOX, SO2 and volatile organic compounds, should be undertaken.

14A-3

SIZE DISTRIBUTION OF ATMOSPHERIC AEROSOLS IN KOLKATA, INDIA AND THE ASSESSMENT OF PULMONARY DEPOSITION OF PARTICLE MASS,

SUBHANKAR NAG, A. K. Gupta, Indian Institute of Technology, Kharagpur, Kharagpur-721302, WB, India; U. K. Mukhopadhyay, West Bengal Pollution Control Board, Salt Lake City, Kolkata, WB, India

Kolkata City, the second-largest metropolis in South Asia is centred on latitude 22° 34’ N and longitude 88° 24’ E. In this study, the relationship between inhalable particulate (PM10), fine particulate (PM2.5), coarse particulate (PM2.5-10) and Aerosol size distributions were measured at three stations during December 2003 to February 2004 by using nine stage cascade impactors followed to assess the pulmonary deposition of particles in different tracts of human respiratory system. The impactor effectively separates the particulate matter into nine sizes ranging from 0.0-0.43 micron to 9.0 -10.0 micron. Thermo Andersen hi-volume samplers were used at all three sites for measuring PM2.5 and PM10 concentration. The results indicate that the total average number distribution in the size range of 0 to 10 micron can be represented as Junge distribution dN/d log(Dp) = 1282.6 (Dp) ^-3.803. Aerosol mass distribution in size had shown that the highest fraction in PM10 was of the aerosols size of 0 size of 0.43 trimodal with fine mode Dp<1.1 micron (MMAD = 0.51 micron, GSD = 2.15), medium mode 1.1 of PM2.5 and PM10 were in the range of 96.31-363.63 microgm/m3 and 140.50 -637.70 microgm/m3 respectively. Correlation analysis result shows that the highest correlation (0.91) was observed between the particle range of 9.0-10.0 micron and 3.3-4.7 micron followed by
0.79 between 9.0-10.0 and 5.8-9.0 micron respectively. Regression analysis shows that PM2.5 is about 60% of PM10 concentration. Advanced and widely used ICRP model was used for estimation of pulmonary deposition. The result shows that 36% of deposited PM10 were deposited in the alveolar region and nearly 49% of deposited PM10 were deposited in tracheobronchial region.

14B-1

SOURCE APPORTIONMENT OF DETROIT FINE PARTICULATE MATTER USING POSITIVE MATRIX FACTORIZATION, AMY E. GILDEMEISTER, Philip K. Hopke Center for Air Resources Engineering and Science, Clarkson University, Box 5708, Potsdam, NY

Fine particulate matter has been shown to be an important causal factor for serious chronic health problems in urban populations, in particular, childhood asthma. Using receptor modeling to determine the sources of fine particulate matter in urban areas provides crucial information to determine the most effective way to address this problem. In this study, fine particulate matter has been collected at two sites in southeast Michigan and analyzed for a suite of 56 trace elements and compounds. The Allen Park sampling site is located south of Detroit, near the most heavily industrialized region. Sources local to the Allen Park site include coal-fired power plants, coke refineries, iron smelters, and waste incinerators. The second sampling site is located in Dearborn, an urban residential area west of Detroit. Receptor modeling applies multivariate statistical methods based on the assumption that chemical species are emitted from sources in characteristic ratios and these atmospheric species that are characteristic of a particular source covary. Positive matrix factorization (PMF) addresses shortcomings of other models by constraining the model output to conform to known physical reality. In particular, PMF does not allow sources to contribute a negative mass or to emit a negative species contribution and permits realistic individual data point weights. Using PMF and comparing source contributions at Allen Park to those in Dearborn, contributions made by local industrial sources (power plants, coke refineries, iron smelting, waste incineration) local area sources (automobile and diesel truck) and long range sources of PM2.5 can be distinguished in greater Detroit.

14B-2

APPORTIONMENT OF AMBIENT PRIMARY AND SECONDARY PM2.5 DURING A 2001 SUMMER INTENSIVE STUDY AT THE CMU SUPERSITE AND NETL PITTSBURGH SITE USING PMF2, DELBERT J. EATOUGH, Nolan F. Mangelson, Department of Chemistry & Biochemistry, Brigham Young University, Provo, UT; Richard R. Anderson, Donald V. Martello, National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA; William K. Modey, Argonne National Laboratory, Argonne, IL

Apportionment of primary and secondary pollutants during a July 2001 summer intensive study at the Carnegie Mellon University Supersite about 5 km east of downtown Pittsbuerg and at the National Energy Technology Laboratory (NETL) PM characterization site, located about 18 kilometers south of downtown Pittsburgh is reported. PM2.5 was apportioned into primary and secondary contributions using the PMF2 multivariate receptor model and analysis software. program. Data were available for five samples collected each day at the Supersite and four samples collected each day at NETK during the summer intensive, three samples during the day and either two or one, respectively at night. Input to the PMF2 analysis included the concentrations of PM2.5, measured both with a PC-BOSS and a TEOM monitor, the nonvolatile and semi-volatile organic material, elemental carbon and PIXE determined trace metal components of the PM2.5, and volatile gas phase organic material, NOx, NO2 and O3 concentrations for the various four-per-day samples. A total of nine sources were identified in the PMF analysis. These included primary emissions from crustal material, mobile emissions(both gasoline spark source and diesel), and three near-by sources high in trace metals. These three sources were assocaited with very specific back-trajectory conditions which indicated the emissions were coming from coal-fired power plants south of the city and a mix of incinerator, power plant and chemical industry emissions from northwest of the city. In addition, three secondary sources were identified, two of which were associated with local secondary products of local emissions and were dominated by organic material and one of which was dominated by secondary ammonium sulfate transported to the NETL from the west to southwest. The major source of PM2.5 at both sites was identified as secondary transported material (dominated by ammonium sulfate) from the west and southwest. The latter source has also been identified from trajectory analysis of regional distributed PM concentrations measured by TEOM continuous monitors. These findings are consistent with the bulk of the secondary ammonium sulfate in the Pittsburgh area being the result of contributions from distant transport, and so decoupled from local activity involving organic pollutants in the metropolitan area. In contrast, the major local secondary sources were dominated by organic material. Secondary material was the dominant contributor PM2.5 in the Pittsburgh area during the summer intensive study.

14B-3

SOURCE APPORTIONMENT OF FINE PARTICLES IN POTSDAM AND STOCKTON, NY, UTILIZING THE COMPOSITION OF WATER-SOLUBLE SHORT-CHAIN ORGANIC ACIDS,

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Samples collected to measure the concentrations of chemical constituents in fine particulate matter (PM2.5) in southwestern (Stockton) and northern (Potsdam) New York from November 2002 to June 2004 have been used for this study. Samples were collected on multiple filters at both sites, every third day for a 24- hour interval in an Andersen RAAS speciation network sampler. The Teflo filters were analyzed for PM2.5 mass and elemental composition by XRF. Nylasorb filters were leached and analyzed for anions and cations. Punches of the quartz fiber filters were analyzed for organic and elemental carbon (OC and EC) and the remaining filter was leached and analyzed for short-chain, water-soluble acids using a procedure described in a companion poster. Positive Matrix Factorization (PMF) was applied to the combination of elemental, ion, and OC/EC data as well as the water-soluble short-chain organic acids at both sites for source apportionment. The usefulness of short-chain organic acids in source resolution, identification of secondary organic formation events and identification of anthropogenic sources of these organic acids upon inclusion in PMF will be discussed.

14C-1

ESTIMATING AMMONIA FLUX AND DRY DEPOSITION VELOCITY OVER NATURAL SURFACES FROM AN INTENSIVELY MANAGED ANIMAL AGRICULTURAL FACILITY IN NORTH CAROLINA,

Sharon B. Phillips, Office of Air Quality Planning and Standards, US Environmental Protection Agency, RTP, NC; S. Pal Arya, VINEY P. ANEJA, North Carolina State University, Raleigh, NC

An experimental study was conducted on the emission and dry deposition fluxes of ammonia (NH3) under different meteorological conditions, using a micrometeorological technique (micrometeorological gradient and modified Bowen-ratio methods in conjunction with the Monin-Obukhov similarity theory) over natural surfaces in North Carolina where intensively managed agriculture/animal farms are located. Ammonia concentrations were measured simultaneously with mean wind speeds, wind directions and temperatures during Fall 2001, Winter, Spring and Summer 2002 at two heights (2 and 6m) employing a technologically advanced mobile laboratory. Diurnal and seasonal variations of ammonia flux and dry deposition velocity were investigated under a wide range of wind and atmospheric stability conditions yielding hourly variation of NH3 flux and deposition velocity. Greater NH3 concentrations were measured during the fall measurement campaign, which were directly related to spray-effluent irrigation practices; whereas the winter season had the lowest overall concentrations, collected during each seasonal campaign (effect of colder temperatures). The largest average NH3 deposition velocities were estimated during the summer measurement campaign, whereas the winter season estimated the lowest daytime velocities. This evaluation of nitrogen species was extended to addressing the total nitrogen budget for North Carolina during summer season. The portion of atmospherically deposited nitrogen, which reaches either land or water bodies is highly variable depending upon meteorological and seasonal conditions. Modeled dry deposition rates of NO (nitric oxide), NO2 , HNO3 and NH3, using a third generation Eulerian model (the United States Environmental Protection Agency's Models-3/Community Multiscale Air Quality (CMAQ) modeling system) in conjunction with measured wet deposition rates of nitrate (NO3-) and ammonium (NH4+), were evaluated in order to characterize the factors controlling the total nitrogen budget. In North Carolina, approximately 50% of NHX or NO3- flux occurs in the form of dry and wet deposition during the summer season. In addition, the Neuse River watershed's largest contributor to dry deposition flux of nitrogen (nitrogen loading) was determined to be NH3, making up approximately 47% of the total atmospheric deposition.

14C-2

AN ECOLOGICAL SCHEME FOR DEPOSITION VELOCITY ESTIMATES FOR REGIONAL AIR QUALITY MODELING, DEV NIYOGI

A dry deposition modeling approach that includes vegetation-atmosphere interactions through photosynthesis/carbon assimilation relationships was recently developed by Niyogi et al. (2003). In this approach, gas deposition velocity (Vd) is calculated using an electrical resistance-analog approach in a coupled soil-vegetation-atmosphere transfer (SVAT) model. For this, a photosynthesis-based surface evapotranspiration and gas exchange model is dynamically coupled to an atmospheric model with prognostic soil hydrology and surface energy balance. The effective surface resistance (composed of aerodynamic, boundary layer, and canopy-based resistances) is calculated for a realistic and fully interactive estimation of gaseous deposition velocity over natural surfaces. Results from the coupled model studies to estimate observed deposition velocity estimates for ozone over a soybean field (C3 photosynthesis pathway) and a corn field (C4 photosynthesis pathway), and nitrogen measurements over a grassland are presented. The coupled results of the 3D model analyses and intercomparison with different vegetation schemes is also presented.

14C-3

EFFECT OF VENTILATION SYSTEMS AND AIR CLEANERS ON DECAY RATES OF PARTICLES PRODUCED BY INDOOR SOURCES IN INDIAN URBAN HOUSEHOLD, Suresh K. Varghese, Centre for Environmental Science and Engineering, IIT Bombay, Mumbai, India. Gangamma S., Chemical Engineering Department, NITK, Surathkal, India

The decay rate of indoor air particulates represents their removal rates and is an important process in the context of indoor air quality. The decay rate of air particulates is also signifies the magnitude of the exposure to the occupants. The proposed paper describes an experimental study to determine the particulate deposition rate in indoors. The experiments were conducted in typical Indian urban household kitchens. The rate of decay and deposition of the particles with various control techniques used in India on particulate removal was determined in the study. The infiltration rate was determined by carbon monoxide tracer. The overall decay rate of particulate was determined by raising the particle concentration by smoldering of Benzoin then measuring the concentration variation with time for various size (3.2- 0.05 μm) particles with a quartz crystal microbalance impactor. The decay rate is varied in a wide range under the forced and natural ventilation conditions (maximum coefficient of variation 68 and 77 percentages respectively) compared to no ventilation conditions (maximum coefficient of variation 14 percentage). Even though, there is considerable variation in the observed decay rate between houses, the exhaust fan decay rates were greater than that of natural ventilation. On contradictory, the electric chimney shows very low particle decay rates. This was found true for both the recirculation and exhaust operating modes. The infiltration studies also showed large variation for natural and forced ventilation conditions. The natural ventilation with favorable wind conditions gave infiltration values comparable with forced ventilation. Also Study indicated that aerosol dynamics, especially evaporation/ condensation may play significant role in determining size segregated particle decay rate. A deposition model for particulate was developed including Brownian, gravitational and thermophoresis settling mechanisms. The observed particle decay rate was compared with model results. The trends of observed indoor particle deposition with particle size were matched with the theoretical predictions based on particle deposition mechanisms. But the magnitude of observed deposition rate was found to be significantly different from the predicted values. Differences of the observed values increases as particle size increases. This may be pointing to the significant role by aerosol dynamics. Therefore, the coagulation effects of particulate deposition estimation were examined using a coagulation model. Results shows that proper design of the experiment is required to avoid the coagulation of the particles to affect the decay rate calculations.

15A-1

POLLUTION PROCESSING BY RADIATION FOGS DURING THE CALIFORNIA REGIONAL PM10/PM2.5 AIR QUALITY STUDY (CRPAQS),

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During winter 2000/2001 an extensive fogwater study was conducted in the San Joaquin Valley (SJV) in California, within the framework of the California Regional California Regional PM10/PM2.5 Air Quality Study (CRPAQS). Colorado State University collected fog samples at 3 locations in the valley with a main focus on the study anchor site, Angiola. The fog chemistry was nitrogen dominated, consistent with findings from previous studies in the region. Nitrate and ammonium concentrations in bulk fog samples collected at Angiola ranged as high as 1870 and 2200 µN, respectively. Observed fog pH values were high, ranging from 5.85 to 8.04 (median 6.73). Organic species were also observed to be important contributors to fog composition, with concentrations of total organic carbon as high as 41.9 ppmC. Efforts to characterize organic matter in these fogs reveal that the most abundant species are typically low molecular weight carboxylic acids and aldehydes. These species have been observed collectively to account for roughly 20-30% of the total organic carbon. Dicarboxylic acids, frequently used as model compounds for organic CCN, typically account for only 1-2 % of the organic carbon, with oxalic acid the most important contributor. Measurements by GC/MS, HPLC, and H-NMR reveal that many other organic compounds are present, including aerosol source markers and compound families frequently detected in aerosol particles including n-alkanes, n-alkanoic acids, and polycyclic aromatic hydrocarbons. These latter compounds were detected in both dissolved and undissolved forms in droplets. Although more than 100 organic species have been quantified in many samples, the majority of the organic carbon mass remains unspeciated. Separation of the dissolved organic carbon into molecular weight fractions via ultrafiltration, suggests that much of this material is contained in compounds with molecular weights in excess of 500 Daltons. Drop size-fractionated fog samples (obtained with 2- and 5-stage collectors) showed little variability of pH with drop size, but indicated that most other fog solutes were strongly enriched in small fog drops. One noted exception was nitrite, which was enriched in large drops. Drop sedimentation in these fog episodes is an important mechanism for deposition of fog borne materials, estimated to decrease airborne concentrations of key species (nitrate, sulfate, ammonium, organic carbon) by amounts on the order of 0.5-1 µg/m3-hr. Deposition velocities for fog solutes were observed to be of the order of 1-2 cm/s, much higher than typically observed for the same species in aerosol form. Deposition velocities were observed to vary significantly between individual solutes in the pattern nitrite > water > ammonium > sulfate ~ TOC > nitrate. The observed trend can be explained in terms of the degree of enrichment of each species in small, slower settling fog drops.

15A-2

LINK BETWEEN ISOPRENE AND SOA: FATE OF PYRUVIC ACID IN DILUTE AQUEOUS SOLUTION,

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Biogenic secondary organic aerosol (SOA) sources have been estimated to contribute to the global particle load between 20 -270 Tg yr-1. In addition, SOA accounts for 20-50% of annual average organic aerosol concentrations in polluted urban and regional environments, more during summertime smog episodes. Thus understanding SOA formation is critical to linking emissions to aerosol concentrations and to effects on climate, visibility, urban air quality and health. Isoprene accounts for roughly half of non-methane volatile organic compound emissions. Homogenous, gas-phase, reactions involving isoprene are not considered a source of atmospheric PM. However, a growing body of evidence suggests that isoprene oxidation products can form SOA through oligomerization on particle surfaces. In addition, two recent modeling investigations predict that aqueous reactions in cloud/fogs form SOA from water-soluble products of isoprene, other alkenes and aromatic organic emissions (Ervens, et al., 2004 and Lim et al., 2004a,b). A major difference between these two modeling studies is the fate of pyruvic acid, and therefore, the importance of isoprene as a precursor for in-cloud SOA formation. In the chemical mechanism by Ervens et al (2004), methylglyoxal forms pyruvic acid and is subsequently oxidized to acetaldehyde. Lim et al., (2004a, b) draws from work of Stefan and Bolton (1999), who propose that dissociated pyruvic acid (pyruvic acid is predominantly present in dissociated form at the pH of cloud and fog droplets) forms acetic acid, then glyoxylic acid and finally oxalic acid. Oxalic acid is a low vapor pressure organic compound likely to remain in the particle phase after droplet evaporation, while acetaldehyde will not. Acetaldehyde is not presented as an intermediary product in the work of Stefan and Bolton (1999) and their total organic carbon measurements and calculations support this. Understanding the fate of pyruvic acid in clouds is critical to evaluating the importance of isoprene as an SOA precursor. Therefore, we recently conducted aqueous-phase batch reactions of H2O2 and pyruvic acid in photochemical reaction vessels at pH values (2-5) typical of cloud and fogs concurrent with UV and H2O2 controls. Products were analyzed by electrospray ionization mass spectroscopy, high performance liquid chromatography (HPLC) with a UV-vis detector and total organic carbon (TOCan). Products identified included acetic acid, glyoxylic acid, formic acid and oxalic acid, supportive of the Stefan and Bolton mechanism. Time profiles of initial reactants, intermediates and products will be provided. The resulting kinetic model (rate and reaction order) will be compared with previously proposed mechanisms and implications for in-cloud formation of SOA will be presented. This work demonstrates the formation of particulate matter

15A-3

FOG PROCESSING OF ATMOSPHERIC ORGANIC MATTER,

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During winter 2003/04 we conducted a field study in Fresno (CA) to characterize organic matter in fog and to study the processing of carbonaceous material by radiation fogs. These fogs are frequent in the Central Valley of California during wintertime. Previous studies, focusing on inorganic compounds, have shown that fogs impact the local particulate matter concentrations through scavenging of volatile species followed by in cloud transformation into nonvolatile species, creating new particulate material. On the other hand fogs also constitute a major deposition pathway of particulate matter through scavenging followed by droplet deposition. The focus of the current study was specifically on carbonaceous material. Particulate organic carbon concentrations ranged from 1 to 12 ug/m3 at the study site. During fog events we observed aqueous phase carbon concentrations of up to 5 ug/m3 illustrating the importance of organic matter scavenging by fogs. About half of the fog carbonaceous material results from scavenging of organic gases including small molecular weight acids (formic, acetic acid..) and carbonyls (formaldehyde, glyoxal,..). Nevertheless, semi-continuous measurements of ambient and interstitial particulate carbon suggest scavenging efficiencies of up to 40% for organic carbon and slightly less for elemental carbon. We will also discuss how different molecular marker species including levoglucosan partition during a fog event between the fog droplets and interstitial aerosol particles. Different scavenging efficiencies of the marker species suggest a preferential scavenging of particulate mater of one source relative to another source. This selection will lead to preferential cleaning of the atmosphere of particles from select sources compared to others. Finally we measured wet deposition fluxes of organic matter in these radiation fogs. The deposition velocities ranged from 0.6 to 7 cm/s, illustrating the efficient removal of carbon from the atmosphere by fogs. The net effect of fogs on ambient particulate matter remains difficult to determine experimentally. The removal of carbonaceous material from the fog layer might be compensated by entrainment of new material from above the fog layer. In addition one can not exclude in cloud processes converting organic volatile species into non volatile species in a similar fashion than SO2 oxidation into sulfate. These last mechanisms would explain why the boundary layer is not depleted as fast in carbon as suggested by the deposition fluxes.

15B-1

ESTIMATING UNCERTAINTIES IN FACTOR ANALYTIC MODELS,

SHELLY EBERLY, U.S. Environmental Protection Agency, RTP, NC; Pentti Paatero, University of Helsinki, Finland; Philip K. Hopke, Clarkson University, Potsdam, NY

When interpreting results from factor analytic models as used in receptor modeling, it is important to quantify the uncertainties in those results. For example, if the presence of a species on one of the factors is necessary to interpret the factor as originating from a certain emission source category or source region, then that species should be present on that factor with high certainty. In this work, we examine three methods for determining uncertainties of computed factors, F, and their respective time series, G, in the non-negatively constrained factor analytic model X=G*F+E, as applied in atmospheric sciences. The methods include linear error propagation of uncertainties of X separately to G and separately to F, bootstrapping, and bootstrapping enhanced with random rotational forcing to provoke rotations in G and F. Linear error propagation is simple to describe and implement. However, since the errors in X are not always well known in environmental applications and since the factor analytic model is non-linear by definition, the uncertainty estimates from linear error propagation are questionable. Bootstrapping is also simple to describe although computer intensive when implemented, but it, similar to linear error propagation, assumes that the solution is unique and therefore ignores the uncertainty that arises from the rotational ambiguity in the results. The methods are applied to simulated data where X, F, and G, and the uncertainties in X are known. By using simulated data, we can compare the F and G uncertainties, as estimated by the three methods, with the differences (estimated value minus true value) of F and G. When tested on simulated data with low errors and without rotational freedom, all three methods agree favorably. When the error levels are increased, the bootstrap methods produce better uncertainty estimates than linear error propagation. Finally, when rotational freedom is introduced to the simulated data, bootstrapping with rotational forcing reproduces the uncertainties in computed F and G most accurately. Next the methods are applied to a real atmospheric data set where unknown errors are present. Real aerosol data from Phoenix (1995-1998) are analyzed. Computed error limits are compared with source profiles that have been used in previous source apportionment studies for Phoenix. Bootstrapping with rotational forcing is applied with parameters as optimized based on the simulated data. The computed confidence intervals mostly cover the true values, although a confidence percentage cannot be quoted. Lastly, we show how the uncertainty estimates are impacted by the assumed errors in X. For some species, even if the assumed errors are doubled, the uncertainty estimates from bootstrapping remain the same. Disclaimer: Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

15B-2

EXAMINING ROTATIONS FOR THE POSITIVE MATRIX FACTORIZATION MODEL USING EDGES AND TARGET SHAPES,

MICHAEL RIZZO, United States Environmental Protection Agency Region 5; Peter Scheff, University of Illinois - Chicago, School of Public Health

The use of factor analytic techniques such as Positive Matrix Factorization (PMF) has been increasing due to the fact that these types of models do not require any a priori information regarding source composition as models like the Chemical Mass Balance (CMB) model does. They do, however, have other requirements which need to be explored in depth in order to obtain reasonably interpretable results. These include the proper assignment of species uncertainties, the number of possible sources to solve for and the possibility of rotational ambiguity in the results. Of these, examining the rotational ambiguity of the results is done when an initial solution has been found. The purpose of rotating factor analytic results is to maximize the values of the matrices in order to make the results more easily interpretable without changing the original solution. This work took the results of a PMF solution for two sites from Chicago, Illinois collected by the United States Environmental Protection Agency's Speciation Trends Network. The data set contained a total of 372 observations collected over the period from 2001 through 2003. For each observation the CMB model was solved for nine sources to serve as a comparison to the rotated PMF results. Two different rotational techniques were examined: edge rotation where values in the source contribution matrix are rotated to an edge in a two dimensional plane and target shape rotation where a priori information associated with the source compositions is used. The results of these rotational methods were compared to the original PMF solution as well as the CMB solution for each day. The edge rotation showed little change in the average fine particulate contribution from source to source, but an improvement in the correlation between the PMF and CMB Vehicle sources was seen without substantially altering other contributions. The target shapes method allowed for the incorporation of established source profile information utilized for CMB. This analysis demonstrated the ability to use a priori CMB information to direct PMF toward a particular solution without dramatically changing the original results.

15B-3

QUANTITATIVE STUDY OF SENSITIVITIES AND UNCERTAINTIES OF MOLECULAR MARKER-BASED CMB MODELING,

BO YAN, Mei Zheng, Armistead Russell, Georgia Institute of Technology, Atlanta, GA

Chemical mass balance (CMB) source apportionment modeling using molecular markers takes advantage of the additional information provided by having a large number of individual organic molecules, some having relatively unique sources. This approach has been successfully developed and applied to apportion the source contributions to fine organic carbon (OC) and PM2.5 in a number of areas, and the number of applications is growing. However, applications of this method are still influenced by the lack of locally-specific emission source profiles, inconsistent choices of fitting species, and unknown uncertainties caused by ambient measurements and modeling itself. In order to evaluate and improve the performance of the molecular marker-based CMB modeling, it is very important to make a thorough and quantitative uncertainty and sensitivity analyses. As such, this study aims to: a) examine the sensitivity of CMB outputs to the source profiles used in the model; b) test the sensitivity of CMB outputs to different combinations of fitting species in the model; c) quantify uncertainties from CMB modeling using a Monte Carlo approach; d) study the possibility of combining additional inorganic species to the molecular marker-based CMB modeling currently applied and e) conduct a comparison of molecular marker-based CMB modeling and inorganic-based CMB modeling. Here, we have used ambient data from the Southeastern Aerosol Research and Characterization program (SEARCH) to address the above issues. Preliminary results indicate that the selection of different organic tracers and source profiles in CMB is a key factor for CMB modeling, which can cause significant variability in the source apportionment results. When different source profiles are used, it was found that the contribution of road dust to primary organic carbon (OC) at Jefferson Street can vary from 1.1% to 2.8%. However, the contribution of meat cooking to primary OC can vary from 14.0% to 47.6% for the same sample due to different selections of source profile. Similarly, selecting different organic tracers as fitting species in the CMB model can also lead to variations in source apportionment results. In addition, significant differences in source categories and source contributions can be seen between molecular marker-based CMB method and inorganic-based CMB method. The details of this investigation will be presented and discussed in the presentation.

15B-4

UNDERSTANDING THE IMPACT OF “UNKNOWN” POINT SOURCES ON MOLECULAR MARKER CHEMICAL MASS BALANCE MODELS,

MIN-SUK BAE, James J. Schauer, Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, Wisconsin, Jay R. Turner, Chemical Engineering, Washington University, St. Louis, MO

Particle-phase organic tracers (molecular markers) have been shown to be an effective tool at assessing the impact of sources of carbonaceous aerosols. These molecular markers have been used in chemical mass balance (CMB) models to apportion primary sources of organic aerosols in regions where the major organic aerosol source categories has been identified through emissions inventory efforts. As in the case of all CMB models, all important sources of the tracer compounds must be included in the model or the CMB model is subject to significant biases. To this end, the application of the molecular markers CMB models to apportion carbonaceous PM in locations where good emissions inventory of organic aerosols has not been developed must be done with extreme caution. Of great concern is the presence of industrial point sources, which emit carbonaceous aerosols and have not been well characterized. Emissions from such sources can greatly bias CMB models if their emissions are not correctly addressed. In addition to the ubiquitous urban sources of carbonaceous aerosols, such as mobile sources, wood burning, food cooking, secondary organic aerosol, and resuspended road dust; emissions of carbonaceous particulate matter from industrial point sources also impact the St. Louis Midwest Supersite. Since these sources are not well characterized, it is important to identify periods when these point sources are impacting the Supersite to avoid obtaining biases source apportionment results. The use of supplemental real time measurements and molecular marker analyses as a screening tool to identify when poorly characterized point sources are impacting a receptor site will be discussed. As the application of molecular marker CMB modeling is growing, it is important that such screening tools be employed to assure that CMB modeling results are not erroneously biased.

15C-1

SEMI-VOLATILE SECONDARY AEROSOL IN URBAN ATMOSPHERES: MEETING A MEASUREMENT CHALLENGE,

William E. Wilson, Russell W. Long, U.S. Environmental Protection Agency, Research Triangle Park, NC; BRETT GROVER, Norman L. Eatough, Delbert J. Eatough, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT; William K. Modey, Argonne National Laboratory, Argonne, IL

Ammonium nitrate and semi-volatile organic compounds (SVOC) are significant components of fine particles in urban atmospheres. These components, however, are not properly determined with current U.S. EPA accepted methods such as the PM2.5 FRM or other single filter samplers due to significant losses of semi-volatile material (SVM) from particles collected on the filter during sampling. Continuous PM2.5 mass measurements are attempted using methods such as the R&P TEOM monitor. This method, however, heats the sample to remove particle-bound water which also results in evaporation of semi-volatile material. Research at Brigham Young University has resulted in samplers for both the integrated and continuous measurement of total PM2.5, including the semi-volatile material. The PC-BOSS is a charcoal diffusion denuder based sampler for the determination of fine particulate chemical composition including the semi-volatile organic material. The RAMS is a modified TEOM monitor which includes diffusion denuders and Nafion dryers to remove gas phase material which can be absorbed by a charcoal sorbent filter. The RAMS then uses a “sandwich filter” consisting of a conventional particle collecting Teflon coated TX40 filter, followed by an activated charcoal sorbent filter which retains any semi-volatile ammonium nitrate or organic material lost from the particles collected on the TEOM monitor Teflon coated filter, thus allowing for determination of total PM2.5 mass including the semi-volatile material. R&P has recently developed a TEOM based monitor, the FDMS TEOM to measure fine particulate mass, including the semi-volatile material. The results obtained using these state-of-the-art samplers have been compared to results obtained with either an PM2.5 FRM sampler or a TEOM monitor in studies conducted during the past five years in Atlanta, GA, Philadelphia, PA, Pittsburgh, PA, Salt Lake City, UT, Seattle, WA, Riverside and Rubidoux, CA, Bakersfield, CA and Fresno CA. The results of these studies have shown that: · Results obtained using the PC-BOSS, RAMS and FDMS TEOM are all comparable. Each instrument measures both the nonvolatile and semi-volatile (nitrate and organic material) aerosol. · This semi-volatile fine particulate material is not retained on the heated filter of a regular TEOM monitor and hence is not measured by this sampling technique. · Much of the semi-volatile aerosol is also lost during sampling from single filter samplers such as the PM2.5 FRM sampler. · The amount of semi-volatile aerosol lost from single filter samplers can vary from less than 1/3 that lost from heated TEOM filters during cold winter conditions to essentially all during warm summer conditions. · Semi-volatile organic aerosol can only be reliably collected using an appropriate denuder sampler. · Either a PM2.5 FRM sampler or the IMPROVE sampler can be easily modified to a denuder sampler with filters which can be analyzed for semi-volatile OC, nonvolatile OC and EC using existing OC/EC analytical techniques. The research upon which these statements are based for the various urban studies listed above will be summarized.

15C-2

MASS BALANCE CLOSURE AND THE FEDERAL REFERENCE METHOD FOR PM2.5 IN PITTSBURGH, PENNSYLVANIA,

ALLEN L. ROBINSON; Carnegie Mellon University, Pittsburgh, PA; Sarah L. Rees, Washington State Department of Ecology, Olympia, WA; Andrey Khlystov, Duke University, Durham, NC; Charles O. Stanier, University of Iowa, Iowa City, IA; Spyros N. Pandis, Carnegie Mellon University, Pittburgh, PA

Daily ambient aerosol samples were taken in Pittsburgh, Pennsylvania from the July 2001 through June 2002 as part of the Pittsburgh Air Quality Study (PAQS). The study measured PM2.5 mass by the Federal Reference Method (FRM) and the PM2.5 chemical composition by a variety of filter-based and continuous instruments. This talk examines the mass balance between the FRM measured mass and the sum of the aerosol chemical components. For the twelve month study period, the average FRM-measured mass is 11% greater than the sum of the mass of the aerosol chemical components. This mass balance discrepancy varies seasonally, with the average FRM-measured mass 17% greater than the sum of the chemical components for the summer months, with discrepancies as large as 30% during certain periods. Meanwhile, the FRM-measured mass was at or slightly below the sum of the chemical components for the winter months. The mass balance discrepancy and its seasonal shift cannot be explained by measurement uncertainty; instead the discrepancy is due to combination of retained aerosol water on the conditioned FRM filters and volatilization losses. The relative importance of these different effects varies with aerosol composition and causes the observed seasonal variation in the mass balance. The contribution of the aerosol water to the FRM measured mass is estimated using continuous measurements of aerosol water at the site; volatilization losses are estimated from other filter-based instruments. Water contributes 16% of the FRM mass in the summer, and 8% of the FRM mass in the winter; it also appears responsible for episodes where the FRM-measured mass is significantly greater than the sum of components. Retention of water is greatest during acidic conditions, which commonly occur during the summer months. Volatilization losses are estimated at 5% of the FRM mass during the summer, and 9% for the winter. Volatilization losses appear to be most significant on days dominated by organic aerosol, or winter days with relatively high nitrate concentration. Accounting for the effects of water and volatilization losses close the mass balance between the FRM and the sum of the chemical components, providing insight into the FRM measurements. S.L. Rees, A.L. Robinson, A.Y. Khlystov, C.O. Stanier, and S.N. Pandis, “Mass Balance Closure and the Federal Reference Method for PM2.5 in Pittsburgh, Pennsylvania,” Atmospheric Environment, 38: 3305-3318, 2004.

15C-3

SHORT-TERM VARIABILITY OF FINE PARTICULATE-NO3-, NH4+ AND SO42- AT 2 SEARCH SITES,

ERIC S. EDGERTON Atmospheric Research & Analysis, Inc., Cary, NC; Benjamin E. Hartsell Atmospheric Research & Analysis, Inc., Plano, TX; John J. Jansen Southern Co, Birmingham, AL, Callie J. Waid, Atmospheric Research & Analysis, Inc., Plano, TX

This presentation compares and contrasts real-time measurements of fine particulate NO3-, NH4+ and SO42- at a rural site (Yorkville) and urban site (Jefferson Street, Atlanta) in north Georgia, USA. Fine particulate NO3- and NH4+ are measured continuously using a 3-channel chemiluminescent NO analyzer. Sample air is drawn through a 2.5 micron Dp50 inlet, then through two annular denuders and a carbon honeycomb denuder to remove acidic and basic gases as well as the preponderance of NOy species. Sample flow is then split into three channels. Channel 1 flow enters a 600C Pt-mesh converter followed by a 350C Mo-mesh converter, which convert particulate NO3-, particulate NH4+, plus any residual NOy not retained by the denuders, to NO. Channel 2 flow enters into a 350C Mo converter, which reduces only particulate NO3- and residual NOy. Channel 3 flows through a particulate filter followed by an annular denuder, then through a third 350C Mo converter. This channel “sees” only residual NOy. Particulate NH4+ is defined as the difference between channels 1 and 2, while particulate NO3- is defined as the difference between channels 2 and 3. Fine particulate SO42- is measured using a modification of the HSPH approach. Sample air is drawn through the same inlet used for NH4+ and NO3-, then into a 30 cm length of ¼” Inconel 600 tubing heated to 1000C in a tube furnace. This converter configuration reduces particulate SO4 to SO2 with > 70-80% efficiency. The air stream exiting the furnace is then filtered and SO2 is quantified via UV fluorescence. In order to minimize baseline uncertainty filtered air zeros are performed every 90 minutes. This approach reduces the baseline uncertainty to an estimated +/- 25 ppt (as SO2) or the equivalent of +/- 0.1 µg/m3 (as SO42-). Results will be used to: 1) discuss short-term contributions to PM2.5 mass; 2) examine SO42- neutralization by NH3 under a variety of conditions; and 3) investigate formation mechanisms and plume chemistry.

15C-4

COMPARISON OF CONTINUOS AND INTEGRATED AEROSOL COMPOSITION AT A BACKGROUND SITE: IS HOURLY RECONSTRUCTION OF AEROSOL MASS NOW POSSIBLE?

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Several comparisons have been reported in the literature continuous measurements of PM2.5 mass and its major constituents (organic and elemental carbon, sulfates, nitrates). These comparisons usually involve XY plots of daily averages of hourly averaged continuous data vs 24-h filter data. Correlations are generally fair (r2 = 0.7-0.8) to excellent (r2 >/ = 0.95) but often with slopes that differ significant from unity. This paper presents several such comparisons in which FRM or IMPROVE sampler mass and component speciation are compared with the results of continuous measurements of mass (TEOM), sulfate (two continuous methods), nitrate (R&P 8400N), organic and total aerosol carbon (two methods), and elemental carbon (Aethalometer). The comparisons show that the slopes of these comparison plots differ from unity largely because of differences in accuracies of the continuous methods in quantifying specific components and uncertainties in the abilities of the filter methods to account for positive and negative artifacts. Addition insights which have been gained from these comparisons at Look Rock include the following: o Comparisons indicate that the slope of plots of sulfate using TVA’s version of the HSPH continuous thermal analyzer (now commercialized as TEII Model 5020) vs. IMPROVE filter sulfate are closer to unity than slopes of plots of R&P 8400 vs. filter sulfate. o Comparisons with continuous and filter measures of organic and elemental carbon indicate that only total carbon can reliably be used from the R&P 5400 outputs, that the Aethalometer data above its effective MDL is the more reliable measure of elemental carbon. Additional evaluation of the Sunset Labs instrument is needed at this or other sites before comparisons with filter data are meaningful. Our preliminary conclusions are that is areas in which diurnal variations in trace elements and/or soil components of fine mass are relatively constant (i.e., 24-h data can be combined with hourly data for other constituents), meaningful hourly reconstruction of fine mass is now feasible in some cases. This paper will include an evaluation of error terms which must be further quantified in order for hourly reconstructions of fine mass to become a useful reality.

16A-1

USE OF THE AERODYNAMIC PARTICLE SIZER TO MEASURE PM-COARSE,

THOMAS PETERS, The University of Iowa, Iowa City, IA; Robert Vanderpool, US EPA, Research Triangle Park, NC

The aerodynamic particle sizer (APS 3321, TSI, Inc.) measures particle size distributions from 0.5 µm to 20 µm by determining the time-of-flight of individual particles in an accelerating flow field. A complete particle size distribution may be determined in a matter of seconds, making the APS ideal for assessing rapid fluctuations in atmospheric PM-coarse. Recent laboratory tests show that the APS 3321 can sample PM-coarse-sized particles with near 100% efficiency if they are solid; however, this efficiency becomes substantially lower for liquid droplets. This work compared PM-coarse measurements made with 24-hr, filter-based PM samplers to that measured with an APS. Two APS 3321 instruments with PM-10 and PM-2.5 samplers were deployed in four field campaigns in three US cities: Gary, IN, Riverside, CA, and Phoenix, AZ. To collect representative aerosol samples, each APS sampled isokinetically from the downtube of a standard 16.7-Lpm, FRM PM-10 inlet. In addition to comparing 24-hr measurements, the APS data were investigated to observe trends in temporal and size variability of the PM-coarse aerosol.

16A-2

A NEW HYBRID REAL-TIME PARTICULATE MASS MONITOR, KEVIN J. GOOHS, Pedro Lilienfeld, Wayne Harmon, Thermo Electron Corporation, Franklin, MA; Juergen Wilbertz, Thermo Electron Corporation, Erlangen, Germany

A new hybrid nephelometric/radiometric particulate mass monitor capable of providing real-time measurements is described. The SHARP (Synchronized Hybrid Ambient Real-time Particulate) monitor incorporates a high sensitivity light scattering photometer whose output signal is continuously referenced to the time-averaged measurements of an integral beta attenuation mass sensor. This system achieves heretofore-unattained short-term precision and accuracy of both PM10 and PM2.5 determinations. The SHARP monitor incorporates advanced firmware to optimize the continuous mass calibration of the nephelometric signal, ensuring that the measured mass concentration remains independent of changes in the particle population being sampled. The SHARP monitor incorporates a “smart heater” system designed to maintain the relative humidity of the air passing through the filter tape of the radiometric stage well below the point at which the collected particles accrete and retain liquid water. This heating system minimizes the internal temperature rise ensuring negligible loss of semi-volatiles from the collected sample. The SHARP monitor is operable at ambient temperatures and uses frequent sample filter changes to mitigate aerosol artifacts. Preliminary laboratory and field tests indicate that the SHARP monitor provides PM short-term, i.e., one minute- to one hour-resolved measurements with a precision of better than ±0.5 µg/m3 over total monitoring periods of several months, without maintenance. Winter and summer field tests indicate acceptable daily accuracy (1.0 + 0.1) and correlation > 0.95 compared against a USEPA PM2.5 Reference sampler. The principle of operation, performance of the instrument, and further refinements of the measurement technique are presented, and potential applications in the field and research studies are discussed within.

16A-3

A NEW METHOD FOR PARTICLE MASS CLASSIFICATION – THE REVERSE ELECTROSTATIC FIELD AEROSOL PARTICLE MASS (REFAPM) ANALYZER, JASON S. OLFERT, Cambridge University Engineering Department, Cambridge, UK

In recent years, a particle mass classifier, called the aerosol particle mass (APM) analyzer, has been used to accurately measure particle mass. Particle mass can be combined with aerosol size data to determine particle mass distributions or a particle's effective density and fractal dimension. The APM was first conceived by Ehara et al. (1996), and consists of two rotating coaxial electrodes. Charged particles pass between the two cylindrical electrodes that are rotating at an equal angular velocity. A voltage is applied between the two cylindrical electrodes creating an electrostatic field. As the particles flow through the device, they will experience a centripetal and electrostatic force acting in opposite directions. Particles of a certain mass-to-charge ratio will pass through the APM. Other particles will either be forced to the outer electrode if the centripetal force is stronger than the electrostatic force or they will be forced to the inner electrode if the electrostatic force is dominant. By adjusting the voltage and angular velocity, particles of different mass-to-charge ratios will pass through the device. If the charge on the particles is known, then the mass of the particle passing through the APM is known. However, the APM suffers from particle losses in the classifier due to unstable external forces. The centripetal force is proportional to r2 while the electrostatic force is proportional to 1/r (where r is the distance from the centre of the APM). Therefore, particles that enter the APM above or below the center of the gap will be forced into the walls. The unstable external forces in the APM cause many particles to impact the walls and the transfer function of the classifier is reduced because of these losses. The transfer function of the device can be greatly improved by creating a stable system. Reavell & Rushton (2004) have suggested two concepts to create stable forces within the APM: 1) change the geometry of the electrodes so that the electrostatic field increases with radius rather than decreases, or 2) increase the rotational speed of the inner cylinder so that the centripetal force decreases with increasing radius. The concepts will be referred to as the reverse electrostatic field aerosol particle mass analyzer (REFAPM) and the centripetal particle mass analyzer (CPMA), respectively. Both of these concepts create a stable system since particles will be forced toward the centre of the gap rather than being forced toward the walls. This presentation will compare the performance of the APM and REFAPM. A theoretical model for the REFAPM will be presented and compared to the theoretical model of the APM developed by Ehara. The results show that the REFAPM has a significantly higher transfer function when classifying large particles, while its performance with small particles is almost identical to the APM.

16A-4

A COMPREHENSIVE PARTICULATE MATTER MONITORING SYSTEM,

YouSheng Zeng

A numerical PM measurement model is developed to characterize and evaluate PM sampling methods. The model is simple and includes only two parameters. When it is used to represent the Federal Reference Method (FRM), the sum of the squared deviations of the modeled PM concentrations from the FRM specifications is as small as 0.04% and 3.9% for FRM PM2.5 and FRM PM10, respectively. The model provides meaningful ways to characterize PM measurement methods, assess biases in PM monitoring, and simplify the descriptions or specifications of PM measurement in related regulations. The numerical model can be used in conjunction with two types of commercially available PM monitoring devices to form a Comprehensive Particulate Matter Monitoring System (CPMMS). The first type of the device can be either the FRM PM2.5 sampler or any dichotomous PM samplers (manual or continuous). The second type of the device is one capable of providing particle size distribution with good relative accuracy between size categories but not necessarily accurate in absolute mass concentration estimates. An example of the CPMMS can be a system consisting of a FRM PM2.5 sampler, an Aerodynamic Particle Sizer (APS), and the numerical model described in this paper. The data collected by the FRM PM2.5 sampler and the APS will be processed by the model to create a virtual aerosol sample. The virtual sample is then passed through the sampling system again to numerically correct PM measurements for both PM2.5 and PM coarse particles (PMc) and to reconstruct an ambient PM mass distribution. It is demonstrated in this paper that CPMMS can provide substantially better PM measurement than the two measurement devices used separately. It can achieve the better measurement with a high level of tolerance in deficiency that may inherently exist within the sampling and sizing components of the CPMMS. In addition to being more flexible and less demanding in PM sampler physical design, the CPMMS has various potentially significant benefits. The results of the ambient monitoring by CPMMS include reconstructed ambient PM mass concentrations with size distributions. Therefore, the monitoring data remains valid and can be reprocessed to meet future needs even if PM ambient standards or related regulations change. After several years of implementing the CPMMS at a particular location, some atmospheric particle size distribution patterns can established for the location. If the previous PM samplers for this location can also be characterized by the model discussed in this paper, it will be feasible to use the CPMMS to bridge the gap between the valuable PM monitoring data collected by the old PM samplers and new monitoring data collected by new PM samplers, providing continuity in an ambient PM trend analysis. With a PM penetration effectiveness curve representing human respiratory system, the CPMMS approach makes it easier to establish ambient PM standards based on human health effect rather than a somewhat artificial particle diameter cutpoint due to sampler design limitations.

16B-1

SOURCE CONTRIBUTIONS TO ORGANIC CARBON IN PM2.5 IN URBAN AND RURAL AREAS IN THE SOUTHEASTERN UNITED STATES,

MEI ZHENG, Bo Wang, Lin Ke, Georgia Institute of Technology, Atlanta, GA; James J. Schauer, University of Wisconsin-Madison, Madison, WI; Eric Edgerton, Atmospheric Research & Analysis, Inc., Cary, NC

The contributions from primary emission sources to organic carbon (OC) in PM2.5 in urban and rural areas in winter on a daily basis were investigated using the organic tracer-based CMB receptor model. Seven of 24-hour high volume (Hi-Vol) ambient samples were collected from each of three urban sites (N. Birmingham, AL (BMH), Jefferson Street Atlanta, GA (JST), and Pensacola, FL (PNS)) and one rural site (Centreville, AL (CTR), a paired rural site with N. Birmingham, AL) in the SEARCH air quality monitoring network during winter (November 2003 to January 2004). The advantage of the day to day comparison using the Hi-Vol sampling over the month to month comparison using the Low-Vol sampling between sites is that the environmental variability can be taken into account between sites so that the comparison may be more accurate. The concentration of OC as well as elemental carbon (EC) were recorded the highest at the BMH site (Average 6.16 and 3.03 µg m-3), followed by JST (5.02 and 1.47 µg m-3), and PNS (4.38 and 1.39µg m-3). The rural CTR site, a designated paired rural site of BMH, however, had relatively high concentration of OC (4.97 µg m -3) but very low concentration of EC (0.78 µg m-3). Comparing the source contributions to OC between the BMH and the CTR sites, the important emission sources of diesel exhaust, gasoline exhaust, meat cooking, and wood combustion appeared different distribution patterns. The sources of diesel exhaust, gasoline exhaust, and meat cooking had significant urban-rural patterns, while the pattern for wood combustion was insignificant. Comparing the source contributions to OC between the three urban sites, it is found that the BMH is characterized by high levels of diesel exhaust and gasoline exhaust, while the JST site was characterized by high levels of gasoline exhaust. The PNS site received lesser amount of diesel exhaust and gasoline exhaust but similar (or even higher) amount of exhaust from wood combustion.

16B-2

SOURCE CONTRIBUTIONS TO SOA CONCENTRATIONS DURING A SEVERE PHOTOCHEMICAL SMOG EVENT, MICHAEL J. KLEEMAN, Qi Ying, Department of Civil and Environmental Engineering, University of California, Davis, Davis CA 95616; Robert J. Griffin, University of New Hampshire, Durham, NH

Secondary organic aerosol (SOA) formation can account for a significant fraction of the total organic aerosol concentration during severe photochemical smog events. Traditional source apportionment techniques such as the Chemical Mass Balance model can not identify the source origin of this secondary material so that appropriate control measures can be implemented. Recently, a mechanistic source apportionment method has been demonstrated that tracks the evolution of precursor gases from different sources separately in the atmosphere including the formation of semi-volatile products and secondary particulate matter. Previous studies have used this technique to identify source contributions to secondary inorganic aerosol (nitrate, sulfate, and ammonium ion) in California. In the present study, the mechanistic source apportionment method is extended to calculate source contributions to secondary organic aerosol. The severe photochemical smog episode that occurred in the South Coast Air Basin surrounding Los Angeles on September 8-9, 1993 will be studied in detail. Ozone concentrations during this episode exceeded 250ppb, and estimated SOA concentrations exceeded 20 μg m-3. Basecase model performance will first be validated by a rigorous comparison between predicted and measured pollutant concentrations. Source contributions to major SOA species will then be quantified.

16B-3

ORGANIC CARBON MASS BALANCE AND SOURCE APPORTIONMENT OF PRIMARY ORGANIC CARBON IN THE PITTSBURGH REGION USING MOLECULAR MARKERS, R SUBRAMANIAN, Allen Robinson, Carnegie Mellon University, Pittsburgh, PA; Anna Bernardo-Bricker, Wolfgang F. Rogge, Florida International University, Miami, FL

Primary organic aerosol emitted during both anthropogenic and biogenic activities form a significant component of ambient PM2.5 in the Pittsburgh region. We use the EPA’s Chemical Mass Balance (CMB) model to apportion the Pittsburgh primary organic carbon (OC) using a combination of organic molecular markers and selected bulk species as tracers for different sources. This approach is applied to a data set of over one hundred daily samples collected at the Pittsburgh Supersite and an upwind satellite site (Florence, PA). The CMB model requires source profiles. As part of the Pittsburgh Air Quality Study (PAQS), speciated source profiles have been developed for emissions from coke production, road dust, and vegetative detritus. For other major sources such as motor vehicles, wood burning and cooking, we use published emission profiles. At least two sets of vehicular profiles can explain the ambient data: the first, “NFRAQS” from Watson et al. [1998], and the second, “Fraser/Schauer” using the results of Fraser et al. [2002], Schauer et al. [1999] and Schauer et al. [2002]. Using a combination of the newly obtained source profiles and literature source profiles, we perform a CMB calculation on the PAQS data. With either set of vehicular profiles, gasoline and diesel vehicles are the largest primary sources. Using the “NFRAQS” vehicle profiles, gasoline sources contribute 13% and diesel engines contribute 8% of the ambient OC on an annual average basis. However, there is a large seasonal variation in the gasoline contribution, which is 21% in the winter and 3% in the summer. The “Fraser/Schauer” scenario apportions significantly greater amounts of the ambient OC to gasoline sources at 37% of the annual average ambient OC, while the diesel contribution remains about the same at 6%. Seasonal variation is also observed in the gasoline OC contribution in the "Fraser/Schauer" scenario, which varies from 48% in the winter and 29% in the summer. Possible reasons for the large uncertainty in the gasoline contribution are seasonal variations in emission profiles or photochemical aging of the molecular markers. Comparison of the Pittsburgh and Florence wood smoke OC indicates that softwood smoke is regional, with hardwood emissions the urban excess. Coke production dominates the ambient PAH concentrations in both Pittsburgh and Florence, but coke emissions are just 2% of the ambient OC.

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16B-4

APPORTIONMENT OF THE ELEMENTAL CARBON COMPONENT OF SOUTHERN CALIFORNIA AEROSOL TO LIGHT-DUTY VEHICLES USING SELECTED POLYCYCLIC AROMATIC HYDROCARBON TRACERS,

ARANTZAZU EIGUREN-FERNANDEZ and Antonio H. Miguel, Southern California Environmental Health Sciences Center and Southern California Particle Center and Supersite, Institute of the Environment, University of California, Los Angeles, CA

Elemental Carbon (EC) in atmospheric particles is formed as a product of incomplete combustion processes of organic material; some of the major sources include spark ignition and diesel fuel combustion. Recent studies suggest that about one-half of the global atmospheric EC emission is estimated to arrive from fossil fuel combustion. EC is an important contributor to the aerosol radiative forcing. As a component of the atmospheric carbonaceous aerosol EC plays an important role in visibility reduction. EC and polycyclic aromatic hydrocarbons (PAHs) are found together in particles with diameters in the nano-, ultrafine, accumulation (and coarse) size ranges. Significant recent health research interest has been focused on EC-containing ultrafine particles. Thus, it is important to apportion the different sources that contribute EC to the atmospheric burden. EC and PAH emission profiles vary depending on the source, a characteristic that makes PAH suitable for use as source signatures in receptor modeling. The Chemical Mass Balance model (CMB) has been extensively used for source apportionment using different organic compounds as tracers. In this study the CMB-8 is applied to estimate the EC that is attributed to light-duty vehicles (LDV) in the air of Southern California using particle-phase PAHs as tracers. Selected PAH/EC ratios, measured in samples collected in the Caldecott tunnel (East Berkeley, California), were tested as potential LDV fingerprints. Our results indicate that the chemically more stable high molecular weight PAHs may be used as tracers. PAH reactivity and/or partitioning during transport affect the source contribution estimates (SCE), as a result of these atmospheric processes. Our ambient PM2.5 data taken during all seasons at sites located in six rural and urban communities of the CARB-funded Children Health Study suggest that benzo[ghi]perylene (BGP) and indeno[1,2,3-cd]pyrene (IND) are less susceptible to these effects and thus suitable for use as LDV tracers. The EC portion of PM2.5 attributed to LDV combustion emissions at the sites varied depending on season, generally increasing the SCE with decreasing air temperature. At all sites, higher contributions of LDVs to the EC component in PM2.5 were observed during winter. The estimated EC attributed to LDV varied between 8.3 and 30% for early summer, 9.0 and 39% for spring/autumn, and 33 and 76% during winter. These results are similar to values reported by Manchester-Neesvig et al., (2003). The observed differences in the estimated LDV contribution to EC during the three seasons may have resulted from several factors, including, i) a decrease in the number of LDVs on the road during summer, ii) higher photochemical PAH reactions during spring and summer, and, iii) an increase in the number of cold starts in winter. Supported by the SCPCS (USEPA Grants #R827352-01-0 and CR-82805901) and the SCEHSC NIEHS Grant #P30 ES07048. Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

16C-1

OPTICAL LIGHT SCATTERING VERSUS CHEMICAL SCATTERING AND PM-2.5 CONCENTRATIONS AT URBAN AND RURAL LOCATIONS IN THE SOUTHEAST,

IVAR TOMBACH, Consultant, Camarillo, CA; Benjamin Hartsell, Atmospheric Research & Analysis, Inc., Plano, TX

Since 1998, the Southeastern Aerosol Research and Characterization (SEARCH), network has been making aerosol mass concentration, chemistry, and light scattering measurements at eight urban and rural locations in the southeastern United States. Mass concentrations and chemical composition of fine and coarse particulate matter fractions are determined from 24-hr filter samples on multiple media and, in several locations, from semi-continuous measurements of chemical components. Integrating nephelometers, with Nafion dryers on the inlets and measurement of the relative humidity at the instruments' optical chambers, are used at most locations to measure the light scattered by the dried aerosol. The optical measurements at five sites in both urban and rural areas have been compared to the particulate matter measurements over all seasons of the year. Nephelometer-measured light scattering was compared against two properties – (1) light scattering estimated from concentrations of the chemical components of the particulate matter; and (2) PM2.5 mass concentrations from filter sampling and TEOM measurements. For the first comparison, light scattering for the dried aerosol was estimated from the mass concentrations of particulate matter components, using the standard EPA/IMPROVE formula and alternative refinements that have recently been developed. The standard chemical extinction estimates correlated relatively well with the optical measurements, although the estimates were roughly 15 to 30% less than the optically-measured values and the slopes of the regression lines differed from urban to rural areas. In particular, the standard chemical extinction formula underestimated the measured extinction most greatly on hazy days, a characteristic that has also been observed with IMPROVE measurements of ambient, non-desiccated aerosol. Potential causes for this underestimate were investigated. For the second comparison, the efficacy of using integrating nephelometers to estimate FRM PM2.5 mass concentrations was investigated. The correlation between 24-hr average optical measurements and modified TEOM measurements was quite good. Here, again, the slope of the regression line, which represents the local light scattering efficiency of the aerosol, varied from one location to another, which implies that using an integrating nephelometer as an indicator of the variation in FRM2.5 concentrations requires site-specific calibration. Potential causes for this site-to-site variability were investigated. Not surprisingly, agreement was poorer when hour-to-hour measurements were compared instead of 24-hour averages. Measurement of the relative humidity of the atmospheric sample at the optical chamber of the nephelometer was essential for obtaining reliable data. When it was very humid, the Nafion dryers were sometimes not able to keep the relative humidity below the point where particles commence hygroscopic growth, a fact that would not have been known without the chamber measurements.

16C-2

OPTICAL REMOTE SENSING TECHNOLOGIES FOR PM STUDIES AND MONITORING,

Gary Gimmestad, DAVID ROBERTS, Georgia Institute of Technology

Atmospheric laser radar (LIDAR) is a very versatile tool for characterizing the atmosphere, but it has not yet lived up to its full promise. At Georgia Tech, we are developing LIDAR technology to make the technique eye safe, automated, reliable, cost effective, and capable of producing real-time reduced data. For example, we monitored vertical profiles of ozone concentration in downtown Atlanta, Georgia throughout much of the 2004 smog season. The improvements that we are making are intended to make LIDAR much more commonplace for both research studies and for routine monitoring. One obvious application is to PM. LIDAR is very sensitive to PM for measuring geometrical properties such as the altitudes of layers, and in conjunction with sun photometer data, LIDAR can accurately measure extinction coefficients. On the other hand, the retrieval of aerosol size and composition information from LIDAR data is notoriously difficult. An assessment of the reasons for the difficulty is presented, along with a strategy for maximizing LIDAR's usefulness in PM research.

16C-3

VERTICAL PROFILES OF AEROSOL AND PARTICULATE MATTER OBTAINED FROM A MULTISTATIC LIDAR,

EDWARD NOVITSKY, C. Russell Philbrick, The Pennsylvania State University, Department of Electrical Engineering, University Park, PA

The vertical distribution of aerosols and particulate matter in an urban environment has been captured by the use of a multistatic receiver imaging system. By forming a ratio of the measured parallel and perpendicular scattering images produced by a lidar beam, profiles of aerosol concentrations were obtained of the nighttime sky within the planetary boundary layer (i.e., below ~1 km). Analysis of the images, in conjunction with other independent instruments and observations, revealed the presence of aerosol layers with highly structured vertical distributions. Using a trimodal lognormal distribution, scattering models showed that large concentrations of very small particles (< 10 nm) and concentrations of highly absorbing elements (such as carbonaceous elements) produce similar, and thus indistinguishable, results, thereby preventing detailed decomposition of the atmosphere into distinct layers or elements.

16C-4

CHARACTERISTICS OF AEROSOLS AND THEIR VERTICAL DISTRIBUTIONS USING RAMAN LIDAR,

C. RUSSELL PHILBRICK, Sachin J. Verghese, Penn State University, Department of Electrical Engineering, University Park, PA

Molecular profiles of the primary well-mixed species obtained using Raman lidar provide one of the best techniques for describing the aerosol distributions. Because the gradient of vertical profile of the primary constituents is well known, the difference in the slope of the measured profile from the molecular scale height can be used to determine the incremental extinction and thereby generate an aerosol extinction profile. The PSU Raman lidars have been used for a number of years to measure the profiles of molecular nitrogen, molecular oxygen and the rotational Raman scatter (the mixture of all molecular species) at both visible and ultraviolet wavelengths. The effects of variations in aerosol size distribution can be described based upon the comparisons of optical extinction profiles obtained at different wavelengths. Results are selected from many years of observations at different locations to summarize the characteristics of the aerosols that are distributed in the lower atmosphere. Most of the observations have been obtained in the eastern region of the US, where the aerosols present are dominated by sulfate components. These extinction profiles are strongly influenced by the local water vapor concentrations since the sulfate aerosol size is strongly dependent on its hygroscopic properties. One interesting aspect of Raman lidar observations of aerosols is our ability to observe the growth of clouds based upon the increase in the sub-visual aerosol extinction observed in the vertical profiles, and conversely we can observe the diminishing extinction at several wavelengths to describe the dissipation of cloud layers.

17PB-1

FINE PARTICLE EMISSION PROFILE FOR ROAD DUST IN PITTSBURGH, PENNSYLVANIA,

ALLEN L. ROBINSON, Eric M. Lipsky, Natalie Pekney, Carnegie Mellon University, Pittsburgh, PA; Wolfgang F. Rogge, Anna Bernado-Bricker Orhan Sevimoglu, Florida International University, Miami, FL

This poster presents a fine particle road dust profile developed in Pittsburgh Pennsylvania. Road dust samples were collected from three urban and three suburban roads. The dust samples were resuspended in a chamber, passed through a PM2.5 cyclone, and collected on a series of filters for offline chemical analysis. Samples on quartz filters were analyzed for organic and elemental carbon using a thermal optical transmittance analysis using a variant of the NIOSH profile. Samples on Teflon filters were extracted and analyzed by Ion Chromatography for major ions including sulfate, nitrate, ammonium, calcium, and potassium. Samples on Teflon filters were extracted and analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine concentrations of Al, As, Ba, Ca, Cd, Cr, Cu, Fe, Ga, K, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Ti, V and Zn. Samples on quartz filters were solvent extracted and analyzed by Gas Chromatography Mass Sectrometery (GC-MS) for more than 100 individual organic compounds. In this poster we will present the profiles developed from the Pittsburgh dust samples; we will also compare these profiles to road dust profiles developed in Los Angeles (Rogge et al., 1993).
Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R. and Simoneit, B. R. T. (1993). "Sources of Fine Organic Aerosol .3. Road Dust, Tire Debris, and Organometallic Brake Lining Dust - Roads As Sources and Sinks." Environmental Science & Technology 27(9): 1892-1904.

17PB-2

FINE PARTICLE EMISSION PROFILE FOR A LARGE COKE PRODUCTION, Emily Weitkamp, Eric Lipsky, ALLEN ROBINSON; Carnegie Mellon University, Pittsburgh, PA; Andrea Polidori, Barbara Turpin; Rutgers University, New Brunswick, NJ; Patrick Pancras, John Ondov, University of Maryland, College Park, MD; Anna Bernado-Bricker, Oskar R. Vasquez, Wolfgang F. Rogge, Florida International University, Miami, FL

This poster presents a fine particle emission profile for a large coke production facility near Pittsburgh, PA. The profile is developed from highly time resolved, ambient air quality measurements made at a fence line site adjacent to the plant. A fence line approach was employed because the coke plant has hundreds of stacks and other emission points, making it difficult to develop an integrated, facility-wide emission profile using stack sampling techniques. Continuous or semi-continuous measurements of PM2.5 mass, PM10 mass, SO2, NOx, organic and elemental carbon (OC and EC), particle size and number, 11 trace metals, wind direction and wind speed were made. Background pollutant levels were also measured. A combination of highly time resolved meteorology and air quality data were used to determine when the coke facility emissions were influencing the sampling site. Concentrations for most pollutants at the fence line site were one to two orders of magnitude higher than background levels when the fence line site was being heavily impacted by the facility plume. For example, organic carbon levels 10 times background and elemental carbon levels 40 times background were observed. Highly time resolved measurements are essential for resolving these relatively short-duration, large spikes in pollutant concentrations. Simply measuring wind direction is insufficient. From these high time resolved measurements an average PM2.5 emission profile for the coke facility was developed. The profile is dominated by organic (40% ± 9% of PM2.5 mass emissions) and elemental carbon (25% ± 5% of PM2.5 mass emissions). Filter samples were also collected for detailed speciation by GC-MS. The results indicate that organic emissions dominated by PAH. Significant contributions of inorganic ions and select trace metals were also observed. The particle emissions are dominated by the fine fraction, with PM2.5 estimated to contribute 84% ± 14% of the PM10 mass. Weitkamp, E. A., Eric Lipsky, Patrick Pancreas, John Ondov, Andrea Polidori, Barbara Turpin, Allen Robinson (2004). "Fine Particle Emission Profile for a Large Coke Production Facility Based on Highly Time Resolved Fence Line Measurements" Atmospheric Environment: submitted.

17PB-3

FUEL-BASED PARTICULATE MATTER AND GASEOUS EMISSION FACTORS DETERMINED FROM VEHICLES IN PITTSBURGH, PA'S SQUIRREL HILL TUNNEL, Andrew Grieshop, Eric Lipsky, ALLEN ROBINSON, Carnegie Mellon University, Pittsburgh, PA

In-use fuel-based vehicle fleet average emission factors were determined using measurements taken in the west-bound bore of the Squirrel Hill Tunnel on Interstate-376 in Pittsburgh, Pennsylvania during two weeks in November, 2002. The west-bound tube of the tunnel has a 2.5% rising grade and is subject to rush-hour traffic in the morning hours. Gas-phase concentrations of CO, CO2, NO, NOX, and SO2 were measured continuously. PM emissions were measured by a suite of filter-based and continuous methods; a TEOM continuously measured PM2.5 mass concentrations while filter-based measurements resulted in mass measurements of total PM2.5, organic and elemental carbon (OC and EC) and size-resolved PM, OC and EC. Background concentrations were simultaneously measured at remote, un-impacted sites. Vehicle volume, traffic speed and fleet composition (fraction of heavy duty diesel vehicles) were determined using microwave sensor traffic counting and the analysis of traffic video taken during the time period of the study. The fleet composition varied throughout the day with the fraction of fuel consumed by heavy duty diesel vehicle (HDDV) traffic ranging from 36 ± 8% diesel fuel in the early morning hours (12 AM to 6 AM) to 11 ± 2% diesel fuel during rush hour (7 AM – 9 AM). Fuel-based emission factors (grams pollutant/kg fuel) were calculated using a fuel carbon balance based on measured, background-corrected CO2 and CO concentrations. A strong positive correlation was found between the calculated NOX emission factor and the fraction of the fuel burned by HDDV traffic during high traffic periods. OC and EC emission factors were also found to have a strong positive correlation with traffic composition, consistent with previous studies. These correlations are used to estimate the emission factors for both the automobile fleet and the heavy duty vehicle fleet. Automobile EC emission factors estimated from this study match well with previous tunnel and dynamometer measurements of automobiles, but the HDDV EC emission factors measured here are significantly lower than most EC emission factors cited for heavy duty diesel vehicles. These differences may be due to differences in operating mode in the tunnel compared to a full driving cycle. Finally, the TEOM (operated at 30 degrees C) was found to significantly underestimate the PM2.5 mass in the tunnel because of particulate mass losses from the volatilization of organic matter.

17PD-4

EUROPEAN CONTRASTS IN PARTICULATE MATTER COMPOSITIONS RELATED TO HEALTH (PAMCHAR),

MARKUS SILLANPÄÄ, Risto Hillamo, Sanna Saarikoski, Anna Frey, Ulla Makkonen, Finnish Meteorological Institute, Helsinki, Finland; Zoya Spolnik, Rene van Grieken, University of Antwerp, Antwerp, Belgium; Erik Sandell, Technical Research Centre of Finland, Espoo, Finland; Arto S. Pennanen, Raimo O. Salonen, National Public Health Institute, Kuopio, Finland

Ambient air particulate pollution and associated human health risks are currently assessed on the basis of measured mass concentrations. The EU-funded PAMCHAR-project investigates European contrasts in the chemical and toxic properties of ambient air coarse (PM10-2.5), fine (PM2.5 -0.2), and ultrafine (PM0.2) particles. A series of 7-week sampling campaigns were conducted in six cities during selected seasons: Duisburg (autumn), Prague (winter), Amsterdam (winter), Helsinki (spring), Barcelona (spring) and Athens (summer). Samplings of the three size classes were made with a modified Harvard high-volume cascade impactor (Sillanpää et al, J Aerosol Sci 2003;34:485-500) and three virtual impactors (PM10-2.5 and PM2.5) in 3+4-day periods per week. Total elemental compositions in the different PM size classes were analyzed by x-ray fluorescence (ED-XRF), soluble elements by inductively coupled plasma mass spectrometry (ICP-MS), ions by ion chromatography (IC), and elemental (EC) and organic carbon (OC) by thermal optical carbon analyzer. The constituents anticipated to have low toxic potency − secondary ions (non-seasalt-SO42-, NO3- and NH4+) and sea salt − constituted together roughly an equal portion (35-49%) of PM2.5 whereas the sum of corresponding portions (11-55%) of PM10-2.5 varied considerably. The portions of particulate organic matter (POM=1.4xOC) (17-54%), total polycyclic aromatic hydrocarbons (PAH) (0.0071-0.16%), soluble transition metals (Fe, Zn, Cu, Ni, V) and As of PM2.5 showed also large variations, while that of EC (5-9%) was relatively constant. There were large differences in the portions of insoluble crustal elements (13-38%), POM (9-27%), EC (1-6%), total PAH (0.0053-0.12%), transition metals, As and Cd in PM10 -2.5. None of the concentrations of major constituents (>5%) in either PM2.5 or PM10-2.5 correlated well with the respective total mass concentration. The differences in the toxic potencies (inflammation, cytotoxicity, genotoxicity, lung damage) of PM10-2.5, PM2.5-0.2 and PM0.2 samples between the six selected PM pollution situations are currently investigated in a series of cell and animal studies.

17PD-5

NITRATE CONCENTRATIONS RETAINED BY THE PM2.5 FEDERAL REFERENCE METHOD IN THE EASTERN US,

NEIL FRANK, US Environmental Protection Agency

The Federal Reference Method PM2.5 monitoring protocol includes many features such as filter temperature control, rapid retrieval of collected samples and cold filter shipping designed to provide reproducible fine particle concentrations with reduced losses of semi-volatile components. By design, however, the FRM only provides an indicator measurement of ambient PM2.5. Therefore, it is important that FRM measurements of PM2.5 be chemically characterized in terms of its retained mass, which reflects losses of collected ammonium nitrate and other semi-volatile materials. This results in mass balance concentrations and percent contributions to PM2.5 mass which may be different than the ambient levels for some of its chemical constituents. This paper presents the results of a sampling study in the Eastern US designed to focus on the nitrate component of PM2.5 gravimetric mass measured by the Federal Reference Method. Twelve months of measurements are provided from a single location in each of six urban areas during calendar year 2003 (Mayville, WI; Chicago, IL; Indianapolis, IN; Cleveland, OH; New York, NY and Birmingham, AL). The nitrate concentrations derived from the teflon filter of the FRM are compared to those from denuded nylon filters of routine EPA speciation sampling. FRM nitrates are always less than speciation nitrates. The differences among sites and by month are presented. The smaller quantity of these measured FRM nitrates is then shown to be accurately estimated by an evaporation model which describes the dissociation of ammonium nitrate as a function of 24-hr speciation nitrate concentrations, hourly temperature and relative humidity. This follows the work by Hering for non-FRM measurements in southern California and shows that excellent estimates can also be derived for Eastern aerosols. Limited FRM ammonium measurements were also produced at the six study sites for comparison to the speciation measurements.

17PD-6

CARBONACEOUS PM2.5 ESTIMATED BY FRM MASS BALANCE, NEIL FRANK, US Environmental Protection Agency

This paper characterizes the major chemical components of PM2.5 at six urban locations in the Eastern U.S. Mass closure is achieved by reducing PM2.5 mass lost due to volatilization, increasing mass from water absorption in hygroscopic particles and deriving the carbon content by subtracting the sum of non-carbonaceous components from measured PM2.5 mass. Crustal material and other constituents such as passively collected PM2.5 are considered. The mass balance approach is applied to 12 months of 24-hour measurements at collocated FRM and EPA PM2.5 speciation monitoring network sites produced during 2003. Retained semivolatile nitrates are derived from FRM Teflon filter measurements. Water adsorbed by sulfates and nitrates are estimated by an equilibrium/hygroscopicity model applied to the measured ionic concentrations at filter weighing equilibration temperatures. The paper describes the large uncertainties in organic carbon measurements (unquantifiable blank levels, volatilization during and after sampling on Teflon and quartz filters, OC multipliers to account for associated hydrogen and oxygen, differences in OC measurement methods, hygroscopicity) and argues that carbon by mass balance is a reasonable alternative to an estimate of carbon mass derived from carbon measurements. This results in concentrations and percent contributions to PM2.5 mass which may be different than the ambient levels for some of its chemical constituents. For National Ambient Air Quality Standards implementation and air quality model predictions, this may provide a better depiction of the major components of FRM mass than methods previously published that focused on characterization of ambient concentrations and relied on direct use of speciation data and uncertain adjustments to ambient carbon measurements. The net change in estimated PM2.5 components, however, is shown to be relatively small when expressed as ug/m3, but can be a large percent change for individual constituents.

17PD-7

URBAN AEROSOL STUDY FOR CAMPINAS-SAO PAULO, BRAZIL, REGINA MAURA DE MIRANDA, Edson Tomaz, University of Campinas, SP, Brazil. Maria de Fátima Andrade, University of São Paulo, Brazil

The Campinas' urban aerosol was collected from August, 2003 to August, 2004, using a fine and coarse particles sampler and a cascade impactor, being the former used for a specific period. PM10 average concentrations for winter and summer were about 40 and 25 ug.m-3, respectively. Due to fact that the samples were collected nearby a location with intense vehicular traffic, the black carbon concentration (BC) was very high, with mean value of 7 ug.m-3 for the whole sample period, being concentrated in the fine fraction of the particulate material. Volatile Organic Compounds were analyzed by means of chromatography with the means compounds being the n-pentene, n-hexene, benzene, toluene and mix-dietilbenzene. The elementar concentration analysis also shows that, in that sampled environment, BC, S, Al, Si, Ca and Fe are the predominant elements.

17PD-8

SIZE DISTRIBUTIONS OF THE ATMOSPHERIC AEROSOL IN THE METROPOLITAN AREA OF SÃO PAULO: A CASE STUDY FOR THE WINTER OF 2003,

TACIANA T. A. ALBUQUERQUE, Maria de Fátima Andrade, Institute of Astronomy, Geophysics and Atmospheric Sciences. São Paulo-SP, Brazil

An aerosol sampling campaign was performed during the winter of 2003 (Jul, 07 – Sep, 05) in the Metropolitan Area of São Paulo (MASP). The following equipments were used: a cascade impactor type MOUDI (MD), which allows the determination of aerosol mass concentration deposited in different sizes distributions (d50%: 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.10 µm), and a Mini Vol (MV), which collects the coarse (2.5<da<10 µm) and fine aerosol (da<2,5 µm). The material collected by the two equipments was analyzed through gravimetric procedures, reflectance (for Black Carbon determination), and the PIXE (Particle Induced X-ray Emission) technique (for elemental composition determination). As the processes associated to aerosol are mainly related to its size, an important property to be discussed is the Size Distribution of Particle Number (SDN) and Size Distribution of Mass (SDM) functions. Using the data collected by MD, it was possible to characterize the SDM of the particles as a function of the size. A SMPS (Scanning Mobility Particle Sizer) was used to obtain the SDN, which provides the particle number concentration for size intervals. In this study it was used the interval of 0.009 to 0.414 mm. The total sampled concentration of PM10 shows that meteorological conditions have a large influence in the total volume suspended aerosol in the atmosphere of São Paulo, with significant differences in the particle mass between August and September, which presented different meteorological conditions. Through the PIXE technique it was identified the following trace elements: Al, Si, P, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Se, Br, Sr, Zr, Pb. The majority of the chemical elements presented in the sample are of composites derived from dust resuspension, as for example: Al, Si, Ti, Ca, Fe, Mn. It was estimated the oxide concentration of these elements. The obtained results show that the fine particles mass is mainly composed of BC, followed by soluble and insoluble compounds, during day and night periods. The coarse mode is mainly characterized by insoluble compounds, followed by soluble compounds and BC, also during day and night time periods. A statistical analysis of the identified elementary composition was performed using Factor Analysis with the VARIMAX rotation, which provides information about the sources of the pollutants. By means of the analysis performed, corroborated by the SDN, the vehicular emission source was identified as being the most significant of the particles ultrafine in the region. The resuspended soil dust accounted for a large fraction of the coarse mode aerosol mass. Automobile traffic and urban soil dust are the main air pollution sources in São Paulo Mega city area.

17PD-9

TIME AND SIZE-RESOLVED CHEMICAL COMPOSITION OF SUBMICRON PARTICLES IN PITTSBURGH – IMPLICATIONS FOR AEROSOL SOURCES AND PROCESSES,

QI ZHANG, Jose-Luis Jimenez, CIRES, University of Colorado, Boulder, CO; Manjula Canagaratna, John Jayne, Douglas Worsnop, Aerodyne Research Inc., MA

An Aerodyne Aerosol Mass Spectrometer (AMS) was deployed at the Pittsburgh EPA Supersite from September 6 to 22, 2002, as part of the Pittsburgh Air Quality Study (PAQS). The main objectives of this deployment were to characterize the concentrations, size distributions, and temporal variations of non-refractory (NR) chemical species in submicron particles (approx. PM1) and to further develop and evaluate the AMS data analysis procedures and information content. Total NR-PM1 mass concentration in Pittsburgh accumulates over periods of several days punctuated with rapid cleaning due to rain or air mass changes. Sulfate and organics are the major NR-PM1 components while the concentrations of nitrate and chloride are generally low. Significant amounts of ammonium, which most of the time are consistent with sulfate being present as ammonium sulfate, are also present in particles. However there are periods when the aerosols are relatively acidic and more than 50 % of sulfate is estimated to be in the form of ammonium bisulfate. Size distributions of particulate sulfate, ammonium, organics, and nitrate vary on time scales of hours to days, showing unimodal, bimodal and even trimodal characteristics. The accumulation mode (peaking around 350 – 600 nm in vacuum aerodynamic diameter for the mass distributions) and the ultrafine mode (< 100 nm) are observed most frequently. The accumulation mode is dominated by sulfate internally mixed with oxidized organics, while hydrocarbon-type organics are often the main component of the ultrafine particles (except during nucleation events). The ultrafine-mode organic aerosols are mainly associated with combustion sources (likely traffic).

17PD-10

RELATIONSHIP BETWEEN NOY, PM_NITRATE AND PM2.5 AT A MOUNTAIN SITE IN UPSTATE NEW YORK DURING THE PMTACS-NY PROGRAM, U. K. ROYCHOWDHURY, R. A. Lamica, J. Schwab and K. L. Demerjian, Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY; O. Rattigan, H.D. Felton, Department of Environmental Conservation, Division of Air Resources, Albany, NY

NOy, PM2.5 and particulate matter nitrate (PM_nitrate) measurements performed at Whiteface Lodge ((WFML), 44o 23.597' N, 73o 51.531' W, 634 m above msl) as part of PMTACS-NY “Supersite” program are presented for the years 2002 – 2003 and discussed. The 2002 PM_nitrate (July – December) ranged from 0.0 – 3.74 □g m-3, (N=3686) when all available hourly averaged data (valid data capture=88.1%) are included. Only 36.0% of this data were above the minimum detection limit (mdl) of 0.15 □g m-3. The mean PM_nitrate was 0.57 □g m-3, with □=0.602. In 2003, the PM_nitrate ranged from 0.0 – 5.79 (N=7139) □g m-3 (valid data capture=81.5%). The data above mdl were 38.1% of the total data set, with mean=0.53 □g m-3 and □=0.533. Particulate nitrate represents a small fraction of PM2.5 at WFML with a mean value of 3.3% for 2002 and only 1.1% over the warm season. For 2003, the corresponding values were 3.4 and 1.1% respectively. Co-located hourly averaged annual NOy mixing ratios were 2.52 (N=3203, □=1.648) and 2.56 (N=6638, □=1.910) ppbv, for 2002 and 2003 respectively. Moderate correlation could be identified between the gas phase NOy and PM_nitrate when all available hourly averaged data for a year was considered. Reported (r2) for the correlation of PM_nitrate and NOy measurements at WFML are 0.358 for 2002 and 0.471 for 2003. Correlation coefficients between hourly averaged PM_nitrate above 0.15 □g m-3 and NOy, when parsed month wise, showed highest r2 value of 0.566 in January and lowest r2 value of 0.008 in September for 2003 with systematic cyclic variation of r2 throughout the year. Partial year data available for 2002 conforms to this trend with r2= 0.001 in October and 0.412 in December. Correlation coefficients for summer months are generally close and the pattern is similar for winter months. For both 2002 and 2003, the monthly mean values of NOy and PM_nitrate track each other closely (r2=0.754 and 0.829 respectively) for all data, with pronounced maxima in February and minima in August. For data above mdl, r2=0.776 and 0.843 for 2002 and 2003 respectively. When all hourly averaged PM_nitrate data above 0.15 □g m-3 are parsed into day time (6:00 – 17:00) and night time (18:00 – 5:00) components, no significant difference between NOy and PM_nitrate scatter plots could be identified. For 2002, r2Day=0. 220 and r2Night=0.402. The corresponding values are r2Day=0.394 and r2Night=0.358 for 2003. The observed seasonal differences between NOy and PM_nitrate are discussed. The influence of meteorological variables will be investigated. It is planned to incorporate 2004 data in the final presentation.

17PD-11

ELEMENTAL COMPOSITION OF PM2.5 IN URBAN AND BACKGROUND AIR MONITORING SITES IN EPA REGION V, MICHAEL COMPHER, U.S. Environmental Protection Agency Region V, Chicago IL; Serap Erdal, University of Illinois at Chicago School of Public Health / EOHS, Chicago, IL

The U.S. EPA has been collecting speciated PM2.5 data at various monitoring sites in Region V since 2000. However, there has not been an integrated and comprehensive effort to analyze and compare the elemental composition of PM2.5 mass collected at unique urban and rural sites with potentially varying source signatures. Such analysis is essential to understand the meteorological conditions leading to higher concentrations of metals found in fine particulate matter, to provide valuable information for PM2.5 source apportionment and receptor modeling efforts, and to evaluate exposures and health risks associated with metals residing in the PM2.5 matrix. From the respiratory health effects perspective, metals within PM2.5 are important due to the role of transition metals in catalyzing redox reactions in human lung epithelial cells, resulting in oxidative stress and increased production of mediators of pulmonary inflammation. We have compiled and analyzed PM2.5 speciation data for metals measured at a total of seven air monitoring stations within EPA Region V. Five of the sites were located within the Gary, IN-Chicago, IL-Milwaukee, WI corridor (i.e., North-South corridor) with the Chicago metropolitan urban area at the center of this airshed. The remaining two sites, which are IMPROVE sites, are situated in Minnesota near the Canadian border, and can be classified as representing background concentrations of metals. The urban vs. background comparative analysis including spatial and temporal patterns focused on the data collected in 2002-2003 due to concurrent availability of data only for these two years for the aforementioned seven stations. The sampling locations are expected to have different source markers due to their varying proximity to industrial and mobile sources and human activity. The sampling frequency at the sites was, at a minimum, on a one every six day schedule. Our results indicate that there are seasonal species-specific differences in metal concentrations between the five urban sites and two background sites. The analysis initially focused on copper, chromium, arsenic, lead, zinc, vanadium, nickel, and manganese content of PM2.5. In general, urban concentrations were 3-30 times higher than the background concentrations with largest differences observed for chromium, copper, and nickel. Zinc had the highest mean concentration among all the metals studied both in urban (in the order of 10-2 µg/m3) and background sites (in the order of 10-3 µg/m3) in 2002/2003. Vanadium appears to be uniformly distributed in the region with small difference in magnitude between the rural and urban sites (Mean-urban: 7.23e-04 µg/m3; Mean-background: 2.19e-04 µg/m3). In urban sites, chromium, copper, lead, manganese, and arsenic concentrations were one order of magnitude higher than vanadium and nickel concentrations. Although these eight metals constitute only about 0.1% in weight of total PM2.5 mass it is very important to characterize spatial and temporal distribution of urban/background ratios of metals of importance by analyzing the speciation data. Such effort as demonstrated here will aid in delineating the effect of sources on observed measurements in a more informed manner, which should lead to effective source control and regulatory programs.

17PD-12

ESTIMATION OF THE SIZE OF A HIGHLY POLLUTED AREA OF SANTIAGO USING THE LIGHT ABSORPTION COEFFICIENT,

ERNESTO GRAMSCH. Universidad de Santiago; Avenida Ecuador 3493; Santiago; Región Metropolitana; Chile

Santiago de Chile is a large city that has high levels or particulate material during winter1. In order to assess the size of the most polluted area in the city, we have performed a two year measuring campaign using the light absorption coefficient (sa). The measurements were carried out with several low cost instruments recently developed at the University of Santiago2. The coefficient is obtained by measuring the light absorption of particles collected on a 0.2 mm pore size filter. In addition, the mass absorption coefficient for elemental carbon (EC) was obtained by measuring simultaneously with a carbon monitor located in one of the city monitoring stations. This coefficient allowed the determination of black elemental carbon concentration in other parts of the city where there are no standard carbon monitors. The monthly averages vary from 15 mg/m3 in July to 3 mg/m3 in October. Strong correlation with the traffic has been found in all monitoring sites in the morning hours, with a large increase during morning rush hour. In the afternoon (14:00 19:00 hrs) there is a decrease in all stations mostly due to increased wind. During the night, there is a large increase in EC concentration in the western and central part of Santiago, and a moderate increase towards the north and south. The results indicate that on average, during the winter period (May August) most of he EC and particulate material is located in the central and western part of Santiago. An inspection of the wind pattern suggests the possibility of transport of pollutants from the center to the western part of Santiago.

17PD-13

PILS-IC (PARTICLE INTO LIQUID SAMPLING ANALYZED BY ION CHROMATOGRAPHY) OVERVIEW OF RESULTS FOR THE PM2.5 TECHNOLOGY ASSESSMENT AND CHARACTERIZATION STUDY IN NEW YORK (PMTACS-NY),

KEVIN RHOADS, Douglas Orsini, Chemistry Department, Siena College, 515 Loudon Road, Loudonville, NY; Sarah Peters, Olga Hogrefe, James J. Schwab, Yongquan Li, Silke Weimer, G. Garland Lala, Kenneth L. Demerjian, Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY

As part of PMTACS-NY, measurements of the soluble inorganic fraction of PM2.5 aerosol were conducted using ion chromatography coupled to a Particle-Into-Liquid-Sampler (PILS-IC)(Orsini et.al., 2003). Data were collected continuously during three approximately month-long field campaigns: Queens College(QCS), Queens, NY, July 1-August 8, 2001; Whiteface Mountain(WFS), Wilmington, NY, July 7 - August 7, 2002; and Queens College(QCW), Queens, NY, January 10 - February 6, 2004. An additional month of field measurements were undertaken from July 7-August 10 2004 in support of the NEAQS/ITCT campaign at Pinnacle State Park (PSS) in Addison NY. Inter-comparisons of the data from the three measurement sites will be presented for the following: urban seasonal (QCS / QCW), rural baseline (WFS/PSS), and contrasting observations from urban and rural environments (QCS/ WFS). The rapid (15 min.) semi-continuous data (Cl-, NO2-, NO3-, SO42-, Na+, NH4+, K+, Ca2+) taken at all three sites allowed for a diurnal characterization of the inorganic aerosol composition. Diurnal trends are especially affected by local sources, meteorology, and seasonal variations. Observations of a recurring daily patterns is key in understanding the sources and mechanisms behind aerosol formation and transport. An evaluation of the overall performance of the PILS-IC instrument using various sampling configurations will also be presented. Atm. Environ., Vol 37, 1243-1259, 2003

17PD-14

REGIONAL TRENDS IN FINE PARTICLE ELEMENTAL AND ORGANIC CARBON CONCENTRATIONS IN THE MIDWEST, REBECCA J. SHEESLEY, James J. Schauer, University of Wisconsin-Madison, Environmental Chemistry and Technology Program, Madison, WI; Donna Kenski, Lake Michigan Air Directors Consortium, Des Plaines, IL; Hilary R. Hafner, Sonoma Technology, Inc., Petaluma, CA; Jeff DeMinter, University of Wisconsin-Madison, State Lab of Hygiene, Madison, WI

Trends in elemental and organic carbon (ECOC) concentrations across a region give an indication as to the relative impact of local and regional sources of carbonaceous particulate matter. To help understand particulate matter control strategies in the Midwestern United States, fine particulate matter collected every 6th day was analyzed for ECOC at 5 urban sites and 1 rural site. The urban sites included Allen Park, MI (suburb of Detroit), Cincinnati, OH, Indianapolis, IN, Northbrook, IL (suburb of Chicago), and St. Louis, MO. Bondville, IL, outside of Champaign-Urbana, was chosen as the rural/remote site. For most of the sampling days, there exists little correlation in the EC and OC pattern across sites. However, select regional PM events can be discerned. Midsummer high OC concentrations occur at all six sites and could potentially be attributed to regional meteorology and increased secondary organic aerosol. The EC concentrations show an increase in the midsummer period, but it is not as correspondingly high as OC. However, the scale of OC concentrations in midsummer does vary by site. All of the urban sites have higher OC concentrations in summer as compared to spring by about 1 μg m-3. In contrast, OC concentrations in Bondville, the regional background site, only show a 0.3 μg m-3 increase in the summer average. Additional relationships can be made between the ambient carbon concentrations, site locations and meteorology. These will be discussed in relation to regional versus local trends in carbonaceous aerosol.

17PD-15

URBAN AND RURAL MEASUREMENTS OF AMBIENT AEROSOL COMPOSITION IN NEW YORK STATE USING AN AERODYNE AEROSOL MASS SPECTROMETER, KENNETH L. DEMERJIAN, Silke Weimer, James J. Schwab, Atmospheric Sciences Research Center, U-Albany, NY; Frank Drewnick, Department Cloud Physics and Chemistry, Max Planck Institute of Chemistry, Germany; Douglas R. Worsnop, Aerodyne Research Inc., Billerica, MA

Aerosol Mass Spectrometer (AMS) measurements of particulate matter conducted at Queens, Whiteface Mountain and Pinnacle State Park in New York State as part of the PM2.5 Technology Assessment and Characterization Study (PMTACS-NY) field intensive studies in conjunction with other chemical and physical semi-continuous ambient aerosol measurements carried out during these campaigns. Data analysis focuses specifically on the regional and urban composition and compositional size distribution of PM through correlation of AMS data with gaseous precursor measurements in terms of secondary PM production and contrasting local versus regional contributions of key PM chemical constituents. The transported PM compositional components are assessed for NYC urban and two rural sites with specific attention given to the contribution from primary and secondary sources. Analyses indicate that urban and rural environments show very similar compositional backgrounds under clean air mass conditions. While analyses of polluted air mass, show similar significant contributions of secondary PM sulfates to PM mass irrespective of region (urban/rural) or season (summer/winter). This is in contrast to secondary PM nitrate and organics which show significant seasonality and regional differences.

17PD-16

ESTIMATES OF PM2.5 AEROSOL ACIDITY FROM INORGANIC ION BALANCE MEASUREMENTS AT URBAN AND RURAL NEW YORK STATE LOCATIONS FROM STN INTEGRATED FILTERS,

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The inorganic ion balance of PM2.5 as measured with ion chromatography gives a measure of the “strong acidity” of the particles. This acidity provides indications of the formation process and the potential for further reaction and/or deposition of the aerosol particles. While the IMPROVE program has many years of chemically speciated filter measurements, inorganic cations (predominantly ammonium) have not been measured for most locations in their network. The IMPROVE network consists of mainly rural sites, although some additional urban sites have been added recently. Speciation Trends Network (STN) data from New York state has the two advantages that ammonium ion is measured, and New York sites consist of both urban and rural locations. The paper will first survey the literature for measurements of strong acidity in the Eastern U.S. There are numerous ways to present the acidity/ion balance measurements and these will be discussed and evaluated. Then data from six sites in New York state (mainly from 2001-2004) will be presented as a function of site and season. The implications of the data will be presented, as will comparisons with previous work.

17PD-17

INFLUENCE OF REGIONAL PARTICULATE MATTER ON SELECTED URBAN AREAS ACROSS THE US,

TRACY KLAMSER_WILLIAMS, Paul A. Solomon (EPA, ORD), Las Vegas, NV; Peter Egeghy (ORD), Research Triangle Park, NC; Dennis Crumpler (OAQPS), Joann Rice, (OAQPS), OAR; James Homolya (OAQPS), Research Triangle Park, NC; Chuck McDade, Crocker Nuclear Laboratory, University of California, Davis, CA.

Over the next few years, States will be required to develop State Implementation Plans for reducing concentrations of fine particles in air where PM2.5 annual and or daily standards are exceeded. It is now well recognized that high concentrations of PM2.5 in urban areas is in part due to transport of fine particles from up wind locations and that the problem is in fact regional, especially in the eastern US. To better understand the sources of PM2.5, the US EPA has established a national chemical speciation trends network (STN) in urban areas, which provides information on the major and some minor chemical components of PM2.5. This network was initiated in 1999. In conjunction with the STN, EPA has enhanced significantly the number of rural IMPROVE[1] monitoring sites nationally. These two combined networks provide a fairly comprehensive picture of PM mass and its chemical composition throughout the US. EPA is currently evaluating the comparability between these two networks through a series of three paired urban-rural monitoring locations where collocated samplers from both networks operate based on each networks specific protocols for sampling and analysis. These sites are located in the areas of Washington, DC, Phoenix, AZ, and Seattle, WA. The sites were chosen to expose the samplers to different ambient chemical and meteorological conditions. The standard IMPROVE sampler was located at all six sites. However, each urban-rural pair used different STN monitors. The Washington, DC sites employed the Anderson RASS 401. MetOne SASS was used at the two Phoenix sites, while the Seattle sites employed URG MASS samplers. Previous comparisons among the three different STN monitors indicated that comparable results were obtained for most species (Solomon et al. 1999, Solomon et al. 2003), although not all across all three samplers. Currently three years of data have been collected at the three urban-rural pairs. This paper describes the chemical characteristics observed between the urban-rural pairs and the variation of those pairs in different parts of the country during the first year of the study. Annual average, seasonal, and daily data are examined to better understand the regional nature of PM2.5 at these different sampling locations and to estimate the general fraction of urban PM by chemical component that is superimposed above the regional component, recently referred to as the urban excess. The regional component dictates the fraction of the local component that needs to be lowered due to local emissions controls on primary PM and PM precursors and allows for a suggestion of how regional controls may benefit areas out of compliance with current PM standards.

1. Interagency Monitoring of Protected Visual Environments Solomon, P.A., et al. 2003. "Comparison of Integrated Samplers for Mass and Composition During the 1999 Atlanta Supersites Project." JGR - Atmospheres, Special Issue for the Atlanta Supersites Project, 108(D7), 8423, doi:10.1029/2001JD001218. Solomon, P.A., et al.. 2000. Evaluation of PM2.5 Chemical Speciation Samplers For Use In The U.S. EPA National PM2.5 Chemical Speciation Network. EPA Report No. EPA-454/R-01-005 / NTIS PB#2001-105814. http://www.epa.gov/ttn/amtic/pmspec.html

17PD-18

ELECTRICAL AEROSOL DETECTOR (EAD) MEASUREMENTS AT THE ST. LOUIS SUPERSITE,

HEE-SIEW HAN, Stanley Kaufman, TSI Inc., Shoreview, MN; Jay Turner, Washington University, St. Louis, MO; William Wilson, U.S. Environmental Protection Agency, Research Triangle Park, NC; David Y. H. Pui, University of Minnesota, Minneapolis, MN

The Model 3070A Electrical Aerosol Detector (EAD) measures a unique aerosol parameter called total aerosol length. Reported as mm/cm3, aerosol length can be thought of as a number concentration times average diameter, or simply as d1 weighting. This measurement falls between number concentration (d0) and surface area (d2). The EAD is a robust, easy-to-use, low-cost aerosol measurement instrument. It provides fast response and displays data in real time. An EAD was operated for about two years at the St. Louis supersite. A second EAD was co-located for about 6 months. Information on precision, reliability and consistency will be discussed. Diurnal profiles of the EAD signal for several days, daily averages for several months, and monthly averages for the entire period will be reported. Correlations of the EAD signal with SMPS measurements of DX for X from 0 to 3 will be reported. Reasons for the correlation being better for X around 1.5 instead of 1.0 will be discussed. Earlier studies have suggested that the EAD signal is highly correlated with the calculated deposition of particle surface area to the lung. Correlation of the EAD signal with the calculated deposition of particle surface area for several breathing patterns will be presented. The possibility of using the EAD as an indicator of PM surface dose to the lung will be considered.

17PD-19

INFLUENCE OF ATMOSPHERIC STABILITY ON PARTICLE NUMBER CONCENTRATION IN TORONTO, CANADA AND ROCHESTER, USA,

CHEOL-HEON JEONG, Greg Evans, Mike Fila, University of Toronto, ON, Canada; Philip K. Hopke, Clarkson University, Potsdam, NY; David Chalupa, Mark Utell, University of Rochester Medical Center, Rochester, NY; Henry Felton, New York State Department of Environmental Conservation, Albany, NY

In a previous study of ultrafine particle number and size distributions in Rochester, NY in 2002, significant diurnal and seasonal differences in the number concentration of ultrafine particles have been found (Jeong et al., Environ. Sci. Technol. 38: 1933 - 1940, 2004). The differences were ascribed to differences in nucleation events, sources, atmospheric dispersion conditions. Atmospheric dispersion is influenced mainly by wind speed and by mixing height causing the thermal turbulence and horizontal transport of ambient pollutants. Mixing height increases as the sun heats the ground in the morning and reaches its maximum depth during the afternoon. There are also seasonal variations in mean dispersion conditions of the atmosphere. With a measure of both wind speed and mixing height, the normalized concentrations can be estimate such that the diurnal and seasonal variations due to differences in atmospheric dispersion are removed. The results of such estimations for particle size distributions measured in Rochester and comparable measurements in Toronto will be presented. During the period of January to December, 2003, fine and ultrafine particle number concentrations were measured by a condensation particle counter in downtown Toronto, Ontario and by a scanning mobility particle sizer (SMPS) in downtown Rochester, New York, respectively. Continuous measurements of PM2.5 mass and gaseous pollutants (CO, SO2, NOx, O3) were also performed at the urban sites. Three-hour interval mixing height data based on the Eta Data Assimilation System (EDAS) of the National Center for Environmental Prediction were obtained from the NOAA Air Resource Laboratory. Meteorological data were available from the Environment Canada and the New York State Department of Environmental Conservation. The product of wind speed times mixing height was determined to estimate a normalization factor, the average ratio of the product in summer (afternoon) to that in winter (morning). Diurnal and seasonal variations in the normalized number concentrations of fine and ultra fine particles as well as PM2.5 mass and gaseous pollutants were compared. In order to relate potential particle sources in the areas, the relationship between number concentrations and PM2.5 mass or gaseous pollutants was also investigated. The spatial variation of ambient pollutants was explored to evaluate the correlation of pollutants sources between two sites. Detailed results over the measurement periods will be presented and discussed.

Reference: Jeong, C.H., Hopke, P.K., Chalupa, D., and Utell, M. (2004). Characteristics of Nucleation and Growth Events of Ultrafine Particles Measured in Rochester, NY. Environmental Science and Technology 38:1933-1940.

17PD-20

UTRAFINE PM IN NEAR GROUND LAYER OF URBAN ATMOSPHERE, PRAGUE 2002/2003,

JAN HOVORKA

Ultrafine PM is of increasing concern nowadays due to its effect on human health and catalytic properties in smog build-up in urban atmosphere. Here we present a measurement of ultrafine PM sampled in a breathing zone of urban atmosphere in a sampling site, which serves as a “green refuge” area in the city centre. Diffusion battery connected to an ultrafine condensation particle counter was used to measure 15 minute integrates of number size distributions. Concurrently with the size distributions, NOx, CH4, non-methane hydrocarbons - NMHC, O3, and meteorological parameters were measured during springs 2002/2003. All the measurements were conducted at 1.8 m height above a lawn surrounded by flowerbeds, trees and bushes in the Botanical garden of the Charles University. The garden is situated in the Prague city centre, near an intersection of medium traffic density (up to 15000 cars/day), within 100 metres from 40 meters tall chimney of the University hospital heating plant. Total number 374 of selected size distributions were separated into two size ranges: 3-10 nm as nanoparticles and 10-200 nm as particles of the accumulation mode. Total number of the nanoparticles was in the range 0-31240 cm-3 (geomean 1848 cm-3), while the accumulation mode particles were in the range 3018-42093 cm-3 (geomean 14960 cm-3). The nanoparticles formed on the average about 23% of the total. There were significantly more accumulation mode particles suspended in the air during weekdays than on weekends and also near mid-day time (10-11 a.m.) and late afternoon (5-6 p.m.) in comparison with daily averages. Nanoparticles had significantly higher concentrations than daily values just in late afternoon (5-6 p.m.). This points to the importance of the traffic density, traced by NO concentrations, which exhibit similar pattern of temporal variation. Concerning relation of gaseous pollutants and particulate matter, concentration of nanoparticles increased with CH4, NO in the 0-3 ugm-3 range but not with NO peak values and decreased with temperature; concentration of accumulation mode particles increased with sun radiation and with all gaseous components measured except of NMHC and decreased with ozone concentration during weekdays but not during weekends. There was no correlation observed between wind speed, humidity, air pressure and particulate matter of both the size ranges.

17PE-21

CHARACTERIZATION OF NH3, NO3, NO2 AND SO2 AT AGRICULTURAL AND URBAN SITE OF NORTH INDIA,

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Abstract Gas and particulate samples were collected from agricultural site and near by urban area of north central part of India during the period of 1999-2002. NH3, NO3, NO2 and SO2 were analyzed in the gaseous samples, however NH4, NO3 and SO4 were analyzed in the particulate matter. The concentrations were ranged between 0.62-35.8 μg m-3 for NH3, 11.62-8.25 μg m-3 for NO3, 8.6-45.2 μg m-3 for NO2 and 4-10.3 μg m-3 for SO2, 1.01-6.5 μg m-3 for particulate NH4, 0.95-5.2 μg m-3 for particulate NO3 and 1.02-10.05 μg m-3 for particulateSO4. Ammonium concentration was higher at agricultural site. Gas phase NH4 were always higher than the particulate phases, however reverse is true for the NO3 due to contribution of resuspended dust. Their seasonal variation indicate the higher levels of NO3 in gas phase during summer. NO2 concentration were higher in urban air. Correlation of SO2 with Sulphate indicates that that major sulphate concentration in the particulate phase were due to soil re-suspension. NH3NO3 product exceeds value predicted by theoretical value due to high ammonium concentration.

17PE-22

AN ANALYSIS OF SO2 ABSORPTION BY A STATIONARY ATMOSPHERIC WATER AEROSOL,

WEI-HSIN CHEN, Department of Environmental Engineering and Science; Fooyin University, Taliao, Kaohsiung Hsien 831, Taiwan, ROC

Sulfur dioxide absorption by aerosol droplets plays a crucial role in forming acid rain and acid fog in the atmosphere. In addition, it is also a basic unit in removing air pollutants in some equipment such as spray towers and scrubbers. In order to recognize this fundamental behavior, sulfur dioxide uptakes by an atmospheric water aerosol under various conditions are predicted and analyzed in the present study. The absorption characteristic due to the solute chemical dissociation in the aerosol is of particular emphasis. By varying some parameters such as initial aerosol pH value, surrounding gaseous SO2 concentration, as well as environmental temperature, the absorption amounts of the aerosol will be evaluated and compared with that of a pure water droplet. The parameters mentioned above will simultaneously cover the situations in the atmosphere and spray towers. For example, atmospheric SO2 concentration is generally in the range of 1 to 200 ppb. However, when attention is placed on flue gas in stacks, the order of SO2 concentration is larger than the previous one by a factor of about 2 to 3. This difference in SO2 concentration will have a significant influence on the uptake result. For this reason, an analysis on sulfur dioxide absorption by a stationary aerosol will be performed. The variations of equilibrium pH value, H2SO3, HSO3-, and SO32- concentrations due to varying the various parameters will be examined in detail. A dimensionless parameter will also be proposed to illustrate the impact of the aforementioned parameters on the aerosol uptake. The obtained results will be capable of providing a fundamental insight into the atmospheric aerosol absorptions.

17PE-23

THE CHEMICAL COMPOSITION AND QUANTITATIVE RELATIONSHIP BETWEEN METEOROLOGICAL CONDITION AND FINE PARTICLES IN BEIJING,

Jingli Wang, Institute of Urban Meteorology, CMA, Beijing. Yuanhang Zhang, State Joint Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences, Peking University, Beijing. Min Shao, State Joint Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences, Peking University, Beijing

The recent year's monitor results of Beijing indicate that the pollution level of fine particles PM2.5 shows an increasing trend. To understand pollution characteristics of PM2.5 and its relationship with the meteorological conditions in Beijing, a one-year monitoring of PM2.5 mass concentration and correspondent meteorological parameters was performed in Beijing in 2001. The PM2.5 levels in Beijing were very high, the annual average PM2.5 concentration in 2001 was 7 times of the National ambient air quality standards proposed by US EPA. The major chemical compositions were organics, sulfate, crustals and nitrate. It was found that the mass concentrations of PM2.5 were influenced by meteorological conditions. The correlation between the mass concentrations of PM2.5 and the relative humidity was found. And the correlation became closer at higher relative humidity. And the mass concentrations of PM2.5 were anti-correlated to wind speeds, but the correlation between the mass concentration of PM2.5 and wind speed was not good at stronger wind.

17PE-24

INFLUENCE OF METEOROLOGICAL PROCESSES ON AEROSOL IN AN URBAN ENVIRONMENT,

N. SHANTIKUMAR SINGH, IIA Observatory, Skara, Leh-Kadakh(J&K) 194101;G.R.Aher, Department of Physics, Nowrosjee Wadia College, Pune-411001;Sanjay D. More, V. V.Agashe, Department of Environmental Sciences, University of Pune-411007

Influence of Meteorological Processes on Aerosols in an Urban Environment N. Shantikumar Singh3, G. R. Aher2, Sanjay D. More1 and V. V. Agashe1 Department of Environmental sciences, University of Pune, Pune - 411 007, India ABSRACT Ground-based intensity measurements of direct solar radiation at multiple wavelengths have been carried out under clear sky conditions by the authors with the help of an indigenously developed sun-tracking MWR from the Department of Environmental Sciences of Pune University during 1998-2001. These data have been used by the authors to investigate the influence of meteorological processes on aerosol optical depth (AOD) and aerosol size distribution. The instrument consists of a sun-tracking plane mirror for continuously imaging the solar disc on the entrance aperture of the diffusely reflecting integrating sphere, which converts the incident radiation into diffuse radiation. The radiation emerging from the integrating sphere passes through a narrow band optical filter (HBW ~ 10 nm) and is detected by a photo-detector, whose output is recorded. The recorded output is proportional to the intensity of monochromatic solar flux imaged by the tracking mirror. Total optical depth is obtained from the measured intensity of direct solar radiation using Beer-Lambert-Bouguer law. Aerosol optical depth (AOD) is then calculated from the total optical depth by subtracting the contribution of molecular (Rayleigh) scattering and an estimated contribution from ozone absorption. Study of the Langley plots has shown the occurrence of 2-segment Langley plot at Pune. These occur all through the observing season with higher frequency in winter. The two linear segments, one for the forenoon period (FN) and the other for the afternoon period (AN) define corresponding AODs viz. $\tau p\lambda$ (FN) and $\tau p\lambda$ (AN). Usually it is found that $\tau p\lambda$ (FN) > $\tau p\lambda$(AN). This variation of $\tau p\lambda$ is regarded as the diurnal variation of AOD. The spectral variation of AOD shows significant small changes from forenoon to afternoon, indicating a change in the aerosol size distribution. Hygroscopic aerosols have their particle size affected by the presence or absence of moisture in the atmosphere surrounding them. Moisture characterized by the relative humidity has been shown to be an important parameter in determining the growth rate of aerosol particle. Other parameters, such as pressure, temperature, wind speed and direction influence the growth rate by mixing different types of air masses. Indications are strong that the diurnal variation of AOD is related to the diurnal cycle of variation of relative humidity (RH) and temperature at the ground in clear sky condition. Some of the surface weather parameters at Pune have special characteristics such as (i) large difference in daily maximum and minimum values of temperature, T(Max.) is almost twice the T(Min) practically round the year; and (ii) large difference in the morning and afternoon values of RH. Morning RH is often three times its value in the afternoon. From the tabulation of daily AOD values for different days of observation, it is noticed that the daily AOD magnitude has significant day-to-day variation. To investigate this variation, relationship between local weather parameters and the daily AOD magnitude is examined by studying their correlation. It is found that the relationship depends on the composition of aerosols. In the urban air the origin of aerosol particles is complex. It is well known that traffic and other anthropogenic combustion sources make important contribution, including the fine particles, to the ambient aerosols. It is found that during drought conditions anthropogenic aerosols predominate resulting in different pattern of behaviour and more complex relationship with local weather parameters.

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17PE-25

CHARACTERIZATION OF REACTIVE OXYGEN SPECIES TRENDS IN FLUSHING, NEW YORK,

PRASANNA VENKATACHARI, Philip K. Hopke, Clarkson University, Potsdam, NY; William H. Brune, Xinrong Ren, Robert Lesher, Jingqiu Mao, Michael Mitchell, Penn State University, University Park, PA

The concentrations of particle-bound reactive oxygen species (ROS) were determined for various size fractions of the ambient aerosol ranging from 10 nm to 18 µm, in Flushing, NY during the period of January and early February 2004. Samples were collected at 3 hour intervals using the MOUDI and Nano-MOUDI sampler. Dichlorofluorescin (DCFH), a non-fluorescent probe that fluoresces when oxidized by the presence of ROS, was used to analyze the collected samples. Diurnal profiles of the ROS concentrations will be examined. Further, correlations of the particulate ROS concentrations with the intensity of photochemical reaction, and gas phase OH and HO2 radical concentrations will also be examined. Comparisons will be made with earlier measurements made during July 2003 in Rubidoux, CA.

17PE-26

HCL UPTAKE BY A CONVECTIVE AEROSOL DROPLET WITH DRAG FORCE, WEI-HSIN CHEN, Department of Environmental Engineering and Science,^M Fooyin University, Taliao, Kaohsiung Hsien 831, Taiwan, ROC

Mass transfers around liquid aerosols in the presence of motion are widely encountered in environments and industries. In the past, in order to recognize these fundamental phenomena, a considerable number of efforts have been performed through various methods. For example, on account of rapid progress in computer simulating capability as well as advanced development in numerical algorithm, computational fluid dynamics (CFD) has become an important tool to provide a framework for predicting aerosol dynamics. When a moving aerosol is examined in detail, it is known that the relative motion between the two phases will elicit drag forces, as a consequence of fluid viscosity and non-uniform pressure distribution along the particle surface. Furthermore, with the impact of the drags, the aerosol velocity tends to decay in the course of movement, except for particles falling at terminal velocities. In the present study, hydrogen chloride absorptions by an aerosol droplet at moderate initial Reynolds numbers are investigated numerically. Particular emphasis is placed on the uptake mechanisms in the droplet under the impact of drag force. An examination of the mass transfer inside the droplet, in view of the solute transport delay from the gas-liquid interface to the droplet interior, a maximum distribution in concentration difference between the particle surface and the internal minimum concentration is exhibited. Regarding the effect of the decelerating motion, the numerical predictions reveal that the variation of the droplet velocity due to drag force is faster than that of the uptake process. Therefore, the absorption rate of the decelerating aerosol is substantially decreased when compared with that of a constant-speed one. As a whole, increasing the initial Reynolds number will cause faster decay in the droplet velocity which further reduces the mass transfer rate in the aqueous phase. This results in that the larger the initial Reynolds number, the more significant the droplet uptake rate decreased.

17PH-27

CORRELATING PARTICULATE MATTER AMBIENT CONCENTRATIONS WITH VEHICLE TRAFFIC VOLUMES, KEVIN BLACK, Federal Highway Administration; Frank Divita, E.H. Pechan and Co.; Richard Margiotta, Cambridge Systematics, Inc; Randall Guensler, Trans AQ, Inc.

Correlating Particulate Matter Ambient Concentrations with Vehicle Traffic Volumes Kevin N. Black, Federal Highway Administration: Frank Divita, E.H. Pechan, Inc; Richard Margiotta, Cambridge Systematics; Randall Guensler, Trans/AQ Inc. Federal Highway Administration (FHWA) has developed its research needs for understanding particulate matter (PM) emissions resulting from vehicle traffic on transportation facilities. Particulate Matter is a pollutant that impacts transportation project development and highway usage due to air quality regulations that have been implemented to protect human health. Laws and regulations such as the Clean Air Act and the transportation conformity rule as well as other initiatives covered by the National Environmental Policy Act are highlighting the need for a better understanding of PM and its association with the transportation sector. In an effort to expand the understanding of mobile source PM emissions, the FHWA established an integrated research program to investigate the contribution of mobile source induced PM pollution, including both PM10 and PM2.5, the two size fractions currently being regulated. This effort was initiated with a strategy document listing fourteen different projects that the transportation community should undertake to understand and apportion PM emissions from vehicles. One of these projects involved working with the EPA Supersites to collect traffic and air quality data. The PM Traffic-Air Quality Supersite Project was initiated in the summer of 2001 establishing the locations and procedures for collecting and analyzing traffic, ambient PM concentrations, and meteorological data obtained from transportation departments, EPA Supersite investigators and other EPA monitoring programs, and state and local air quality agencies. Data from six EPA Supersite cities and from the City of Detroit was collected to serve as representative samples from different geographical regions. Findings from the first year of the two-year collection period have been studied but initial correlations of vehicle traffic and ambient PM concentrations have been inconclusive. These results likely are caused by a variety of factors including monitor locations and meteorological conditions. Additional data collection and analysis will be performed to refine the first year findings and establish trends or anomalies resulting from influence factors such as weather. The study is investigating the contribution from regionally transported vehicle emissions and the fugitive dust component generated locally by vehicle traffic where this information is available. Reporting from this study has been made during the same time periods at all sites to the best degree possible offering regional comparisons. Attempts are being made to investigate regional, time of day and seasonal variations as these factors are important when developing mitigation strategies. This data and the results of this project are intended to serve as a planning resource for State and local agencies responsible for developing mobile source PM inventories and reducing PM emissions.

17PH-28

MODIFYING 50 DEG C TEOM DATA TO BE MORE "FRM LIKE" FOR AQI REPORTING USING A NON-LINEAR CORRECTION BASED ON THE JULIAN DAY, HENRY D. FELTON, Department of Environmental Conservation, Division of Air Resources, 625 Broadway, Albany, NY

The 1400AB TEOM (Tapered Element Oscillating Microbalance) manufactured by the Rupprecht and Patashnick company is in wide use for near real time reporting of ambient PM-2.5. The instrument is easy to operate in State Agency networks and provides hourly data suitable for use for AQI calculation and for the EPA's AirNow website hourly reporting requirements. The most prevalent configuration of the instrument is the base instrument with a size selective inlet, and sample conditioning consisting of constant heat. The instrument heats the sample flow and the sampling filter to 50 DegC. This sample conditioning lessens the instrument sensitivity to short term swings in atmospheric humidity and PM-2.5 volatility but causes the resulting data to under predict the FRM in periods when the PM-2.5 contains a significant proportion of volatile material. Experience with the TEOM and FRM data shows that in general the bias is greatest in the colder months in the Northeast United States. Looking at the daily average difference of FRM minus TEOM over a calendar year shows that the difference is indeed highest at the beginning and end of the year. A non-linear equation can be fitted to the difference based on the Julian Day. Once the calculated daily value for how much the TEOM under predicts the FRM is known, it can be added back to the TEOM value to make the TEOM data more closely resemble FRM data. A second linear regression is used to remove any additional bias between the measurements from the FRM and the TEOM. Each set of equations presented here is based on annual data from a pair of collocated PM-2.5 FRMs and TEOMs. These correction equations vary significantly from urban to a rural areas as well as from one geographical area to another as illustrated by the five sites examined for this study. The equations can be installed on most data loggers as math channels. This allows for Air Quality Reporting Agencies to automatically submit adjusted TEOM data necessary for public reporting purposes. AQI: Air Quality Index AirNow: EPA sponsored website graphically displaying hourly AQIs for most of the States in the USA. http://www.epa.gov/airnow/

17PH-29

ANALYSIS OF ALTERNATIVE PM2.5 NATIONAL AMBIENT AIR QUALITY STANDARD LEVELS AND FORMS, PHILIP R.S. JOHNSON, John J. Graham, Jr., Northeast States for Coordinated Air Use Management

The U.S. Environmental Protection Agency (EPA) is currently engaged in a PM2.5 standards review cycle and expects to release the final draft PM Staff Paper early in 2005 recommending PM National Ambient Air Quality Standards (NAAQS). This paper explores the spatial and temporal variability of PM2.5 levels in the northeastern U.S. and assesses the various aspects of averaging times and forms for PM NAAQS. Specifically, three areas were addressed. First, the relationship of the stringency or "protectiveness" of annual and 24-hour averaging times was analyzed across the entire distribution of PM2.5 values in an eight-state study area (CT, ME, MA, NH, NJ, NY, RI, CT) as well as for the continental U.S. Across broad areas, we found that both annual and daily standards may fail to constrain PM2.5 levels and that the concept of a controlling standard could leave substantially large populations unprotected. Second, we analyzed the behavior of PM2.5 24-hour maxima using a 98th percentile form and alternative forms in the northeastern U.S. This enabled us to assess the effect of various PM2.5 standard forms and high peak day exemptions on annual and 24-hour design values. Third, we analyzed multi-year continuous PM2.5 datasets for two Northeast urban sites. We found that elevated short-term concentrations varied by time of day, day of week, and season, showing that current 24-hour design values mask periods of peak sub-daily exposures. In order to understand the effect of alternative 24-hour standards on controlling peak sub-daily levels, we compared the 24-hour metric with 1-hour and 3-hour average metrics above a prescribed PM2.5 baseline. The magnitude of 1-hour and 3-hour average PM2.5 elevated values was substantially higher than the 24-hour averaged mass value during all seasons. In populated areas, short-term PM2.5 levels are important to consider in light of plausible acute biological mechanisms such as increased inflammation, allergenicity, and cardiopulmonary reactivity given the extensive prevalence of heart and lung disease in the U.S. population.

17PH-30

IMPROVING EMISSION INVENTORIES FOR EFFECTIVE AIR-QUALITY MANAGEMENT ACROSS NORTH AMERICA -- A NARSTO ASSESSMENT,

J. David Mobley, US Environmental Protection Agency; Marc Deslauriers, Environment Canada; Howard Feldman, American Petroleum Institute; Chris Frey, North Carolina State University; Leonora Rojas-Bracho, National Institute of Ecology of Mexico; Susan Wierman, Mid-Atlantic Regional Air Management Association; Arthur S. Werner, MACTEC

The NARSTO Ozone and Particulate Matter Assessments emphasized that emission inventories are critical to the success of air quality management programs and that emissions inventories in Canada, Mexico, and the United States need improvement to meet expectations for quality, timeliness, and cost effectiveness. Accordingly, NARSTO sponsored a workshop to address new and innovative methods for emission inventory development and evaluation. Findings and recommendations from the workshop led NARSTO to undertake an assessment of the emission inventory programs across North America. The assessment, slated for completion in Spring 2005, identifies emission inventory programs needed for the 21st century, recognizes the capabilities and limitations of current programs, and recommends enhancements needed to move the programs forward. Preliminary findings and recommendations will be presented. The authors of this poster are CoChairs of the NARSTO committee that oversaw preparation of the Emissions Inventory Assessment report. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

17PI-31

EVALUATION OF IN VITRO BIOLOGICAL EFFECTS INDUCED BY PARTICULATE MATTER FROM MEXICO CITY COLLECTED WITH THE VERSATILE AEROSOL CONCENTRATOR (VACES) SYSTEM,

ANDREA DE VIZCAYA-RUIZ, Ma. Eugenia Gutiérrez-Castillo, M Uribe-Ramírez, Mariano E. Cebrián, Toxicology Section, CINVESTAV-IPN, D.F., MX; Violeta Mugica-Alvarez, UAM-A, D.F., MX; Irma Rosas, Eva Salinas, Centro de Ciencias de la Atmósfera, UNAM, D.F., MX; Flor Martínez, Claudia Garcia-Cuéllar, Ernesto Alfaro-Moreno, Alvaro Osornio-Vargas, INCan, D.F., MX; Victor Torres-Flores, Fac. de Medicina, UNAM, D.F., MX; (Mexican Consortium for Particle Matter Studies, D.F., MX); Constantinos Sioutas, Dept. of Civil and Environmental Engineering, USC, Los Angeles, CA; Arthur Cho, Department of Molecular and Medical Pharmacology, UCLA, CA; John Froines, Center for Occupational and Environmental Health, UCLA, CA; (The Southern California Particle Center and Supersite, Los Angeles, CA)

Coarse and fine particles were collected using an ambient particle concentrator (VACES system) in the North (N), Center (C) and South (S) areas of Mexico City during the warm and cold-dry seasons. The chemical and biological composition of PM was studied, together with the oxidative potential, in vitro cell toxicity, ultrastructural morphology and DNA damage. Analogous PM collection in filters using low and high volume particle collectors was performed to compare chemical composition and biological effects (DNA damage). The fine fraction of PM showed a higher soluble Zn, Fe, Cu, V, Ni content analyzed by graphite furnace atomic absorption spectroscopy (GFAAS) than the coarse fraction, with higher levels in the N < S < C. When analyzed by induced coupled plasma (ICP), levels of Fe, Zn, Ti, Cu, Cr Cd, Ni, Mn and Pb were higher in the coarse fraction, and were predominately in the N. Bacteria, fungi and endotoxin were present mostly in the coarse samples from the N. Fine PM from the warm-dry season showed a higher redox potential, assessed by the dithiothreitol (DTT) assay a quantitative measure of in vitro reactive oxygen species formation, than those from the cold-dry season as well as from the coarse fraction. Fine PM from the C were more potent in the warm-dry season and fine PM from the N in the cold-dry season. In vitro viability of A549 cells remained unchanged after exposure to coarse and fine PM at a concentration of 50 ug/cm2. Fine PM were internalized in cytoplasm and induced structural damage. All PM samples induced DNA damage assessed by the comet assay on THP-1 cells when exposed to a concentration of 10 ug/cm2, particles from the N were the most potent (median length: 45 um for N; 26 um for C and 34 um for S). Coarse PM from the warm-dry season were more potent than those from the cold-dry season, and the fine PM fraction was more potent in the cold-dry season. Evidence of 8-oxoguanosine adduct formation was demonstrated. In conclusion, PM from the N with higher metal and biological content showed a more extensive DNA damage. Also, the fine PM fraction from the all regions sampled showed a higher metal content, redox potential and cellular cytoplasmic PM inclusions structural damage. In summary, location, season and size of PM collection influence their chemical and biological composition and thus their effect on cell toxicity. (Financed by UC MEXUS-CONACYT Collaborative Grant and the UCLA-Fogarty Program).

17PI-32

INCORPORATING BIOMARKERS AS FORENSIC EVIDENCE IN ASSESSING CHEMICAL EXPOSURE IN ENVIRONMENTAL JUSTICE AREAS,

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Incorporating biomarkers as forensic evidence in assessing chemical exposure in environmental justice areas By Janine M. Legg, MBA Abstract Biomarkers have a role in providing forensic evidence to assess the disease-exposure continuum and provide evidence of environmental and white collar crimes. Residents who live in environmental justice areas are exposed to mixture chemicals and hazardous waste through illegal discharges to air and water or through illegal transportation and dumping of hazardous waste, which may cause lifelong disease or shortened lifespan. Biomarkers are currently used as indicators of the pollution-disease continnum in respiratory diseases, cancer, childhood leukemia, endocrine disruption and neurotoxicity. The disease exposure continuum can only be accurately assessed by the gathering of environmental forensic evidence and human forensic evidence. Biomarker and medical monitoring data can be used to assess the level of exposure of a resident living in an environmental justice area. Examples of reliable biomarkers are PAH DNA Adducts for exposure to Polycyclic Hydrocarbons, PAH metabolites in Urine for exposure to Polycyclic Hydrocarbons, DNA Adducts for exposure to Environmental Mutagens/Xenobiotics, Blood lead levels for exposure to lead, Cholinesterase activity in red blood cells for exposure to Organophosphates, S-Phenylcysteine for exposure to benzene and Urinary trans-trans muconic acid for exposure to benzene. The use of environmental forensic data and biomarker/ medical monitoring data can be used together to evaluate the public health hazard and environmental damage caused by the illegal discharges and used for prosecution. EPA uses a method of environmental forensic science in gathering samples for evidence of environmental crimes which include samples of water, soil and hazardous waste. This differs from the traditional police analyses due to quality management but nonetheless are methods for forensic analyses in environmental crimes. The Pesticides and Toxic Office, the National Enforcement Investigation Center (NEIC) and the Police Laboratory analyze data packages without referring back to a Validated Method. This method is used rather than referring back to a validated method because of the unique compounds being analyzed. Analyses of blood and urine tests for biomarkers and chemical exposure are done within a clinical setting and sent to a limited number of designated medical labs. There are established validated tests for testing individuals for chemical contaminants. Models of validation of biomarkers are the mathematical of Attributable Proportion, Variability Source of Biomarkers and the Quantitative Reproductive Risk Estimation Model. The biggest challenge facing the use of biomarkers is to establish reliable biomarkers of mixture chemicals to validate the pollution-exposure continuum. The use of biomarkers in a clinical setting should enable the physician to include specific environmental toxic exposures within the differential diagnoses of illnesses and screen residents who live in environmental justice areas for toxic exposures. This screening should assist the prosecutor and agency in presenting evidence of chemical poisoning, environmental and white collar crimes. The challenge to the law enforcement officer and detective is to build bridges with the regulatory agencies and public health professionals to assist in recognizing and gathering of environmental and forensic evidence and accurately documenting police reports.

17PI-33

NEW PROBLEMS OF AIR POLLUTION IN ARMENIA WITHIN POST-SOVIET PERIOD,

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Various studies have provided of harmful effect of outdoor and indoor air pollution on health in different groups of population. In this investigation I tried to illuminate the role of air pollution on some indicators of health . As a source of the information we have used the reports of Ministry of Health , Department of Statistics , Monitoring Center. Materials were analyzed by dispersion, regression and correlation methods. The results of our research show that in terms of anthropogenic chemical burden diminution on the human organism between of 1987 –1993, the indexes of still-births as well as up to one year infant mortality have decreased. The sickness rate and the death-rate of breathing pathologies have also diminished . On the background of almost half-decreasing volume of pollutions in the urban the still-births rate decreased from 19.2%o to 10.09%o. Up to 1 year infantile mortality decreased for 8.85%o. Infantile breathing pathologies rate decreased triple At the same period the death-rate in the group of breathing pathologies decreased from 28.2 to 24..05 (per 100 thousand of population).The decrease of summary pollutions index “P”(by M.Pinigin) from 10.7 to 4.8 is correlated with the stillbirth-rate decrease as (r=0.85). Starting in 1993 mainly because of the wide use of bad quality petrol unallowable concentration of formaldehyde and benzene were found in the air of Yerevan. Because of changes in the type of heating system in Armenia the level of indoor air pollution has increased. At the same time breathing pathologies, contributing to a rise in death rate, lung’s cancer , still births, infant mortality and bronchial asthma have increased. Our studies have shown a correlation (r=0.45) between the level of indoor and outdoor air pollution and health of pregnant women and infants because of their more susceptibility to the effect of PM and combustion gases. During energy crisis(1993-1995) indoor air pollution was very harmful, because people used to burn wood, coal oil, polymer materials, clothes for heating intention. The most high rate of stillborn was registered at 1994. The proportion of newborn with low birth weight has increased from 3.46% to 6.55%.Moreover the number of newborn with good physical development decreased. From these results we can conclude that the establishment of quantity dependence between the level of environment pollution and sick rate may be very useful in risk assessment of unfavorable factors. But our Soviet methods are insufficient for correct interpretation and calculation of risks of bad influence in the modern understanding of question. That is why it is important for us to acquire contemporary knowledge in assessing of risk of unfavorable factors to establish the role of each dangerous factors of environment in forming indicator pathologies.

17PI-34

HEART RATE CHANGES IN 24-MONTH OLD FISHER 344 RATS EXPOSED TO CONCENTRATED PARTICULATE MATTER (PM2.5) CLOSE TO A FREEWAY IN DIAMOND BAR, CA,

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Cardiovascular diseases are among the most prevalent causes of mortality and morbidity in the United States. Exposure to elevated levels of ambient particles during air pollution episodes has been associated with cardiopulmonary morbidity and mortality, especially in individuals 65 years of age and older, in epidemiologic studies. In order to test the hypothesis that fine ambient particles could affect cardiac function in an elderly population we exposed 24-month-old rats to concentrated ambient fine paricles (CAPs). The rats were used as models of the susceptible aged human population. Eight 24-month old Fisher 344 rats, implanted with telemetry-based EKG monitors, were exposed to purified air and CAPs in a repeated measures design. The animals were exposed to purified air in week 1 and CAPs in week 2 at a site in Los Angeles with high levels of particulate pollution. In this design, each rat served as his own control. The rats were exposed, whole body, for 4 hours/day for 3 consecutive days. The Diamond Bar, CA exposure site was downwind of a heavily trafficked freeway and in an area impacted by transported regional pollutants. Exposures were performed in a mobile exposure facility. Electrocardiogram tracings were recorded for 20 minutes before and 20 minutes following each daily exposure while the rats were stationary. The data from these tracings are being analyzed for changes in heart rate, frequency of abnormal heart beats and changes in heart rate variability. Preliminary analyses showed an increase in heart rate following exposure to PM2.5 as compared with exposure to purified air. Additional analyses for inflammatory cytokines and acute phase proteins will be performed to test an hypothesis that the increase in heart rate resulted from pulmonary-irritation-induced autonomic nervous system stimulation or proinflammatory cytokine induction of autonomic neural reflexes affecting the heart.

17PJ-35

SAMPLING AND ANALYSIS OF PAHS IN URBAN, SUBURBAN AND RURAL ATMOSPHERE. TEMPORAL VARIATIONS OF CONCENTRATIONS AND GAS-PARTICLE PARTITIONING,

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Atmospheric sampling (Gas and particles) of 16 PAHs on XAD-2 resin (20 grs) and glass fibre filters respectively, were performed between 2002 and 2004 by using “Digitel DA80” high volume samplers. Sampling were performed in Strasbourg (east of France) and its vinicity (Schiltigheim and Erstein). Sites were chosen to be representative of urban (Strasbourg), suburban (Schiltigheim) and rural (Erstein) conditions. Field campaigns were undertaken simultaneously in urban and suburban, urban and rural and suburban and rural sites during all the seasons during 4 hours at a flow rate of 60 m3.h-1 which gives a total of 240 m3 of air per sample. Period of sampling varied between 06h00 to 10h00, 11h30 to 15h30, 17h00 to 21h00 in order to evaluate a variation of concentration during automobile traffic between urban, suburban and rural areas. Gas and particle samples were separately Soxhlet extracted for 12h with a mixture of CH_2Cl_2 / n-hexane (50:50 v/v), concentrated to about 1 mL with a rotary evaporated and finally dried under nitrogen. Dry extracts were dissolved in 1 mL of CH_3CN before analysis. Before use, traps were Soxhlet cleaned for 24 h with the same mixture as used for the extraction. Analysis of each extract were performed by reverse phase HPLC and fluorescence detection and quantification was done with respect triphenylene used as internal standard. Principal results shows that : lower molecular weight PAHs were more enriched in atmospheric gas, whereas high molecular weight PAHs were more abundant in atmospheric particles, sharp peak concentrations of PAHs were observed in early morning (6h -10h) corresponding with a period of high traffic, followed by a reduction during the day time, concentrations in the evening were lower than in morning time. Indeed, the intensity of the traffic was distributed during a more longer period. In the evening time, back return to home was more variable, in general, the concentration of PAHs at the urban sampling site was higher than at the rural and suburban sampling sites. Spatial and geographical variations of PAHs concentrations associated to gas-particle partitioning in function of temperature will be presented and discussed together with climatic conditions.

17PJ-36

IDENTIFICATION OF POLYMERS IN PM2.5 AIR SAMPLES BY LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY,

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The formation of polymers as an important component of the secondary organic aerosol (SOA) has drawn considerable attention in recent years. The mechanisms of polymer formation through ozonolysis of cycloalkenes or by heterogeneous reactions in the atmosphere are not well understood even with a substantial part of the SOA being polymeric. The current study was undertaken to investigate polymer formation in the atmosphere by analysis of the ambient aerosol by liquid chromatography/mass spectrometry (LC/MS). Air samples were collected in Potsdam, New York in the late summer of 2004 at 220 LPM through a PM2.5 inlet. The samples were extracted with methanol prior to the LC/MS analysis. Several groups of polymeric species were found in PM2.5 samples by LC/MS having several different monomer groups. We found polymers group with a base ion m/z value of 356 with addition of units of 44 to form a group of polymers with ion of m/z values of 400, 444, 488, 532, 576, 620, 664, and 708. These species could be a base compound with m/z of 356 with addition of –CH2-O-CH2- or –COO-. We also found polymers group of m/z values equal to 189, 332, 475, 618, and 761 with addition of 143 to the starting species. We found that the formations of polymers were affected by environmental conditions such as daily temperature, presence or absence of sunshine, and etc. Weather would affect what polymers would form and the amount of each polymer formed and can potentially provide additional insights into the mechanisms of formation in future studies.

17PJ-37

SOURCE APPORTIONMENT OF PM2.5 IN PHOENIX, ARIZONA USING POSITIVE MATRIX FACTORIZATION,

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Speciated PM2.5 data collected as part of the Interagency Monitoring of Protected Visual Environments (IMPROVE) program in Phoenix, Arizona from April 2001 through October 2003 were analyzed using the multivariate receptor model Positive Matrix Factorization (PMF). Over 250 samples and 24 species were utilized, including the organic carbon (OC) and elemental carbon (EC) analytical temperature fractions from the thermal optical reflectance (TOR) method. While these fractions are only analytically based, they have been useful in apportioning between combustion sources. Nine factors were identified, with a good comparison between predicted and measured mass (r2 = 0.96) and orthogonality between factors seen. Motor vehicle and diesel particulate matter (DPM) factors were identified; both showed a significant decrease on weekends compared to weekdays, and were predominantly local in origin. Road dust/soil also showed a weekday-weekend decrease, indicative of the importance to off-road mobile sources to the total PM. Mining operations, metal manufacturing, and non-ferrous smelting factors were also determined. These factors were confirmed using trajectory and conditional probability function (CPF) analysis, which showed high contributions of these factors from known source locations. Other factors identified included regional power generation, secondary transport, and winter nitrate formation. Overall the various temporal, spatial and inter-factor analyses made identification of these factors robust.

17PJ-38

CHEMICAL MASS BALANCE MODEL: EPA-CMB8.2,

C. THOMAS COULTER, USEPA, Research Triangle Park, NC and John V. Scalco, Ideal Software, Inc., Apex, NC

The Chemical Mass Balance (CMB) method has been a popular approach for receptor modeling of ambient air pollutants for over two decades. The first interactive, user-oriented software for CMB was programmed in 1978 at the Oregon Graduate Center in Fortran IV on a PRIME 300 minicomputer, which had strict storage memory limitations. CMB Versions 1 through 6 updated this original version and were subject to many of the limitations dictated by the original computing system. CMB7 was completely rewritten in a combination of the C and Fortran languages for DOS-based microcomputers (PCs) with floating-point coprocessors, and took advantage of PCs having much more storage and memory. CMB7 was released by EPA in the early 90s as a tool for PM10 apportionments in State Implementation Plan revisions. For the past few years the U.S. Environmental Protection Agency's Office of Research and Development and Office of Air Quality Planning & Standards have collaborated to develop a new generation of CMB software, CMB8. Developmental work was initiated under EPA contract by the Desert Research Institute. CMB8 created a user interface for CMB7 calculations using the Borland Delphi® object oriented language, and was delivered to EPA in 1998. Work to improve documentation (Users Manual), address reporting anomalies and run-time instabilities continued by Pacific Environmental Services (now MACTEC), and final repairs and enhancements were accomplished by Ideal Software, Inc. The current version, EPA-CMB8.2, incorporates the upgrade features that CMB8 has over CMB7, but also addresses problems identified with CMB8 and adds enhancements for a more robust and user-friendly system. EPA-CMB8.2 features include: (1) full use of Windows® (32-bit) capability for file access/management, (2) a tabbed-page interface that facilitates the sequence of steps for doing a CMB calculation, (3) multiple indexed arrays for selecting fitting sources and species, (4) versatile display capability for ambient data and source profiles, (5) mouse-overs and on-line help screens,(6) increased attention to volatile organic compounds (VOC) applications, (7) correction of some CMB7 flaws, (8) more options for input and output data formats, (9) addition of a more accurate least squares computational algorithm, (10) upgraded linear algebra library, (11) a new treatment of source collinearity, and (12) choice of weights for measure of ‘best fit’. Details of the changes and the procedure for obtaining EPA-CMB8.2 are presented. The CMB model’s apportionment is based on an effective variance weighted, least squares regression. Its formulation constrains it for localized applications for which speciated profiles of impacting sources are known, and for which secondary formation is not explicitly treated. The model is ideal for apportioning localized sources and has seen a lot of application for PM10 and lead. EPA-CMB8.2 also lends itself to localized apportionment of fine particles and VOC. It is being released with an updated Protocol for Applying and Validating the CMB model for PM2.5 and VOC. The model has been subjected to scientific peer review, and is now considered ready to release for regulatory applications. It now joins the family of other receptor models in EPA’s stable: EPA-Unmix and EPA-PMF.

17PJ-39

METHANOL REACTION WITH SULFURIC ACID AND SULFATE SALTS: A SFG AND RAMAN SPECTROSCOPIC STUDY,

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The reaction between methanol and sulfuric acid (SA) was investigated using Raman and vibrational broad bandwidth sum frequency generation spectroscopies. Evidence for the formation of methyl hydrogen sulfate (MHS) was obtained by the presence of a new peak in the 800 cm-1 region, not present in either the neat methanol or concentrated sulfuric acid spectra. This peak is attributed to the singly bonded OSO symmetric stretch of MHS. The maximum yield of MHS with a large SA excess (7 SA/1 methanol) is shown to be (95 ± 5)% at -(15 ± 2) °C. No evidence was found to suggest formation of dimethyl sulfate. An additional study revealed no evidence to suggest formation of MHS for the reaction between methanol and ammonium sulfate or ammonium bisulfate in place of SA.

17PJ-40

VIBRATIONAL SPECTROSCOPY OF AQUEOUS SODIUM HALIDE AND HYDROGEN HALIDE SOLUTIONS,

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Reactions on the surfaces of atmospheric aerosols have been shown to yield active halogen compounds. These reactions can occur in the bulk liquid and/or at the air-liquid interfaces. Vibrational sum frequency (SFG) spectroscopy, which is an interfacial selective spectroscopy was used to investigate the air-liquid interface of sodium halide and hydrogen halide solutions. For comparison of the bulk water structure to that of the interface, Raman and IR spectroscopy was used. Data indicate a decrease in the number of dangling OH bonds at the acid (hydrogen halide) surfaces. However, an increase in the interfacial depth for both the sodium halide and hydrogen halide air-aqueous interfaces is observed.

18A-1

THE ROLE OF NIGHTTIME CHEMISTRY IN WINTER AMMONIUM NITRATE FORMATION IN THE SAN JOAQUIN VALLEY,

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Ammonium nitrate is the most abundant constituent of PM2.5 in winter in the San Joaquin Valley and in many other parts of the western United States. Nighttime chemistry can strongly influence atmospheric composition by removing hydrocarbons and oxides of nitrogen, and by forming ammonium nitrate aerosol. Field observations of NO, NO2, NOy, ozone, and nitrate aerosol concentrations at the Fresno Supersite and at a rural 100m tower located south of Fresno provide evidence for the regional importance of the nighttime NO2, O3, NO3, N2O5 chemistry leading to nitric acid via N2O5 hydrolysis and subsequent formation of ammonium nitrate aerosol. Surface observations alone do not capture the nighttime chemistry aloft because of decoupling of atmospheric layers, deposition, and inhibiting reactions near the surface. Field observations on the tower suggest rapid nighttime ammonium nitrate formation aloft in the San Joaquin Valley. Fresno Supersite measurements show rapid increases in ammonium nitrate in the morning as growth of the mixed layer entrains nitrate laden air from aloft. Nighttime ammonium nitrate formation aloft contribute to the regional nature of wintertime PM2.5 episodes in the San Joaquin Valley.

18A-2

COMPARISON OF PARTICULATE NITRATE FORMATION IN DIFFERENT CHEMICAL REGIMES,

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Recently, concern has developed about the response of the sulfate, nitric acid, nitrate, ammonia-ammonium system when sulfate levels are reduced as a result of declines in SO2 emissions. As sulfate levels decrease, there is a potential for particulate nitrate concentrations to increase, partially compensating for the reduction in sulfate concentrations. The change in nitrate with respect to sulfate can be different in various limiting regimes of the nitrate-sulfate-ammonium system. The changes in nitrate can be estimated using a thermodynamic equilibrium calculation. The SCAPE and ISORROPIA thermodynamic equilibrium models were applied alone or together to three different areas where the chemical regimes are significantly different. These areas include (a) southern and central California—an ammonia and nitric acid rich condition, with low sulfate concentrations; (b) the Great Lakes area—an enriched ammonia regime, with elevated sulfur oxide conditions and; and (c) the Southeast--an ammonia lean and sulfate rich system. Ideally, the application of the model depends on availability of sulfate, nitrate, ammonium, ammonia, and nitric acid measurements, along with temperature and humidity data. Each of the locations of interest had a reasonable record of these components, with the exception of ammonia concentrations at some sites. The results show a different, non-linear response of nitrate change with changes in the other components depending on the limiting conditions in each location. Nitrate formation was sensitive to changes in ammonia levels in the Southeast, but to nitric acid in California. The Great Lakes area showed a sensitivity to both nitric acid and ammonia, which was dependent upon season and varied among sites; after the sulfate levels were reduced by 50 percent, decreases in HNO3 concentrations produced proportional decreases in mean particulate nitrate concentrations. The thermodynamic equilibrium calculations provide useful guidelines for managing changes in nitrate given expected reductions in sulfate, assuming that future changes in ambient nitric acid concentrations can be estimated from photochemical modeling.

18A-3

SYNTHESIS OF RESEARCH ON NEW PARTICLE FORMATION AND GROWTH AT THE PITTSBURGH AIR QUALITY STUDY,

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Homogeneous nucleation, a major source of atmospheric particles, is an important process in shaping the ambient aerosol size distribution. Over 150 days with homogeneous nucleation were observed with Scanning Mobility Particle Sizers (SMPS) during the Pittsburgh Air Quality Study, a 15-month sampling campaign in the Eastern United States. Most of the events occur over a wide geographical area (at least 100s of kilometers) and therefore are important to the regional aerosol size distribution. Field observations from a number of instruments were integrated with modeling studies by a multi-investigator team to understand the chemistry, physics, and meteorology of these events as best as possible. We show (a) good model-measurement agreement for summer conditions (100% prediction of yes/no for new particle formation for 19 modeled days; prediction of final mode size and time of appearance of new particles on the majority of the modeled days); (b) demonstration that NH3 is often a limiting species in summer; (c) encouraging model-measurement agreement under winter conditions (but with less fidelity than summer), showing that H2SO4 production can be limiting during winter; and (d) an increase in the frequency of new particle formation from proposed SO2 reductions and an opposite effect for NH3 controls. The approach was used to test hypotheses regarding the chemistry of nuclei formation and ultrafine particle growth using a suite of gas-phase, aerosol-phase, and modeling tools. Gas-phase observations (including SO2, NH3); particle-phase measurements (including aerosol size distributions at urban and rural sites, PM2.5 inorganic compounds by denuder/filter, steam sampling, and flash volatilization; PM2.5 organic carbon; size resolved chemical composition by Aerodyne Aerosol Mass Spectrometer; and particle hygroscopicity); meteorological data (including solar radiation, wind parameters, RH, and temperature); and modeling (using a 0-D box model with gas-phase chemistry, nucleation, condensation, and coagulation) were used for the analysis.

18A-4

FORMATION MECHANISMS OF ULTRAFINE PARTICLES IN THE BOUNDARY LAYER,

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Ultrafine particles, which usually dominate the number concentrations of atmospheric aerosols, influence the formation and properties of clouds by acting as cloud condensation nuclei. Ultrafine particles may also lead to adverse health effect due to their high number concentration and surface area, high deposition efficiency in the pulmonary regions, and high propensity to penetrate the epithelium. The concentration of ultrafine particles is determined by a number of microphysical processes, of which the nucleation process is critical but least understood. New particle formation has been observed in many field measurements (including field campaigns sponsored by the US EPA supersite programs). A clear understanding of the formation mechanisms of secondary particles is important to improve the predictive understanding of the environmental and climatic impacts of atmospheric aerosols, and recent measurements provide useful data to test different nucleation mechanisms. Most of nucleation events observed in the atmosphere are associated with precursor gas sulphuric acid. Binary H2SO4-H2O homogeneous nucleation (BHN), ternary H2SO4-H2O-NH3 nucleation (THN), and ion-mediated H2SO4-H2O nucleation (IMN) are three different nucleation theories that have been widely used to predict new particle formation. All three mechanisms may contribute to the new particle formation in the atmosphere but different mechanisms dominate the nucleation under different conditions. In this presentation, recent advances in the nucleation theories are discussed, the differences between the theories are described, and the predictions based on different nucleation mechanisms are compared with relevant measurements in the boundary layer (BL). BHN has been recognized to be negligible in the BL ambient atmosphere, however we find that BHN can contribute to significant particle formation in vehicular exhaust when the vehicle is running with fuels contain more than ~ 200 ppm sulphur. Due to the lack of thermodynamic data with regard to ternary solution, THN theory has huge uncertainty. Based on the preliminary THN model which shows that NH3 (of a few ppt) can enhance the nucleation rates by up to 30 order of magnitude, the predicted THN rates are much high than the observed values in the field campaigns. Based on a kinetic THN model with the NH3 nucleation enhancement factor constrained by available laboratory experiments, THN rates are very small in the BL ambient air. It is well recognized that nucleation on ions is thermodynamically favoured over homogeneous nucleation. While our simulations indicate that most of particles nucleated on ions in the ambient atmosphere are neutralized by opposite small ions before they reach around 3 nm, ions play a critical role in the formation of clusters above stable critical sizes and new particles in BL ambient air. IMN appears to be able to account for many nucleation events observed in the boundary layer. The IMN rates are limited by ion concentrations or ionization rates. Most of the new particle formation rates observed in the BL ambient atmosphere are less than 10 cm-3s -1 which is consistent with ionization rates of ~ 10 ion-pairs cm-3 s -1.

18A-5

ASSOCIATIONS BETWEEN PARTICLE NUMBER AND GASEOUS CO-POLLUTANT CONCENTRATIONS IN THE LOS ANGELES BASIN,

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Continuous measurements of particle number (PN), particle mass (PM10) and gaseous pollutants (CO, NO, NOx and O3) were performed at five urban sites in the Los Angeles Basin to support the USC Children's Health Study (CHS) in 2002. The degree of correlation between hourly PN and concentrations of CO, NO and NO2 at each site over the entire year was generally low to moderate (r values in the range of 0.1 to 0.5) with a few notable exceptions. In general, associations between PN and O3 were either negative or insignificant. Similar analyses of seasonal data resulted in levels of correlation with large variation, ranging from 0.0 to 0.94 depending on site and season. Summertime data showed generally higher correlation between the 24-hr average PN concentrations and CO, NO and NO2 than corresponding hourly concentrations. Hourly correlations between PN and both CO and NO were strengthened during morning rush hour periods, indicating a common vehicular source. Comparing hourly particle number concentrations between sites also showed low to moderate spatial correlations with most correlation coefficients below 0.4. Given the low to moderate associations found in this study, gaseous co-pollutants should not be used as surrogates to assess human exposure to airborne particle number concentrations.

18B-1

ATMOSPHERIC MERCURY MEASUREMENTS AT THE ST. LOUIS MIDWEST SUPERSITE,

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Although the adverse effects of mercury (Hg) in the environment and on human health are predominately associated with aquatic environments, the atmosphere is a major route for the transport and transformation of Hg from sources to receptor sites. Increases in anthropogenic emissions of inorganic Hg have resulted in long-range global transport of Hg from sources to remote pristine areas. Hg emissions are expected to continue to increase due to global demands for energy, leading to increases in the number of fish and wildlife Hg consumption advisories in North America. Here we present ground level atmospheric Hg concentrations that were measured in plumes observed at the US EPA funded St. Louis Midwest Supersite, 3 km east of city centre St. Louis, MO. Measurements of elemental Hg (Hg0), reactive gaseous Hg (RGM), and particulate Hg (pHg) were obtained from December 2, 2003 to March 1, 2004 and concentrations vastly exceeded background concentrations of ~1.5 ng m-3, 50-200 pg m-3, and <100 pg m-3, respectively. Elemental Hg concentrations were as high as 560 ng m-3 during an 8-day period in mid February 2003 where Hg0 was elevated. Maximum reactive Hg (RHg; the sum of RGM and pHg concentrations) were observed in early February, with observed concentrations as high as 20000 pg m-3. The high time resolution measurements made at the St. Louis Supersite, including meteorological data, criteria gases, and aerosol chemical components provide an excellent mechanism to identify sources and determine the mercury speciation in the emissions from these sources. In addition, these measurements provide insight into the chemical and physical properties controlling the gas/particle partitioning of reactive mercury. The methods used in this analysis will be presented.

18B-2

SELENIUM IN FINE PARTICLES (PM2.5) OVER METROPOLITAN LISBON (PORTUGAL) -- CANONICAL LEVELS AND RELEVANT EPISODES,

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With the beginning of systematic measurements of air quality within the framework of a surveillance program for an urban-waste incinerator, it has been possible to get a picture of the selenium status in the atmosphere of greater Lisbon. Even though the Se levels are usually low -- which makes the appearance of high values easily noticed -- some relevant episodes of high selenium concentrations have been observed thus far, especially after November, 2001. Such an increase has occurred mainly in the PM2.5 fraction, which is an indication of its anthropogenic origin. This paper aims at i) providing a first assessment of that status in what concerns both background and episodic levels; and ii) discussing the latter in view of other elemental concentrations in airborne particulates, and also some rather unusual meteorological conditions that prevailed through the fall/winter of 2001. Particulate matter has been obtained with Gent-type collectors. Each collector is equipped with a stacked-filter unit (SFU), that carries two Nuclepore, 47-mm diameter polycarbonate filters. The air is sampled at a rate of 15-17 L/min, which enables the collection of coarse particles with 2.5 micron < EAD < 10.0 micron (EAD = equivalent aerodynamic diameter) in the first stage (coarse fraction), and finer particles with EAD < 2.5 micron in the second stage (fine fraction). Sampling was carried out twice a week (working days) for 24-hour periods. Filter loads were assessed gravimetrically, following standard procedures. Half of each filter was then put through instrumental neutron activation analysis (INAA), at the Portuguese Research Reactor. Determination of selenium is based on the measurement of the long-lived Se75 nuclide. Three urban-industrial locations along the NE corridor out of inner Lisbon, and about 5 km from each other, have been selected for this study. The sites are 4, 9 and 14 km from Lisbon city limits, respectively, and they roughly parallel the nearby Tagus river mouth, a major freeway (A1, also E80) and a busy highway (N10). A Solvay-process plant, an urban-waste incinerator, a glass works and an animal-food plant are the largest industrial facilities. Other than being heavily populated, the whole conurbation is dotted with smaller industries as well. A detailed analysis of the most recent (2001-2002) particulate-data time-series places the onset of high selenium levels on November 12, 2001, reaching annual average values in the order of 100 ng per cubic meter. Such an outbreak was found to last until February 21, 2002, in a continuous, consistent manner, and then to have faded down to the usual (background) levels within 0.5-1 ng per cubic meter that every station had been recording thus far. The whole elemental pool determined by INAA was also searched for other elements that could have been experiencing significant changes in concentration, concurrent with selenium's through the same interval. It became apparent that, relative magnitude notwithstanding, something had happened to mercury as well. The episodic, abnormal levels of selenium (and mercury) are discussed in terms of wind patterns through the sampling period and fugitive emissions from major plants.

18B-3

SUMMERTIME AMBIENT FORMALDEHYDE IN FIVE US METROPOLITAN AREAS: NASHVILLE, ATLANTA, HOUSTON, PHILADELPHIA AND TAMPA: WHAT HAVE WE LEARNED? PURNENDU DASGUPTA, Jianzhong Li, Genfa Zhang, William McClenny, Winston Luke, Jochen Stutz, Alan Fried

In this paper, we briefly review the atmospheric chemistry and previous intercomparison measurements for HCHO, with special reference to the diffusion scrubber-Hantzsch reaction based fluorescence instrument used in the present study. Then we discuss summertime HCHO levels in five major US cities measured over 1999-2002. A significant amount of formaldehyde ends up as organic acids and contributes to PM. Land-sea breeze circulations play a major role in observed concentrations for coastal cities. Very high HCHO peak concentrations were observed in Houston (>47 ppb), but the overall median concentration was 3.3 ppb relative to a median concentration of 7.8 ppb and a peak concentration >18 ppb measured in Atlanta. The peak and median concentrations (9.3 and 2.3 ppb) were the lowest for Tampa, where the land-sea breeze also played an important role. In several cities, replicate HCHO measurements were made by different instruments, based on altogether different principles and these were located kilometers from each other. Even under these conditions, there was remarkable qualitative and often quantitative agreement between the different instruments, if the wind direction carried the airmass more or less directly from one instrument to the other in a short period. Local chemistry dominates how HCHO is formed and dissipated. The high concentrations in Houston unequivocally resulted from sporadic emissions near the ship channel, the persistence of these plumes at multiple sites suggest that a 2-4 h lifetime estimate for HCHO in the sunlit troposphere may be too low. Local micrometeorology is another factor. HCHO patterns measured at a high rise site in downtown Nashville were very much in synchrony with other ground sites 8 km away until July 4 celebrations whence nighttime HCHO concentrations at the downtown site remained elevated for several days. The extensive data set represented in this paper not only underscore that such measurements can now be made easily, the agreement between independently calibrated disparate measurements indicate that such measurements can be done reliably and accurately for this very important atmospheric species.

18B-4

INDOOR/OUTDOOR RELATIONSHIP OF PARTICULATE POLYAROMATIC HYDROCARBONS (PAHS) IN CENTRAL PART OF INDIA, ALFRED J. LAWRENCE and Ajay Taneja, School of Chemical Sciences, Department of Chemistry, St. John's College, AGRA

Indoor/Outdoor Relationship of Particulate Polycyclic aromatic Hydrocarbons (PAHs) in Central Part of India. Alfred J. Lawrence and Ajay Taneja School of Chemical Sciences, Department of Chemistry, St. John’s College, Agra - 282002, India. alfred_lawrence@yahoo.com Abstract: Ambient air quality especially aerosol pollution is of serious concern in many cities of the world. In India this problem has attracted increasing attention of policy makers, research institutes, Universities and donor agencies. Many recent policy interventions have been undertaken to lesson ambient air pollution but very little is known about indoor air quality (IAQ). Recent studies have been concerned with sources of atmospheric aerosols because they can be related with global climate changes and serious health hazards such as increasing risk of respiratory and cancer diseases. The impacts on global climate and the toxic effects of aerosols are mainly attributed to particulate poly-aromatic hydrocarbons (PAHs), which are considered possible or probable human carcinogens. In central India few studies have been focused on ambient TSPM, but no studies has been reported about indoor respiratory particles. PAHs in particulates were monitored for a span of one year (2002-2003) in Central part of India. Samples were collected in summer, monsoon and winter and were analyzed to determine the concentrations of 16 PAHs listed as priority pollutants by the U.S. EPA. The mean concentration of total 16 PAHs (□ PAHs) at three different microenvironment i.e. rural, urban and roadside residences were determined and was found maximum at roadside sites viz. 27.3, 14.8, 48.4 ng/m3 for indoors and 29.7, 18.6 and 36.9 ng/m3 for outdoors in their respective seasons i.e. summer, monsoon and winter. Among these 16 PAHs, BaP is believed to be most carcinogenic and was found to be highest in roadside residences viz. mean concentration of indoor BaP in summer, monsoon and winter 2.3, 3.4 and 5.1 ng/m3 respectively. A statistical correlation analysis of indoor concentration with outdoor concentration was also carried, which revealed that indoor environment is positively influenced by outdoors. An activity schedule of inside and outside these homes were also prepared to see its influence and concentration of pollutants. This study was done in order to provide useful information to help understand air pollution and atmospheric chemistry processes in Agra, India (famous for TAJMAHAL) and there by contribute towards and improve strategy for indoor in Asian countries. Keywords: Indoor Air Quality (IAQ), Statistical Correlation, Benzo (a) pyrene (BaP), carcinogenic. Corresponding author: alfred_lawrence@yahoo.com

18B-5

ASSESSMENT OF FREE RADICAL PRODUCTION BY RESIDUAL OIL FLY ASH AND NICKEL SUBSULFIDE USING DNA DAMAGE ASSAY, NICHOLAS RALSTON, John Gallagher, Kevin Galbreath, Energy and Environmental Research Center, University of North Dakota, Grand Forks, ND, Edward Zillioux, Florida Power and Light, Juno Beach, FL

Pathological consequences associated with pulmonary exposure to particulate materials are subjects of increasing public and regulatory concern. Respiratory and cardiovascular effects of exposure to airborne particulates are associated with formation o reactive oxygen species (ROS) occurring at the particle interface or from water-soluble transition metal ions arising from the particulates. Nickel and other ROS-forming metal ions are present in varying distributions in combustion derived particulates such as residual oil fly ash (ROFA). However, the molecular forms of the chemical species present appear to be more important than the mass quantities of the elements themselves. Distinctions in solubility and stability of various forms of nickel influence cellular uptake rates as well as kinetics of ROS formation. As a result, more severe consequences are associated with pulmonary exposure to chemical species such as nickel subsulfide than with nickel oxide. When evaluating potential consequences of exposure to airborne particulates such as ROFA, it is important to consider quantitative differences in the abundance of these forms as well as qualitative distinctions i the nature and chemical mechanisms of the ROS-dependent damage they cause. Using supercoiled circular deoxyribonucleic acid (DNA) from bacteriophage PhiX174 DNA as our test substrate, we employed a highly sensitive assay to evaluate ROS-dependent damage from insoluble forms of nickel in comparison to similarly treated ROFA. Samples of ROFA, nickel subsulfide mixture (Ni3S2 and Ni7S6), “green” nickel oxide (NiO), and the oxide spinel compounds, (NiFe2O4, [Ni, Mg][Al, Fe]2O4, and MgAl2O4 were extracted using 1M NaOAc-0.5M HOAc at pH 5, 25-28 ˚C followed by exhaustive rinsing with deionized H2O. To assess the inherent ROS formation rates of these species, DNA substrate suspensions in aqueous solutions were exposed to identical mass quantities of these residues. Due to its compact hydrodynamic diameter, undamaged DNA (DNA form 1) moves rapidly through a 0.6% agarose gel during electrophoresis. The relative quantities of DNA migrating as either form were visualized using ethidium bromide following separation. Free radical damage creates “nicks” in the DNA molecule, resulting in relaxed, partially unwound forms (DNA form 2) that migrate through the gel at a slower rate than DNA form 1. ROS-dependent damage changes DNA form 1 into DNA form 2 in a time and dose dependent manner. Using this assay, we found ROS formation by ROFA was slightly greater than ROS formation by NiO or the spinel compounds, but ROFA caused far less damage than nickel subsulfide. DNA damage induced by nickel subsulfide was also qualitatively different than that induced by other nickel species. Nickel subsulfide induced a rapid and complete elimination of DNA form 1 and produced a novel form of damaged DNA (DNA form 3) that migrated between DNA form 1 and form 2. The DNA damage assay provides a sensitive and rapid assessment of ROS generating capacity inherent in the materials studied. Potential health hazards associated with exposure to respirable particulate materials may be qualitatively and quantitatively assessed using this technique.

18C-1

QUANTIFICATION OF PRIMARY AND PARTIALLY OXIDIZED ORGANIC PM EMISSION AND THE FORMATION OF SECONDARY ORGANIC AEROSOL QUEENS, NY IN SUMMER AND WINTER, KENNETH L. DEMERJIAN, J. Schwab, G. Lala, O. Hogrefe, S. Weimer, M. Tang, Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY; D. Felton, G. Boynton, Division of Air Resources, NYS Department of Environmental Conservation, Albany, NY; F. Drewnick, Cloud Physics and Chemistry Department, Max-Planck-Institute for Chemistry, Mainz, Germany; W. Brune, X. Ren, R. Lesher, Pennsylvania State University, College Station, PA; D. Worsnop, Aerodyne Research, Inc., Billerica, MA; J. Jimenez, Z.Qi, University of Colorado, Boulder, CO

Applying a combination of PM organic mass fragments measured from an Aerosol Mass Spectrometer (AMS) and empirical estimates of secondary organic particulate matter production using simultaneous measurements of OH and speciated VOCs, we have estimated the contribution of PM organic and partially oxidized organic (POO) PM fractions from primary emission and that portion of POO-PM formed from secondary photochemical transformation processes. The results from the summer 2001 field intensive in Queens, NY suggest that the mean contribution of photochemically produced secondary partially oxidized organic (SPOO) PM, accounts for ~ 42% of the total PM organic contribution or ~ 30% of the total PM mean mass concentration for the period. Similar data collected during the winter 2004 field intensive in Queens, NY indicate that although photochemistry is significantly attenuated under wintertime conditions, there is still some photochemical contribution, ~ 10% and ~ 4% to the PM organic and PM total mass concentration respectively. Comparison of the fractional contribution of POO from primary emission to total PM organic in summer and winter measurements indicate similar contributions, ~ 20% and ~ 25%, respectively. The small increase in winter POO from primary emission may be real and reflect the increased source contribution from residual oil use for residential and commercial heating.

18C-2

SECONDARY ORGANIC AEROSOLS FROM BIOGENIC HYDROCARBON OXIDATION,

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Biogenic volatile organic compounds (BVOCs) such as monoterpenes (MT) and sesquiterpenes (SQT) are known precursors for secondary organic aerosols. However, the contribution of BVOCs to aerosol production on the regional scale is not well known. The goal of our research is to incorporate new data on SQT and MT emissions and responses to environmental and physiological factors into a regional-scale chemistry and transport model. This work will yield estimates of the contributions of BVOC to aerosol production in the eastern United States under current conditions and hypothetical land-use management scenarios. New data on SQT emissions and their light and temperature dependencies are acquired through greenhouse and field studies for critical vegetation species. MT and SQT emission rates have been quantified for loblolly pine at Duke Forest in Chapel Hill, NC, using FEP Teflon film branch enclosures. Air entering the enclosures was cooled with an ice bath and scrubbed of ozone with activated carbon. Outflows were sampled with solid adsorbent tubes, which were then thermally desorbed to a GC/MS system. Late summer and fall measurements indicate that SQT emissions (primarily beta-caryophylene and humulene) contributed significantly to the overall BVOC flux. Temperature-controlled leaf enclosure measurements for several species indicate that SQT and MT emissions exhibit similar temperature dependencies. SQT screening of additional vegetation species is being conducted in the NCAR greenhouse this fall and winter, to be followed by field measurements next spring and summer. The new emissions data, along with data from a comprehensive literature review, are being incorporated into an advanced biogenics emissions model, MEGAN (Model of Emissions of Gases and Aerosols from Nature). In turn, MEGAN provides input to the Community Multiscale Air Quality Model (CMAQ), which has been modified to include gas-phase chemistry and secondary aerosol formation from multiple MT and SQT species. CMAQ results for July 2001 and January 2002 are evaluated through comparison with aerosol data from the IMPROVE, SEARCH and Supersite networks.

18C-3

EFFECT OF TEMPERATURE AND NOX ON SOA YIELDS FROM TERPENES,

NEIL DONAHUE, Spyros Pandis, Kara Huff-Hartz, Albert Presto, Carnegie Mellon University, Pittsburgh, PA

Secondary Organic Aerosols (SOA) are formed in the atmosphere after oxidation of a volatile precursor. SOA comprise approximately 1/3 of the organic aerosol mass, and organic aerosol in turn is often the single most important fraction of total aerosol mass. SOA are also often semi volatile, with substantial mass fractions in both the condensed and vapor phases. The most important source of SOA appears to be ozonolysis of terpenes, including monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$). Our knowledge of SOA mass yields from terpene ozonolysis is limited in two major ways. First, there are few data constraining the temperature dependence of SOA yields, and second, ozonolysis yields are typically only well constrained under low NOx conditions. We shall address both of these limitations here. First, to constrain the temperature dependence of SOA production we must separate the effect of temperature on the chemistry itself from the effect of temperature on the vapor pressure. Our solution is to carry out ozonolysis in a temperature-controlled smog chamber at a fixed temperature ranging from 15 to 40 C and then to vary the chamber temperature through its full range after the chemistry has run to completion. Bulk SOA mass yields are determined through SMPS measurement, while composition is determined via periodic filter sampling followed by solvent extraction derivatization GC/MS. In this way we are able to observe partitioning (vapor pressure) effects in the ozonolysis of d-limonene, culminating in large yields of SOA near 20 C, followed by a shift in chemistry at lower temperature causing lower SOA yields. Second, to constrain the VOC/NOx dependence of SOA production, we also carry out experiments in the presence of NOx, under near UV illumination to maintain a stable NO/NO2 ratio. Basic functional group levels (e.g. carbonyls vs nitrates) are monitored via FTIR analysis of teflon filter samples. Consistent with expectations, SOA yields decrease with increasing NOx, as progressively more nitrates are observed on collected aerosols. Our results suggest that aerosol yields under typical VOC/NOx conditions may be between a factor of 2 and 4 below yields in NOx-free conditions. Not only does this have significant implications for total SOA production from biogenic precursors, but it suggests that NOx controls in regions with high terpene concentrations could lead to increased organic aerosol mass.

18C-4

SECONDARY AEROSOL FORMATION FROM GAS AND PARTICLE PHASE REACTIONS OF AROMATIC HYDROCARBONS,

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Abstract Secondary Aerosol Formation from Gas and Particle Phase Reactions of Aromatic Hydrocarbons, Di Hu and Richard M. Kamens (PI), Univ. of North Carolina-Chapel Hill The overall goal is integrate newly discovered heterogeneous processes with gas phase chemistry, as a unified, multi-phase, chemical reaction mechanism. We are developing and integrating gas and particle phase chemistry to predict secondary aerosol formation from aromatic compounds such as, toluene, xylenes and tri-methyl-benzenes. To develop and test chemical mechanisms that describe SOA formation from aromatics, it is necessary to include in mechanisms the gas phase reactions that generate semi-volatile oxygenated products, which partition between the gas and particle phases and then further react in the particle phase. These products are also very reactive, and produce yet another generation of oxygenated products. Experimental and exploratory model results for toluene-NOx experiments will be shown. The kinetics mechanism provides an acceptable description of the time dependence of NO, NO2 and O3. The model predicts a reasonable toluene decay for the first 2 hours, but is about 30% too low at the end of experiment. For total particle mass, the model simulation is higher than measured after particle mass reaches its maximum. The underestimation of NO2 after its peak suggests that more organic nitrate compounds need to be included in the mechanism. The under-prediction of toluene reveals that there may be an OH radical source missing from the mechanism. There are many uncertainties in particle phase chemistry, such as particle phase reaction rates and amount of polymer formed on the particle phase. A series of chamber experiment are under way to investigate the degradation of the key oxygenated products, such as their particle formation potential, their quantum yields and photo-degradation products.

18C-5

FIELD AND LABORATORY EXPERIMENTS EXAMINING THE STABILITY OF ORGANIC MOLECULAR MARKERS USED FOR SOURCE APPORTIONMENT,

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Individual organic compounds such as levoglucosan and hopanes are often used as tracers for different sources of primary organic aerosol. An important question is the stability of these reduced organic compounds, particularly in the eastern US and other areas where long-range transport is an important contributor to ambient aerosol concentrations. This paper presents evidence of photochemical aging of molecular markers using both in situ observations and laboratory experiments. First, a large in situ dataset of speciated condensed phase compounds is examined for evidence of aging of important tracers including cholesterol and hopanes. The challenge is to separate mixing and aging effects; we apply a dual-ratio chemical coordinate analysis technique to the condensed-phase organics data. This approach has been used extensively in the past constrain photochemical age using gas-phase hydrocarbon data. The ambient data are consistent with significant aging, but a `smoking gun' is difficult to obtain due to the convolved mixing and aging effects, coupled with incomplete or inadequate source profile data. Second, smog chamber experiments have been performed to measure the oxidation of different condensed phase species in complex aerosol mixtures. The speciated smog chamber data are interpreted using a variant of the gas-phase relative kinetics technique. This approach allows us to determine relative oxidation rates for a large number of condensed-phase organic compounds in both model systems and real emissions. Experiments performed with model meat smoke mixtures of varying complexity indicate oxidation of oleic acid cholesterol. Cholesterol oxidation is slow but significant. The apparent rate constant for oleic acid oxidation varies, depending on aerosol composition, ranging from somewhat faster to orders of magnitude faster than cholesterol oxidation. The measured kinetics are fast enough to cause significant decay of cholesterol, an important molecular marker for meat cooking, on time scales commensurate with regional transport. We shall draw parallels between ongoing laboratory studies of model and real systems and the corresponding in situ measurements.

19A-1

USING IN-NETWORK PRECISION DATA AS A BASIS FOR CROSS-NETWORK COMPARISONS,

WARREN H. WHITE, Nicole P. Hyslop, Charles E. McDade, Crocker Nuclear Laboratory, University of California, Davis, CA

Several networks monitor fine particle concentrations, but different networks often employ somewhat different measurement protocols. Where the regions covered by separate networks overlap, improved coverage and resolution can be obtained by merging their data. Such integration of different networks places high demands on the comparability of their data. Some networks have cooperated to conduct side-by-side measurements at selected sites with the expressed purpose of assessing data comparability between the networks. Each network typically applies its own protocols, but measurements are conducted during the same time periods to provide samples of the same airmass. In order to interpret the differences between networks, it is first necessary to understand the precision to be expected within each network. Understanding the in-network uncertainty establishes a baseline for the best cross-network agreement that might be expected. There is little to be gained from detailed analysis of cross-network disagreements that are wholly explained by the imprecision of one or both measurements. IMPROVE (Interagency Monitoring of Protected Visual Environments) and STN (Speciation Trends Network) have been conducting side-by-side measurements at six sites since 2001, with measurements at several additional sites being added during 2003 and 2004. Data from the first two full years from the original six sites have been compared between the two networks, and the findings are the subject of a companion paper at this conference (Solomon, et al., 2005). Both IMPROVE and STN determine measurement precision within their own networks. Precision information is obtained from two principal sources: 1) from collocated measurements within each network, in which identical samplers have been operated concurrently, and 2) from propagation of individual component uncertainties, such as those in flowrate and laboratory calibration. Collocated measurements and propagated estimates each provide different and complementary insights into the overall expected precision, so both are used to reach an aggregate expectation of measurement precision for each reported species. This paper describes a statistical approach developed to incorporate the in-network precision data from both networks in order to evaluate their cross-network differences. Data from each 24-hour sampling period are compared between the networks, and the predicted and observed differences are tabulated for each period. Then, the aggregate root mean square (RMS) predicted and observed differences are determined for the entire two-year period, as well as for individual seasons. This analysis is performed for each reported species. For each species, the results indicate whether or not cross-network agreement lies within our expectations. Where expectations are not being met, further work is warranted to determine the physical reasons for the differences. Reference: Paul A. Solomon, Tracy Klamser-Williams, Warren H. White, Nicole P. Hyslop, and Charles E. McDade, “Comparison of Aerosol Data from the STN and IMPROVE Networks” (2005).

19A-2

RESULTS OF FIELD AND TRIP BLANK FILTERS IN THE PM2.5 SPECIATION TRENDS NETWORK,

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One component of the U.S Environmental Protection Agency’s (EPA) National PM2.5 Monitoring Network is the Speciation Trends Network (STN). The STN consists of 230 samplers deployed across the United States. The samplers collect particulate matter with aerodynamic diameters less than 2.5 microns on filter media with subsequent analysis for chemical composition. In addition to filters used for acquiring 24-hour ambient samples, blank filters are sent to the field sites to assess background levels of analytes. Two different types of blank filters are deployed: Field Blanks and Trip Blanks. Field Blanks are taken to the sampling location and placed into the sampler for a few minutes without the sampler being started. Results of the Field Blank filters will indicate background levels due to shipping, handling, transporting to the site and placement in the sampler itself. Trip Blank filters are sent to the site along with filters that will be used for sampling but the Trip Blank filters are neither opened nor taken to the sampling site. The Trip Blank filters are returned to the analytical laboratory along with the sampled filters. Results of the Trip Blank filters will indicate background levels due to shipping and handling only. This paper will present results of Field and Trip Blank filters during the timeframe of September 2003 through August 2004. These filters have been analyzed for gravimetric mass, 48 elements, anions (sulfate, nitrate), cations (ammonium, sodium, and potassium), organic and elemental carbon. Background levels for the major analytes found on Field and Trip Blank filters will be summarized. The data will also compare background levels of the same analytes for the five different types of samplers deployed in the STN.

19A-3

SPECIATION TRENDS NETWORK: EVALUATION OF WHOLE-SYSTEM UNCERTAINTIES USING COLLOCATED DATA,

JAMES B. FLANAGAN, Edward E. Rickman, Max R. Peterson, Eva D. Hardison, Lisa C. Greene, Andrea C. McWilliams, William F. Gutknecht, and R.K.M. Jayanty, RTI International, Research Triangle Park, NC

Particulate matter (PM) with particle aerodynamic diameters of 2.5 µm and smaller (PM2.5) in ambient air has been associated with respiratory and other health-related problems in addition to contributing to atmospheric visibility impairment and regional haze. Negative health effects have been statistically correlated to total mass concentration (µg/m3) of PM2.5 in ambient air, but whether the correlation is actually to total mass concentration or to concentrations of specific chemical species comprising PM2.5 is a key question. The deployment of a new PM2.5 monitoring networks by EPA is a critical component in the national implementation of the PM2.5 National Ambient Air Quality Standards (NAAQS). The compliance (mass) monitoring portion of the network was established first. Data from the compliance network is used to determine attainment with the NAAQS. EPA has also established the Speciation Trends Network (STN) to provide complementary data on the chemical composition of PM2.5 for the purposes of identifying sources, developing implementation plans, and supporting ongoing health effects research. This program has grown significantly over the last four years and presently RTI supports over 225 PM2.5 monitoring sites throughout the United States and Puerto Rico. Reliable estimates of uncertainty are required for many applications of the speciation data such as source attribution modeling. Estimating these uncertainties is a complex process because there are many different components that affect total uncertainty, including: • Differences between laboratory instruments • Repeatability of laboratory measurements on the same instrument • Differences between sampler models • Differences between samplers of the same model • Sampler flow/volume uncertainties • Sample handling (e.g., filter contamination and damage) The STN database, which now includes over four years of data, is a rich resource for data relevant to estimating whole system uncertainties. This paper will use data from six collocated sites in the STN program to assess total system uncertainties and compare these with analytical uncertainties determined in the laboratories and with previous estimates of sampling uncertainty. Components of uncertainty will be evaluated for the following analytical methods used by the STN program: gravimetry, Ion Chromatography, X-ray fluorescence, and thermal-optical analysis for organic carbon and elemental carbon.

19B-1

DIFFERENT PRE-EXISTING AEROSOL EFFECTS ON SECONDARY ORGANIC AEROSOL YIELDS IN HETEROGENEOUS ACID CATALYZED REACTIONS,

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The secondary organic aerosol (SOA) production from the reaction of α-pinene with ozone was studied in the presence of different seed aerosols. The SOA formation in the ambient atmospheric conditions is often progressed in the presence of pre-existing aerosols. Thus, the additional heterogeneous reaction in the particle phase is expected between the newly created SOA products and pre-existing aerosol components. SOA formation was studied in a 2 m3 Teflon film indoor chamber under darkness. To study acid catalytic effects on SOA growth, humidity and the composition of seed inorganic aerosols were controlled for the heterogeneous reactions of secondary organic products. The particle size distribution and concentration were measured by a scanning mobility particle sizer (TSI-SMPS) and the results were used to calculate the aerosol yields. The SOA yields from a reactive organic compound increased when SOA production took place in an environment associated with acid catalyzed heterogeneous reactions. These reactions result in high molecular weight products having low volatility and are prone to remain in the particle phase. Sulfuric acid was used in this study because sulfuric acid is ubiquitous atmospheric inorganic acid that results from fossil fuel burning associated with photochemical cycles of atmospheric oxidants. In order to demonstrate the additional effects of pre-existing organic compounds in the particle phase, SOA was created in the pre-existing seed aerosol comprising of organic and inorganic compounds. The SOA production associated with heterogeneous reactions was influenced by pre-existing organic compounds in the particle phase. This additional reaction was also accelerated by the presence of an inorganic acid catalyst such as sulfuric acid.

19B-2

INFLUENCE OF PARTICLE ACIDITY AND OH SCAVENGERS TO SOA YIELDS AND PRODUCTS: RESULTS FROM AEROSOL CHAMBER STUDY OF THE ALPHA-PINENE OZONOLYSIS,

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Secondary Organic Aerosol (SOA) is believed to contribute considerably to the atmospheric aerosols burden yet our understanding of its formation mechanism and indirect climate effects is still limited. In order to reduce the uncertainties associated with the role of SOA in the climate system, a number of studies have been carried out to determine the composition of the SOA and the yields of particle and gas phase products, especially from monoterpenes ozonolysis. Although primary oxidation products found from monoterpene ozonolysis have sufficiently low vapor pressure to form SOA, condensation or partitioning of primary oxidation products alone cannot explain the measured organic aerosol concentrations in the atmosphere. The possibility of transformations of gaseous or semi-volatile organic compounds in atmospheric particles or at their surface has been suggested recently [e.g. Jang and Kamens, 2001]. More recently, the evidences of second generation products from the acid-catalyzed reactions of primary oxidation compounds in the particle phase are found [Iinuma et al., 2004; Tolocka et al., 2004]. These evidences suggest that the formation of higher molecular weight compounds through heterogeneous reaction in the particle phase may play a significant role in the formation and growth of atmospheric particles. In order to improve our understanding of the effects of particle acidity to SOA formation gas phase alpha-pinene ozonolysis was carried out in the presence of neutral or acidic seed particles in a 9 m3 Teflon chamber at mixing ratios of 100 ppbv for alpha-pinene and about 70 ppbv for ozone. The resulting particles were sampled by a denuder/PTFE filter for the analysis of individual chemical species using capillary electrophoresis with electrospray ionisation ion trap mass spectrometer (CE-ESI-ITMS). Here we present the results from a series of experiments for alpha-pinene ozonolysis with both acidic and neutral seed particles and the influence of OH scavengers (2-butanol and cyclohexane) to products and SOA yields from alpha-pinene ozonolysis. Iinuma, Y., Böge, O., Gnauk, T. and Herrmann, H., Atmos. Environ. 38, 761-773 (2004). Jang, M. and Kamens, R. M., Environ. Sci. Technol. 35, 4758-4766 (2001). Tolocka, M., Jang, M., Ginter, J., Cox, F., Kamens, R., Johnston, M., Environ. Sci. Technol. 38, 1428-1434 (2004).

19B-3

ACIDITY AND ORGANIC AEROSOL CONCENTRATIONS: AN ANALYSIS OF SEMI-CONTINUOUS OC AND ACIDITY FIELD MEASUREMENTS,

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Jang et al. (2002) suggested that yields of secondary organic aerosols (SOA) in the presence of acidic seed aerosols can be much greater than in the presence of neutral seed aerosols, and implicated inorganic acidity from to SO2 and NOx as sources of acidity that can increase yields. Kalberer et al. (2004) however, found that organic acidity generated endogenously from photo-oxidation reactions of organic compounds is sufficient to allow these acid-catalyzed reactions that lead to increased SOA yields to proceed. The policy-relevant question is whether inorganic acidity is responsible for increased SOA yields in the atmosphere; if such were the case then reductions in SO2 could potentially result in SOA reductions. Previously, correlations of daily average organic carbon (OC) and sulfate have been suggested as possible evidence for acid-catalyzed SOA formation occurring in the atmosphere (Chu et al., 2004); we expand this analysis by examining relationships between high time-resolution measurements of OC and elemental carbon (OC/EC ratios), free acidity (H+) concentrations calculated by a thermodynamic model, GFEMN (Ansari and Pandis, 2004), and wind directions measured at the Pittsburgh Air Quality Study from July 2001 to July 2002. In addition, we examine the Pittsburgh region, where SOA accounts for around 35% of the organic aerosol mass on average (2004), to estimate potential reductions in organic aerosol that can be achieved through reductions in sulfate levels and acidity. References: 1. Jang, M., Czoschke, N.M., Lee, S., Kamens, R.M., Heterogeneous Atmospheric Aerosol Production by Acid-Catalyzed Particle-Phase Reactions, Science, 298, 814-817, 2002. 2. Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U., Identification of Polymers as Major Components of Atmospheric Organic Aerosols, Science, 303, 1659-1662, 2004. 3. Chu, S., PM2.5 episodes as observed in the speciation trends network, Atmos. Env., 38, 5237-5246, 2004. 4. Ansari, A.S. and Pandis, S.N., Prediction of multicomponent inorganic atmospheric aerosol behavior, Atmos. Environ., 33, 745-757, 1999. 5. Cabada, J.C., Pandis, S.N., Subramanian, R., Robinson, A.L., Polidori, A., Turpin, B., Estimating the secondary organic aerosol contribution to PM2.5 using the EC tracer method, Aerosol Sci. Technol., 38, 140-155 Suppl. 1, 2004.

19C-1

HYGROSCOPICITY AND CLOUD CONDENSATION NUCLEUS ACTIVITY OF SECONDARY ORGANIC AEROSOLS,

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Measurements are reported on the hygroscopic growth and CCN activity of secondary organic aerosols generated in chamber studies. Hygroscopic growth is measured by a Hygroscopic Tandem Mobility Analyzer (HTDMA) and CCN activity by a flow CCN instrument. Observed properties are correlated with the nature of the organic aerosol.

19C-2

AEROSOL WATER CONTENT DURING PITTSBURGH AIR QUALITY STUDY: OBSERVATIONS AND MODEL COMPARISON,

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The ability of atmospheric particles to absorb water affects their lifetime, their light scattering properties, and their interactions with semi-volatile compounds. Due to the hysteresis effect of the hygroscopic growth, the physical state (dry or wet) of particles in the troposphere is uncertain, leading to uncertainties in their optical and chemical properties. Aerosol size distributions, dried and at ambient RH conditions, were measured during July - August 2001 and January – June 2002 within the Pittsburgh Air Quality Study (PAQS). The measurements were made using the Dry and Ambient Aerosol Size Spectrometer (DAASS). Most of the aerosol during the study was transported to the region from other areas and its composition and concentration were characteristic of the regional particulate matter in the Northeastern US. The measurements revealed that during summer the ambient aerosol in Pittsburgh always contained water even when the relative humidity was as low as 30%. During the winter, however, aerosol was dry below 60% RH. The spring months showed a transitional behavior. This behavior is consistent with the acidity of aerosol particles. During the summer, particles in the area are acidic retaining water down to low RH. During the winter the aerosol in Pittsburgh is neutral and is expected to crystallize at higher RH. The wet and dry aerosol distributions were used to derive hygroscopic growth factors as a function of particle size. Hygroscopic growth factors were found to vary with size. Smaller particles during rush-hours had smaller growth factors than accumulation mode particles, probably due to a larger contribution to smaller aerosol sizes of water insoluble material from traffic emissions. The observations of aerosol water content during July 2001 were compared with the thermodynamic equilibrium models GFEMN and AIM. The models neglected contribution of organic content to water absorption and under-predicted water content by about 35%. However, no clear correlation between organic mass and the excess water was observed. On average, the contribution of the organics to water absorption appeared to be higher during the afternoon hours than during the night, probably due to the photochemical production of water-soluble compounds.

19C-3

GROWTH OF ATMOSPHERIC AEROSOL PARTICLES IN WATER AND ETHANOL VAPOURS: EFFECT OF SO2 OXIDATION, KAARLE HÄMERI, T. Petäjä and M. Kulmala, Division of Atmospheric Sciences, Department of Physical Sciences, University of Helsinki, Finland; V.-M. Kerminen, Air Quality Research, Finnish Meteorological Institute, Finland; P. Vaattovaara, J. Joutsensaari, A. Laaksonen, Department of Applied Physics, University of Kuopio, Finland; W. Junkermann, Institute for Meteorology and Climate Research, Forschungszentrum Karlsruhe, Germany

Hygroscopic properties of atmospheric aerosol particles are one of the key factors in defining their optical properties and consequently their impacts on climate. Atmospheric aerosols are both internal and external mixtures of several chemical compounds and the mixing state is expected to change during the life tiem of the particles. Condensation of sulphuric acid onto less hygroscopic particles is one of the processes that is expected to increase the aerosol particle hygroscopicity and hence their cloud condensation nuclei formation potential. In this study, differences in the hygroscopic and ethanol uptake properties of ultrafine aerosol particles in the Arctic air masses with a different exposure to anthropogenic sulphur pollution were examined. The main discovery was that Aitken mode particles having been exposed to polluted air were more hygroscopic and less soluble to ethanol than after transport in clean air. This aging process was attributed to sulphur dioxide oxidation and subsequent condensation during the transport of these particle to the measurement site. The hygroscopicity of nucleation mode aerosol particles, on the other hand, was approximately the same in all the cases, being indicative of a relatively similar chemical composition despite the differences in air mass transport routes. These particles had also been produced closer to the observation site typically 3-8 hours prior to sampling. Apparently, these particles did not have an opportunity to accumulate sulphuric compounds on their way to the site, but instead their chemical composition (hygroscopicity and ethanol solubility) resembled that of particles produced in the local or semi-regional ambient conditions.

20A-1

COMPARISON OF AEROSOL DATA FROM THE STN AND IMPROVE NETWORKS, CHARLES E. McDADE, Warren H. White, and Nicole P. Hyslop, Crocker Nuclear Laboratory, University of California, Davis, CA; Paul A. Solomon (ORD), Tracy Klamser-Williams (ORIA), U.S. EPA, Las Vegas, NV; Dennis Crumpler (OAQPS), Peter Egeghy (ORD), US EPA, Research Triangle Park, NC;

Two national chemical speciation-monitoring networks operate currently within the United States. The Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring network operates primarily in rural areas collecting aerosol and optical data to better understand the causes of regional haze in Class I areas. IMPROVE began operation in 1988. The Speciation Trends Network (STN) operates in urban locations collecting aerosol data to better understand the causes of PM2.5 levels that exceed the National Ambient Air Quality Standards for Particulate Matter (PM) established in 1997. STN began operation in late 2000. EPA desires to integrate data from both networks to allow for a regional approach to reducing PM in urban areas since concentrations of PM in urban areas are strongly influenced by regional levels. While both networks are based on 24-hour filter sampling, there are differences in the sampling and chemical analysis methods employed. These differences range from the inlet of the samplers to how data are processed before final concentrations are reported. EPA, in conjunction with UC Davis and others, has conducted collocated sampling since October 2001 at three sets of paired urban-rural sites (Washington, DC; Phoenix, AZ; and Seattle, WA). Collocated STN and IMPROVE samplers were operated at all sites and analyzed for major components (sulfate, nitrate, organic carbon, and elemental carbon) and trace elements (e.g., Fe, Ca, Si). Each network followed its own specific protocols. Comparison results from the first year of sampling (October 2001-September 2002) have been reported previously. This paper expands those analyses by incorporating the second year (October 2002-September 2003). Furthermore, IMPROVE initiated its own in-network collocated sampling program during 2003 to assess the precision of IMPROVE data. Those precision data are utilized to provide a baseline for comparing aerosol data from the two different networks. The approach for doing so is described in a companion paper at this conference (White, et al., 2005). Reference: Warren H. White, Nicole P. Hyslop, and Charles E. McDade, "Using In-Network Precision Data as a Basis for Cross-Network Comparisons" (2005). Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

20A-2

IMPROVE XRF ANALYSIS OF STN FILTERS USED IN STN'S ROUND ROBIN EPA ACCEPTANCE TESTS,

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The IMPROVE committee contracts the University of California at Davis (UCD) to not only maintain and support the IMPROVE PM2.5 speciation network with air monitors and sample collection, but is also to perform elemental analysis of the PM2.5 aerosols. The EPA established another PM2.5 speciation network called the Speciation Trends Network (STN). The EPA contracts Research Triangle Institute (RTI) to provide the air monitoring and sample support. In addition, RTI and subcontractors Cooper Environmental Services and Chester Labnet have provided elemental analysis for the STN. Starting in 2001, the IMPROVE and STN networks have operated 6 collocated sites. Initial comparisons of these collocated sites have shown some differences with respect to species reported by the elemental analysis such as iron, arsenic, calcium and lead. These differences could be attributed to a number of possible reasons. The STN program has used up to five different XRF instruments that have been approved by the EPA. These instruments are from different manufacturers and employ different analysis software. As part of RTI's data quality control, cross comparisons of the STN instruments are done by selecting several "real-world" filters from the STN for use as part of a "round robin" set of analyses. These filters are analyzed by each of the instruments and results compared. Currently, UCD analyzes the aerosol of the IMPROVE 25 mm Teflon filters with a two anode XRF system to provide 24 elements. Because the XRF analysis systems were designed and built at UCD, modifications must be made to the XRF system to accommodate other size filters, including 47mm sized Teflon filers that are used in the STN program. To determine if there were any consistent biases between the XRF analysis used by UCD or STN, UCD analyzed some of the archived STN filters used in past "round robin" inter-laboratory comparisons. The comparison between UCD's XRF analysis and RTI's original round robin analysis data will be presented. Good agreement between the STN and IMPROVE results for certain key elements such as iron, calcium, and sulfur indicates that the filter area and other calibration factors are consistent between programs.

20A-3

SPATIAL REPRESENTATIVENESS OF THE FRESNO SUPERSITE PM AND GASEOUS CO-POLLUTANT MEASUREMENTS,

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An evaluation of neighborhood-scale and urban-scale air pollutant spatial variations was conducted in Fresno and Clovis, California to determine the spatial representativeness of the Fresno Supersite measurements. Measurements of particulate matter, its chemical components, and gaseous co-pollutants were obtained from two mobile vans equipped with continuous and integrated air monitoring equipment similar to those at the Supersite. The mobile vans collected air quality and meteorological data at seven locations within 10 km of the supersite over a one year period. Additional measurements were obtained at 73 residences [Fresno Asthmatic Children's Environment Study (FACES) participants] during the year to quantify PM2.5 and PM10 mass; PM2.5 sulfate, nitrate, organic carbon, and elemental carbon; PM10 trace metals and polycyclic aromatic hydrocarbons; light scattering; and NO2. Four or five residences were sampled concurrently for two week periods, which, in combination with the vans and Supersite, provided up to eight locations on residence measurement days. Kriging was used to spatially map concentrations across the community. Persistent spatial gradients across the community were found. Differences in pollution spatial patterns are primarily due to meteorological conditions. Factor of two variations in daily concentrations with the urban area are common in the Fresno and Clovis area for primary pollutants. The spatial representativeness of the Supersite measurements is good for regional pollutants like sulfate and nitrate, but the Supersite is less representative for pollutants with primary emissions in the urban area.

20A-4

METEOROLOGICAL ASPECTS OF PM2.5 EPISODES USING A MET TOWER AND LIDAR AT THE BALTIMORE SUPERSITE AT PONCA ST.,

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Highly time-resolved measurements of various meteorological variables like wind velocity, wind direction, air temperature, absolute humidity were obtained from February 14th through the end of November, 2002 at the Baltimore Supersite at Ponca St. using commercial and prototype semi-continuous instruments. In addition, the Johns Hopkins Elastic LIDAR was also used to obtain highly resolved temporal and spatial structure of the daytime boundary layer. Based on the PM2.5 measurements made by John Ondov's group from University of Maryland, College Park, the entire study period has been divided into a total of 13 PM2.5 pollution episodes, in each of which the 24-h averaged PM2.5 mass concentrations exceeded 30.0 µg/m3 for one or more days. A detailed analysis of the available meteorological and LIDAR datasets will be performed to characterize the atmosphere boundary layer specifically during these episodes. The preliminary analysis indicates that large PM events occur preferably on hot days. In addition, the relative humidity and pressure for most events is around the 3 month average. The goal of the analysis would be to characterize the importance of local and the synoptic scale climatic patters in the aforesaid episodes. While the LIDAR is used to gain a deep insight of the local spatial and temporal structures in the atmospheric boundary layer, data from soundings, remote sensed data and back-trajectory analysis is used to assess the role of synoptic scale phenomena. A deep understanding of the meteorological aspects of the events would therefore, help us in explaining the origin of the chemicals/species dominating the episodes.

20A-5

EVALUATION OF AMBIENT FINE PARTICULATE MATTER (PM2.5), CO-POLLUTANTS AND MERCURY IN SOUTHEASTERN OHIO,

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This project complements U. S. Department of Energy's National Energy Technology Laboratory's (NETL) overall goal of ensuring that the best science and technology are available for emission control strategies and regulatory decision making related to the health and environmental impacts of PM2.5, regional haze, and air toxics. Ohio University, in collaboration with Consol Energy R&D, Advanced Technology Systems, Atmospheric Environmental Research and Argonne National Laboratory is evaluating individual and regional coal-based power plant emissions and transport issues related to PM2.5 and mercury in the Ohio River Valley Region. As part of this evaluation a surface air monitoring station (SAM) was established in a rural location south of Athens, Ohio. The site is located in the heart of the Ohio River Valley region, which is characterized by a high number of coal-fired power plants. Approximately eleven coal-fired power plants and a significant number of industrial and chemical facilities are within a 60 mile radius of the site. The scope of work for the monitoring campaign involves investigating the ambient fine particulate matter composition along with simultaneous measurement and analysis of ambient and deposited concentrations of mercury, arsenic and gaseous criteria pollutants. This data will be used for validation of regional model simulations and to provide pre-regulatory information that can be used by Ohio River Valley industries to assess performance on multi-pollutant control systems. This presentation will concentrate on the regional nature of PM2.5; Co-pollutants (SO2, NOx, CO and O3) and mercury. Detailed analysis of the data is currently on going which focuses on how concentrations vary with seasons and weather. Preliminary review of the data indicates elevated pollutant levels during episodic events which routinely impact the site, making it an excellent location to capture the transport of pollutants into and out of the valley.

20B-1

DEVELOPMENT OF A HYBRID MODEL FOR PREDICTING PARTICLE NUMBER CONCENTRATIONS,

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We have studied the association between measured particle number concentrations (NC) in different particle size modes against deterministically predicted fine particle (PM2.5) concentrations and meteorological conditions. We have also assessed the contribution of urban and suburban sources and the effect of a nearby motorway to the measured particle number concentrations during a 45 days (15May-30June 2000) monitoring campaign in Helsinki, Finland. The PMx monitoring campaign is described in detail in Hussein et al. (2004). The PM2.5 contribution of the local traffic emissions to NCs is estimated by a finite line source model CAR-FMI (Härkönen, 2002). The long range transport (LRT) contribution is predicted by a statistical method (Karppinen et al., 2004). The measured and preprocessed meteorological variables are based on routine synoptic and sounding measurements by Finnish Meteorological Institute (FMI). The hourly data is grouped to daytime and night time values and also against three flow direction sectors: urban, suburban and local traffic. The Principal Component Analysis (PCA) and the General Linear Model (GLM) are applied to the data using SYSTAT 11 (SYSTAT Software, Inc., 2004) statistical package. Some meteorological parameters, like stability and dew point temperature, explain significantly the variations of the particle number concentrations in each size mode. As expected, the diurnal variations were significant in all three wind flow sectors. LRT-factor had the greatest influence on the accumulation mode number concentration. However, this relation was very sensitive to the grouping of data, obviously, because LRT depends strongly on the flow direction. PM2.5 mass and particle number concentration correlation was strongest when the flow direction was from the nearby motorway. We were able to extract the most important sources and meteorological conditions explaining the observed particle number concentrations in different size modes, so the study demonstrates clearly the usefulness of a combined deterministic and statistical modeling approach Hussein, T., Hämeri, K., Aalto, P., Asmi, A., Kakko, L., Kulmala, M., 2004. Particle size characterization and the indoor-to-outdoor relationship of atmospheric aerosols in Helsinki. Scand J Work Environ Health, vol. 30, no. 2, p. 54 -62. Härkönen, J., 2002. Regulatory dispersion modeling of traffic-originated pollution. Finnish Meteorological Institute, Contributions No. 38, FMI-CONT-38. University Press, Helsinki, 103 p. Karppinen A., Härkönen, J., Kukkonen J., Aarnio P., Koskentalo T., 2004. Statistical model for assessing the portion of fine particulate matter transported regionally and long range to urban air. Scand J Work Environ Health, vol. 30, no. 2, p. 47-53.

20B-2

APPLICATION OF SOURCE AND RECEPTOR MODELS TO ANALYZE SELECTED EPISODES FROM THE ST. LOUIS - MIDWEST SUPERSITE,

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Anderson and Davis (2004) examined the spatiotemporal characteristics of a multiday regional ozone and fine particulate matter event in April 2003 utilizing a combination of advanced receptor modeling and lagrangian particle modeling techniques to elucidate the nature and location of the potential source event. This study documented the influence of a large scale grassland fire across the Central Plains to states as far away as Minnesota and Alabama. Imagery from the MODIS system for April 11-12, 2003 indicated the presence of a smoke over the entire state of Missouri including the St. Louis metropolitan area. Likewise, simple two-dimensional trajectory displays depicted transport from the fires towards St. Louis area. However, detailed examination of the high time resolution carbon data and daily-integrated speciation data from the St. Louis Supersite for this time period did not indicate any influence from the regional smoke event identified in the previous study. Analysis of surface synoptic meteorological charts indicated the presence a stationary frontal boundary located across east-central Missouri which likely mechanically uplifted the smoke. Using the meteorological model MM5 in conjunction with the lagrangian particle dispersion model (LPDM) FLEXPART, we simulated the meteorological and regional dispersive characteristics. The FLEXPART simulations clearly depicted the mechanical forcing of the smoke emissions aloft, accounting for the absence of any biogenic smoke tracers at the St. Louis Supersite in contrast to other chemical speciation sites in Missouri. In this study, we examine the detailed meteorological and physical characteristics associated with this and another event utilizing a combination of meteorological modeling and lagrangian particle modeling in concert with advance receptor modeling using positive matrix factorization (PMF) to develop a conceptual model of select episodes in the St. Louis metropolitan area. Additionally, we examine the importance of the use of LPDM modeling techniques in comparison to traditional ensemble trajectory techniques. Reference: B. Anderson and M. Davis (2004) “Integrating Source and Receptor Oriented Analytical Methods for Fine Particulate and Ozone: A Case Study”, in Proceedings of the A&WMA Visibility Specialty Conference - Regional and Global Perspectives Haze: Causes, Controversies and Consequences, Paper #72, October 26-29, 2004, Asheville, NC.

20B-3

DEVELOPMENT OF A GIS EMISSIONS ANALYSIS TOOL TO ESTIMATE THE PROBABILITY OF REGIONAL SOURCE CONTRIBUTION TO HAZE,

Steven G. Brown, Sean Raffuse, Dana Sullivan and Hilary R. Hafner, Sonoma Technology, Inc.

A customized geographic information system (GIS) spatial mapping tool was developed to aid in the characterization of relationships between emissions trends from 1988 through 2002 and ambient data trends for the chemical components of aerosols. The tool, called the probability of regional source contribution to haze (PORSCH), combines back-trajectory meteorological analyses with emission inventory data to detect and visualize the correlations between days with high ambient pollutant concentrations and probable emissions source regions. PORSCH geographically and temporally weights inventory data, coupling them with trajectory probability distributions. Thus, emissions that are most likely to affect the location of ambient measurement are more heavily weighted in the correlation analyses. Statistical correlations indicate the source categories and geographic distributions of emissions that have historically affected visibility conditions in Class I areas. They may also serve as predictors of the potential effects of future controls or limits on emissions. Analyses based on trend correlations can be valuable components of integrated, corroborative research projects, which, when taken as a whole body of evidence, can be highly effective tools for developing conceptual models of regional haze phenomena, planning photochemical modeling efforts, and selecting control strategies.

20B-4

GENERATION OF CHARGED AEROSOLS BY HIGH-VOLTAGE ELECTRIC-POWER LINES,

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Anthropogenic activity can both create airborne particulate matter (PM) and affect the number of elementary electric charges per particle. Aside from freshly created particles, the electric charge distribution of ambient aerosol PM is close to Boltzmann equilibrium, and is centered on zero net charge. However, changes in the electric charge distribution of atmospheric aerosol PM can modify the subsequent transport, deposition, and fate of PM, due to electrostatic forces and induction of image charges. The number of electric charges per particle influences the lung deposition efficiency of aerosols. The number of elementary charges per particle may be modified by collisions with the air ions created in the vicinity of high-voltage transmission-line conductors (HVTC). The electric field between HVTC accelerates pre-existing air ions, which collide with gas molecules to produce an avalanche of corona ions. We analyzed how aerosol particles in the vicinity of HVTC come into equilibrium with the cloud of corona ions. The ability of corona ions to charge particles decreases with particle size. Although particles greater than 1 µm diameter can accumulate 10 or more charges, the charging probabilities for particles < 0.1 µm are small, and decrease with decreasing particle size. For particles below 0.01 µm diameter, accumulation of more than one charge is prevented by the limited surface area on each particle and electrostatic repulsion. Thus, the natural charge distribution of ultrafine particles remains largely unaffected by air ions. For particles that are created charged (e.g., 218-Po clusters, ~90% of which have a +1 charge), the presence of HVTC lines produces no additional charging. Combustion aerosols in ambient air are generally created with electrical charge (e.g., diesel exhaust particles (~ 0.3 µm), carry an average charge of about +4), and cannot be further charged by corona ions. Charged aerosols are returned to an equilibrium (Boltzmann) charge distribution through interaction with ions in natural background air. The air within several meters of the ground contains background 222-Rn concentrations due to naturally occurring isotopes (238-U) in surface soils. The combination of radon decay, cosmic rays, and gamma-ray emanations from the earth lead to a background air ion concentration that drives the electric charge on aerosol particles toward equilibrium levels. Our analyses showed that, although high-voltage AC and DC transmission lines have increased air-ion concentrations in their vicinity, the effect of such ions on the electric charge of ambient air particles is modest for the PM-1.0 range and smaller.

20B-5

NEW PARTICLE FORMATION ASSOCIATED WITH SO2 EMISSION FROM POWER PLANTS: 3-DIMENSIONAL MODELING,

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It is well recognized that atmospheric particles affect regional air quality, human health, and climate, and these effects depend strongly on the number size distributions and compositions of the aerosols. The number size distributions of atmospheric aerosols are determined by a number of microphysical processes, of which the nucleation process is critical but least understood. To understand the key microphysics controlling the formation and fate of secondary particles and to represent these processes in the models are important to improve the predictive understanding of the environmental and climatic impacts of atmospheric aerosols. In this presentation, we discuss the new particle formation in the lower continental atmosphere over the Eastern United States, using a nucleation sub-model coupled with the Comprehensive Air Quality Model with extensions (CAMx). The evolution of freshly formed particles at selected locations is also simulated with a detailed aerosol microphysics model driven by the time-dependent variables predicted with the CAMx. Our nucleation sub-model includes three different nucleation mechanisms: binary homogeneous nucleation (BHN) of H_2SO_4-H_2O, ternary homogeneous nucleation (THN) of H_2SO_4-H_2O-NH_3, and ion-mediated nucleation (IMN) of H_2SO_4-H_2O. The CAMx is driven by the meteorological fields from the meteorological model and uses the gridded emission inventory prepared with Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System. We find that the temporal and spatial variations of nucleation rates predicted by different nucleation theories are quite different. BHN theory predicts negligible nucleation in the lower atmosphere over Eastern United States. Based on IMN theory, the plumes from Ohio River Valley and some urban centers are significant source of secondary particles. In such plumes, though the pre-existing particle concentration is high, the high production rate of H_2SO_4 as a result of high SO_2 concentration leads to relative high H_2SO_4 (g) concentrations which promote nucleation. The IMN rates are limited by ionization rates (~ 20 ions $cm^{-3}s^{-1}$) in continental boundary layer). The nucleation rates predicted with THN theory depend strongly on ammonia concentrations and THN rates frequently exceed 1E6 $cm^{-3}s^{-1}$ in the regions with high NH_3 concentration. The frequency and nucleation rates predicted with IMN theory are consistent with the results from the Pittsburgh Air Quality Study (from July 2001 to June 2002) which indicate that nucleation occurred on 50% of the study days and the average nucleation rates during the nucleation period never exceeded ~10 $cm^{-3}s^{-1}$. The power plant plumes frequently across Pittsburgh area, and in sunny days IMN theory predicts significant nucleation in such plumes. In our simulations of the evolution of particle number size distributions, the condensation of precursor gases (including sulfuric acid and condensable organic species from both anthropogenic and biogenic sources) and the coagulation scavenging are taken into account. Our simulations indicate that a significant fraction of the freshly formed particles can grow to the sizes in the range of 30-100 nm within 10 hours. These particles may contribute to the regional haze formation and may serve as cloud condensation nuclei.

20C-1

FIELD ASSESSMENT OF THE DYNAMICS OF PARTICULATE NITRATE VAPORIZATION USING DIFFERENTIAL TEOM® AND AUTOMATED NITRATE MONITORS,

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Time resolved PM-2.5 mass data from the Differential Tapered Element Oscillating Microbalance (TEOM), and time-resolved PM-2.5 nitrate concentrations from an automated nitrate monitor are used to examine the dynamics of volatilization under field conditions. Measurements from Claremont, California, a city downwind of Los Angeles, and a region of high nitrate concentrations, are compared with that obtained in the laboratory for sampling of pure ammonium nitrate aerosol, and to vaporization losses predicted by theory. Our analysis specifically examines whether the nitric acid and ammonia gas volatilization from particle-bound ammonium nitrate loaded on the TEOM’s fiber filter occurs over time scales that are longer than the five-minute cycle time for the system. The field data show that the TEOM reference signal obtained when sampling particle-free air tracks ambient nitrate on most days, but with a delay of 40-100 min. The characteristic lag time for ambient data similar is to characteristic evaporation time predicted by theory of Zhang and McMurry (1992) and Furuchinini et al. (2001). The saturation of nitric acid vapor downstream of filter, estimated from the filter temperature and nitrate loss rate, was consistently less than 1. Measurements at two different TEOM filter temperatures, and theoretical analysis, indicate that the filter temperature is generally more important than filter pressure drop to evaporative loss rate. These results support the use of the approach employed by the Differential TEOM, which applies a filter artifact correction based on measurements for particle-free collection during alternating five-minute collection periods, for the accurate assessment of PM-2.5 mass. Furuuchi, M.; Fissan, H.; and Horodecki J. (2001) Evaporation behavior of volatile particles on fibrous filter flushed with particle-free dry air, Powder Technology 118, 171–179. Zhang, X.Q.; McMurry, P.H. (1992) Evaporative losses of fine particle nitrates during sampling, Atmospheric Environment, 26A, 3305-3312.

20C-2

MEASUREMENT OF FINE PARTICULATE MATTER (NONVOLATILE AND SEMI-VOLATILE FRACTIONS) IN FRESNO, CA,

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Semi-volatile material, including ammonium nitrate and semi-volatile organic material, is often not measured by traditionally used sampling methods including the FRM and the R&P TEOM Monitor. An intensive sampling campaign was performed at the EPA Fresno, CA Supersite during December 2003. Measurements of fine particulate matter, including both the semi-volatile and nonvolatile fractions of the aerosol were made. Several real-time mass instruments were employed during the study. The recently developed R&P FDMS Monitor has been shown to measure total PM2.5 mass including both semi-volatile carbonaceous material and ammonium nitrate. The PC-BOSS, an integrated sampler, has also been shown to measure semi-volatile carbonaceous material and ammonium nitrate, resulting in integrated total PM2.5 concentrations. Good agreement was observed between the PC-BOSS and the R&P FDMS Monitor during this study. Several real-time measuring systems including the R&P Differential TEOM, the Met One BAMs, and a GRIMM Monitor were also employed during the study, and comparisons of total PM2.5 mass were made with the R&P FDMS Monitor. Agreement among these various monitors was generally good. However, differences were often seen under conditions of high semi-volatile species concentrations. Reasons for the observed differences in the real-time mass measurement systems are explained by the composition and complexity of the measured aerosol, most importantly the composition of semi-volatile organic material. In contrast, the PM2.5 FRM and the R&P TEOM Monitor (operating at 50 0C) did not reliably measure semi-volatile material. Measurements were also made with several continuous species monitors. A recently commercialized Dionex GP-IC instrument was extensively field tested for the first time during this study. Sulfate, nitrate and ammonium concentrations were determined by the Dionex GP-IC. Comparisons were made between the Dionex GP-IC and an R&P Sulfate Monitor and an R&P Nitrate Monitor. Good agreement was observed between sulfate concentrations measured by the Dionex GP-IC and the R&P Sulfate Monitor. However, significant differences were observed during episodes of high humidity between nitrate concentrations measured by the GP-IC and R&P Nitrate Monitor. Continuous particulate carbon measurements were made by an R&P Carbon Monitor, Sunset Labs Carbon Monitor, and an Anderson Aethalometer. Sums of all the major species of an urban aerosol, as determined by the various continuous species monitors, were made and compared to total PM2.5 concentrations measured by the R&P FDMS Monitor. Differences observed in the measurements can be explained by the ability of the various measurement systems to accurately measure semi-volatile organic material and ammonium nitrate. Comparisons were also made between the R&P FDMS and the FRM, and observed differences are explained. Measurement of Fine Particulate Matter (Nonvolatile and Semi-volatile Fractions) in Fresno, CA

20C-3

CONTINUOUS SIZE SELECTIVE MEASUREMENT OF SEMI-VOLATILE COMPOUNDS,

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Introduction The value of a Particulate Matter (PM) collected by an FRM represents the mass fraction collected on the filter per volume and 24h. This information however does not represent entirely the atmospheric condition, since air temperature and the chemical composition can alter the results. It is therefore desirable to measure continuously the solid and the aerosol dust mass concentration in the atmosphere, since many aerosol consist of semi-volatile components such as sulphate, nitrate, ammonium nitrate and other volatile material such as humidity. It is necessary to determine the aerosol size distribution in combination/ addition with different speciation technologies to get also an insight on the composition of the particulate matter. Method Some optical particle counters (OPC) are capable to measure particle size and concentration nearly independent of the refractive index with the method of orthogonal light scattering. These results are converted to mass of ambient aerosols and expressed as PM-10 or PM-2.5 or PM-c. This new approach of an OPC the Grimm 19 inch rack-mounted dust monitor #280. He has been designed to determinate the particle mass distribution and the different PMx values in real time. Ambient air to be analyzed is drawn into the unit via an internal volume controlled pump at a rate of 1.2 litres/minute. The inlet air is at the same outdoor temperature, however, the inlet air can be heated prior introduction to the optical chamber, if so desired. The scattered signal from each particle passing in the optical chamber through the laser beam is collected at approximately 90 degree by a mirror and transferred to a recipient diode. After a corresponding reinforcement, the signal of the diode is recorded with a multi-channel size classifier. A pulse height analyzer then classifies the signal transmitted in each channel. These counts are stored in the data storage card for future analysis. To prevent condensation, the monitor incorporates a special sample probe with a permapure drying system and does not alter the probe. With this newly developed instrument it is now possible to get a realistic value of PMx and in addition the amount of semi-volatile compound for the different size fractions. The instrument is measuring first the total amount of particles (volatiles and non-volatiles) in the ambient air with the standard non-heated sample inlet and the according PM10 and PM2.5 values are obtained. The sample inlet will then be heated up to 90°C and a few seconds later the non volatile fraction of the sample air is measured (semi-volatiles are stripped out by heating up the sample probe to 100°C). The difference between the two results is the semi-volatile fraction of the ambient air. By processing both measurement cycles, it is possible to get the mass value of the semi-volatile fraction. Results will be shown of Mass and count related changes during measurement.

20C-4

NEW YORK STATE URBAN AND RURAL MEASUREMENTS OF CONTINUOUS PM2.5 MASS BY FDMS TEOM AND BAM: EVALUATION AND COMPARISONS WITH THE FRM,

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The New York State Department of Environmental Conservation in conjunction with the EPA sponsored PMTACS Supersite Program administered by the Atmospheric Sciences Research Center at the University at Albany have operated urban and rural monitoring sites with collocated FDMS TEOM, BAM and FRMs for the past several years. Part of the design of the PMTACS program includes technology transfer from the research arena to routine application. These new instruments are operated in conjunction with academic and State Agency staff with the expectation that the final commercial version of each instrument will be valuable and reliable to routine State Agency air monitoring networks, in addition to research operations. New York City data comparisons between the FDMS TEOM, BAM and FRM are examined for bias and seasonality over a two-year period. Data comparisons for the FDMS TEOM and FRM from a rural site in Addison, NY as well as from Niagara Falls, NY are examined for the same two-year period. Preliminary data from New York City show a higher correlation between the FDMS and BAM than that between the FDMS and FRM or the BAM and FRM. Continuous PM2.5 mass monitoring is performed by State and Tribal Agencies for near real time public health reporting, model and SIP evaluation, trends analysis and in place of FRM monitoring. The continuous mass instruments are currently being evaluated with the assumption that they will eventually be deployed in a public reporting Agency's monitoring network. The comparisons between these continuous methods and the FRM demonstrate that the continuous monitoring methods are not yet adequate for all State monitoring objectives. Data from the continuous mass monitoring instruments is compared to the proposed EPA requirements for Class III Federal Equivalency. State Agencies are interested in this designation because it potentially will allow for a reduction in the labor-intensive manual PM-2.5 FRM monitoring network. Instrument cost, ease of data transfer, routine maintenance procedures and overall reliability will also be examined for each method.

Author Index

(page numbers refer to Abstract Book)

Author Index
(page numbers refer to Abstract Book)