Plenary 1

WHAT SATELLITES CONTRIBUTE TO THE GLOBAL AEROSOL PICTURE. Ralph Kahn, Jet Propulsion Laboratory/ Caltech

Since aerosols generally do not remain in the atmosphere long enough for global mixing, and many respond to changes in relative humidity and other factors, their properties and amounts vary on many space and time scales. However, aerosols contribute to direct radiative forcing, and indirectly by affecting cloud properties, to a degree that must be considered when modeling climate on global, and especially on regional scales. They are also significant players in regional pollution and long-distance material transport.

Compared to in situ measurements, space-borne detectors are relatively blunt instruments for studying atmospheric aerosols. Until recently, only column-averaged aerosol optical depth over dark water, derived from assumed aerosol micro-physical properties, could be retrieved routinely from space. But the enormous range of space and time scales presented by aerosol phenomena of interest creates opportunities for satellites to contribute. Recent advances in spacecraft measuring capabilities, such as those represented by NASA's Earth Observing System MISR and MODIS instruments, are beginning to reliably retrieve particle column amounts over land and water, and to constrain column-average particle size and shape along with spectral optical depth. Polarization, UV, and lidar techniques promise to contribute added sensitivity to particle composition and vertical distribution. Taken together, these new data products are improving our ability to identify and track aerosol air mass types over regional and larger scales, giving added value and context to detailed particle micro-physical properties that can be measured in situ at selected points during the life history of an air mass. This talk will review the strengths and limitations of current space-based aerosol products, and will suggest how they may fit with in situ and surface measurements, to advance our global picture of atmospheric aerosols.

Plenary 2

THE HEALTH EFFECTS OF AMBIENT PARTICULATE MATTER: WHAT WE KNOW IN 2005 AND WHERE WE NEED TO GO IN THE FUTURE. Dan Costa, Environmental Protection Agency

The last decade has seen the accumulation of a large and ever-convincing database that ambient particulate matter can have adverse impacts on health. These impacts range from hospitalization, worsening of pre-existing health impairments, and loss work and school days to mortality. The growing evidence points to certain population subgroups, typically the aged with cardiopulmonary deficiencies or impairments or genetic predisposition or children with asthma, are at unusual risk of adverse effect. Life-threatening risk appears to involve cardiac mechanisms not heretofore appreciated as an impact of air pollution. However, what it is about particulate matte that impacts health remains speculative, although there is evidence that certain attributes related to size and combustion origin are involved. PM-associated contaminants such as metal and organic compounds may impart their effects via oxidant mechanisms or distort neural or humoral balances in the body. Linking health effects to the contaminants most associated with specific source or transformation processes may allow for more effective regulatory control. Linking sources to hazardous components to health outcomes remains a challenge to the air pollution science community.

Plenary 3

FROM ANCIENT ARTWORK TO MODERN FUNCTIONAL AEROSOL-MADE MATERIALS. Sotiris E. Pratsinis, Institute of Process Engineering (IPE), Swiss Federal Institute of Technology

Recent major advances in the scientific understanding of aerosol formation and growth allow now optimal aerosol reactor design and inexpensive production of sophisticated nanoparticles with controlled composition, size and morphology leading to exciting new products. For example, noble metal bearing catalysts that were made for eons by multi-step wet impregnation and costly effluent treatment are made now by one-step liquid-fed flame aerosol reactors. Transparent but radioopaque dental nanocomposite materials can be made, for the first time, in these reactors breaking, somehow, the "tyranny" of thermodynamics. These developments bring new challenges to modern aerosol science and engineering. For example, there is a need to distinguish between hard- and soft-agglomerates as the structure of nanomaterials affects their performance as, for example, in a slurry for chemical-mechanical polishing of microelectronics or as a filler in a dental resin. As with every technology that has to survive the "death valley" of scale-up, there is a need for quantitative understanding of the controlling phenomena during interfacing of fluid and particle dynamics for process design that lead to homogeneous multicomponent products of controlled characteristics. Aside from these promising research areas with aerosol-made nanoparticles, there is concern for their health effects. Do the advanced material properties come with adverse health effects? Scattered data imply a rather vague answer. Some are ready to treat this technology as another "GMO" and even impose a moratorium on such research. Clearly there is a need to place the health effects of aerosol-made nanoparticles on a firm scientific basis to better protect the international investment in this field and guide researchers. Given the current advances in aerosol characterization and the large body of anecdotal data in industry regarding exposure to nanoparticle commodities (carbon black, fumed silica, titania, welding fumes), there is enough knowledge to initiate health effect and, even, epidemiologic research on these materials.

Plenary 4

WHAT ARE WE LEARNING FROM FIELD MEASUREMENTS WITH AEROSOL MASS SPECTROMETRY?. Dr. Jose-Luis Jimenez, Department of Chemistry & Biochemistry and Cooperative Institute for Research in the Environmental Sciences (CIRES), University of Colorado-Boulder

The past decade has seen the emergence of several methods capable of determining the size and chemical composition of aerosol particles in real-time using mass spectrometry, allowing the investigation of aerosol sources, processes, and effects in more detail than was possible before. The Aerodyne Aerosol Mass Spectrometer (AMS) is currently the most widely used instrument of this type. This presentation explores recent applications of the AMS and complementary instrumentation to the analysis of ambient particles at multiple urban, rural, and remote locations. Urban locations include Pittsburgh, Mexico City, New York City, Riverside (California), and Manchester (UK). Rural and remote locations include Storm Peak (Colorado), Jungfraujoch (Switzerland), Trinidad Head (California), Jeju Island (Korea), Okinawa (Japan), and Mace Head (Ireland). Examples include the determination of the composition of growing particles during nucleation events; the characterization of the organic aerosol components based on the entire organic mass, rather than on tracers; and the integration of AMS data with other measurements towards closure of aerosol effects on light scattering and cloud nucleation. The presentation will conclude by summarizing recent improvements to the AMS: high m/z resolution, soft ionization, and light scattering and surrogate morphology measurements.

1PA1

INVESTIGATION OF GLASS FIBER DEPOSITION ONTO INNER WALLS OF STRAIGHT BRASS TUBING.

ZUOCHENG WANG, Philip K. Hopke, Goodarz Ahmadi, Center for Air Resources Engineering and Science, Clarkson University, Potsdam , NY; Paul A. Baron, Gregory Deye, National Institute for Occupational Safety and Health, Cincinnati , OH; Yung-Sung Cheng, Wei-Chung Su, Lovelace Respiratory Research Institute, Albuquerque, NM.

The wide use of man-made vitreous fibers (MMVF) raises the concern over their potentials to induce pulmonary diseases. The deposition density of airborne fibers on a region in the respiratory tract is clearly an important factor in determining the likelihood of diseases. 10 micrometer and 25 micrometer length-classified glass fibers by a dielectrophoretic fiber classifier (Baron et al. 1994) are used to investigate the deposition pattern onto the inner walls of straight brass tubing which has an inner diameter of 0.5 cm and is set up vertically. The theory by Jeffery (1922) predicted the rotational motion of ellipsoidal bodies in shear flow. Rotational interception deposition along airway walls was expected by an extension of Jeffery's solution (Johnson et al. 1993). Our research shows that no deposition happens under flow rates 0.5 liter/min and 3.5 liter/min for a 6 cm long tubing. We suggest that near wall region the fibers incur dramatic increase of local shear rate and hence lengthen the rotation period.

1PA2

VAPOR AND LIQUID PHASE CRITICAL EMBRYOS OF POLYMETHYL METHACRYLATE GENERATED UNDER ILLUMINATION OF LASER ON FREE ELECTRONS.

A.M. BAKLANOV, A. A. Onischuk, T.A. Fedirko, and M.P. Anisimov

Laser ablation of solids is actual problem for current time from the practical as well as scientific points of view (See, for example, article by Lu et al., 2002). Polymethyl Methacrylate (Acrylic Resin) ablation in the nitrogen gas flow is studied. experimentally in the present research. The laser on free electrons is used as powerful light beam source. Sample was placed in the box with the nitrogen gas flow rate about several cc per second. The sodium chloride window was used for the Acrylic Resin sample illumination. Resulting aerosol was analyzed by Chromatograph, Transmission Electron Microscope, and Diffusion Aerosol Spectrometer. TEM image of aerosol particles is represented by two fractions, i.e. small and mach bigger particles. That result is reproduced in the Diffusion Aerosol Size Spectrometer measurements. The particle size distributions as function of the power of laser pulse are obtained. Each spectrum is measured by Diffusion Aerosol Spectrometer.

It can be easily seen the low energy (0.03 j/cm2) beam produce one mode size distribution. It is reasonable to assume that the mode is associated with supersaturated vapor nucleation which generates near 10 nm diameter (solid) particles after sublimation of solid Polymethyl Methacrylate under laser impulse. The bigger in energy laser impulse have chance to create the pressure in the light spot area which is enough to make phase transition from solid to liquid states. Well known that according the phase
state diagram at temperature which is upper the triple point the target substance has chance to be in the vicinity of parameters associated with transition of solid to liquid. That is reason to get melted Polymethyl Methacrylate as well as the mode for droplets at higher energy density for laser beam. One can find the second mode associated with droplets. Chromatography analysis shows monomers of Methyl Methacrylate in the gas phase

We believe that the embryo phase state coincides with the particle phase states. In other case one has no chance to get two separated peaks for size distribution because the interpeak space infilling by particles migrating from one phase state to an other.

Grant RFBR 05-03-32208 is acknowledged.

Lu, Q., Mao, S.S., Mao, X. and Russo, R.E. (2002) Appl. Phys. Letters, 80(17), 3072-3074.

1PA3

IMPACT OF TEMPERATURE FLUCTUATIONS ON NUCLEATION RATE. I.H. UMIRZAKOV and M.P. Anisimov

There are many efforts devoted to influence of various physical phenomena on nucleation rate. Fluctuations of critical nucleus physical parameters have impact for nucleation rate estimations. We consider the temperature fluctuations of the critical size nucleus. One can get averaging the rate of atom evaporation from nucleus of new phase over distribution function of temperature fluctuation. Solution of kinetic equation of nucleation gives equation for the number of molecules in critical nucleus. The temperature fluctuations of critical embryos lead the fluctuations of molecule evaporation rate from cluster.

Taking as example the water vapour nucleation one can estimate the temperature fluctuations on nucleation rate parameters. One can see the considerable influence of the temperature fluctuations on the vapour supersaturation. The difference of two models is bigger when nucleus size is smaller. For the discussed example for water vapour nucleation difference of nine orders of magnitude can be found for nucleation temperature near 300 K and water vapour supersaturation about 3.46. In the same fashion the volume fluctuations can be estimated. It was found that the specific volume fluctuations result mach smaller effect on the vapour nucleation rate.

The present consideration shows the considerable influence of temperature fluctuations on the critical nucleus size. It means the result should be taken in to account for the experimental estimation of the number of molecules in critical nucleus using the slope of the experimental data on nucleation rate introduced, for example, by Anisimov and Cherevko (1982).

Grant RFBR 05-03-32208 is acknowledged.

Anisimov, M.P.& Cherevko, A.G. (1982) Izv. SO AN USSR, Chemical series, 4, No 2, 15-19.

1PA4

DIRECT NUMERICAL SIMULATION OF MICRODROPLET KINETICS IN A TURBULENT FLOW. OLEG KIM, University of Notre Dame, Notre Dame, IN

The spatial – temporal evolution of electrically charged droplets in jet-vortex wakes of heavy airliners is of interest for their visualization in the airport vicinity. This study is important to provide information for the safe take off/landing of the following aircraft.

In the case of many of charged particles, the forces acting upon each of them is the sum of binary interactions. As a result, this problem can not be solved analytically. For this reason, direct numerical modeling is used in the present work.

In the numerical model, the region of an aircraft traveling wake is divided in many cubic cells, and modeling of physical processes occurs within each cell. The droplets are regarded as non-deformable spheres. The dynamic equation for each of them is solved numerically, taking into account their interaction with all other particles. Particles remain attached at the moment of their collision, and the collision process is non-elastic. The classical spectrum by Kolmogorov is used to describe the turbulence of the air.

The temporal evolution of the particle mass spectrum is obtained. The characteristic coagulation time in the case of identically charged particles is much larger than in the case of electrically neutral droplets. This fact increases the life time of an aerosol visualizing the aircraft wake. The developed numerical investigation of the evolution of the particulate mass spectrum makes it possible to calculate the time evolution of optical properties in accordance to the Mie theory. The space - angular distribution of the scattered radiation polarization is obtained.

1PA5

A CRCD COURSE FOR PARTICLE TRANSPORT, DEPOSITION AND REMOVAL. GOODARZ AHMADI, David J, Schmidt, Kambiz Nazridoust, John McLaughlin, Cetin Cetinkaya, Suresh Dahniyala, Jeffrey Taylor, Stephen Doheny-Farina, Clarkson University, Potsdam, NY 13699-5725; Fa-Gung Fan, Xerox Corporation, Webster, NY, 14580

Particle transport, deposition and removal technologies are of crucial importance to the competitiveness of many high tech US microelectronic, imaging and pharmaceutical industries, as well as for solving a number of environmental problems. In the last decade, significant research progress in the areas of particle transport, deposition and removal has been made. The primary objective of this NSF supported combined research and curriculum development project is to make the fruits of these new important research findings available to seniors and first year graduate students in engineering through developing and offering of specialized courses. In the last two years, a course-sequence on particle transport, deposition and removal and re-entrainment has been developed. The course will be available on the web next fall and the plan is to teach it at several campuses simultaneously. The course sequence is composed of four modules:

- Fundamental of particle transport, dispersion, deposition and removal.
- Computational modeling of particle transport, deposition and removal.
- Experimental study of particle transport, deposition and removal.
- Industrial applications of particle transport, deposition and removal.

1PA6

INFLUENCE OF METEOROLOGICAL PARAMETERS ON THE ANGSTRÖM TURBIDITY PARAMETERS AND THE CHARACTERISTICS OF INFERRED AOD. SHANTIKUMAR SINGH NINGOMBAM, Indian Institute of Astrophysics, IAO, LEH, Ladakh, India

A case study was made to study the Angström turbidity parameters with the local prevailing surface meteorological conditions from the inferred aerosol optical depth (AOD). The data was obtained from a multiple wavelengths radiometer (MWR), operated at the tropical urban station, Pune University (18o32/N, 730 51/E, 559m, AMSL) during winter season (Dec-Feb) to pre-monsoon summer season (March-May) of the year 99-2k.

In the visible region of the solar spectrum (400-750nm) aerosols are the major cause of depletion of direct solar radiation through the process of scattering and absorption. Since the tropical observing station Pune is an industrially developing area, various amount of contaminants are continuously inter into the atmosphere through various sources from the main made anthropogenic particles. Due to comparatively short residence time and increased susceptibility from the natural and anthropogenic perturbations, aerosols in the boundary layer and the lower troposphere exhibit more variability in their characteristics with the change of local atmospheric processes. A systematic seasonal variation for atmospheric turbidity was observed with the prevailing surface meteorological conditions.

From the observe data it is found that alpha decreases towards the pre-monsoon summer period (March-May), which indicates the dominance of bigger size particles. During the hot summer season, the strong convective activity would be able to sustain more number of large and giant particles for larger period of time. The maximum value of alpha is occurred at December (0.58 +/- 0.08) and the minimum at May (0.13 +/- 0.02). It is found that 38% correlation coefficient is found between alpha and RH. The good correlation is also found between alpha and maximum temperature of the observing period.

The Angstrom turbidity parameter beta is related to the amount of aerosols present in the atmosphere. There are good correlations between beta vs. maximum surface temperature as well as the Maximum RH values. The maximum value of beta is occurred at April and the minimum at December. The good correlation (95%) is also found between the Linke's Turbidity factor (T) and the Schuepp's turbidity coefficient (B). As the atmospheric transparency increases the values of both T and B are also decreases. The details analyses of these results were described in the paper.

1PA7

CAVITY RINGDOWN SPECTROSCOPY OF AEROSOLS.. MIKHAIL JOURAVLEV

Cavity ringdown spectroscopy is more recently developed laser absorption approach that replaces a multiphase cell with a stable optical cavity.

The system of cavity ringdown spectroscopy consists of the aerosols flow or the single levitated aerosol droplet replaced in open cavity. This method of aerosol spectroscopy based on the principle of measuring of the decay rate of light intensity in aerosol droplets in the double resonant condition of the external cavity.

The nonlinear ringdown spectroscopy of aerosols achieves the higher sensitivities by a factor of at least two separate resonance conditions namely both input-output resonance in the aerosol particle and input-output resonance of cavity [1,2].

In this condition a number of nonlinear effects such as Raman scattering and amplification, lasing, thermal and striction scattering occurs in aerosol droplets under lower threshold intensity [1-3]. The additional concentration of electromagnetic energy in the aerosol droplet by the external cavity enables due to Purcell factor of cavity to decrease the input intensity threshold to more record value. The transparent aerosol droplet is very high Q-factor oscillation systems. The Q-factor can be achieved approximately million. In addition to the total optical losses in stable optical cavity is compensated by the effective gain of nonlinear amplification. The decay rate is proportional to the total optical losses inside the cavity multiplied by Purcell factor and by integral coefficients of an open cavity and droplet electromagnetic modes overlapping.

The effective optical path length of the optical system is proportional Q-factor of aerosol droplet. The effect of the path length enhancement in-depth studied.

This approach permits to create the direct methods of studying of coagulation and sedimentation of the aerosol particle in the volume of aerosol chamber.

It permits to measure the both a single rotational-vibrational absorption line for gas species around of flowing or levitated aerosol particles at atmospheric pressure and separate aerosol chamber or clean room as well the diffusion and the adsorption of the gas or the water. The lower detection limit for ringdown spectroscopy is comparable to the ion mobility spectroscopy. By exploiting its high spectral resolution a lower detection limit can achieve excellent sensitivity and selectivity.

The Fortran programs for calculation of the integral coefficients of couple of an aerosol particle and ringdown resonant modes with the second and third kind nonlinearity are developed.

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1PA8

IMPACT OF PARAMETER REPRESENTATION IN GAS-PARTICLE PARTITIONING ON AEROSOL YIELD MODEL PREDICTION. JANYA HUMBLE, Diane Michelangeli, York University; Paul Makar, MSC, Downsview, ON, Canada; Don Hastie, Mike Mozurkewich, York University, North York, ON, Canada

A continuation of the kinetic box model study reported by Humble et al (23rd Annual AAAR Conference, October 2004) is presented in which the formation of SOA from the photo-oxidation of toluene is simulated using a subset of the University of Leeds Master Chemical Mechanism (MCM) version 3.1, and a kinetically based gas-particle partitioning approach. The model provides a prediction of the total aerosol yield and a tentative speciation of aerosols based on experimental data from York University’s indoor smog chamber. Mixtures of toluene, isopropyl nitrite and NO are added to the smog chamber and the resulting aerosol mass, along with toluene decay, NO concentration and aerosol size distributions are measured. Overall, the aerosol yield is predicted reasonably well for all experiments, with high aerosol loading resulting in better predictions. Early sensitivity experiments indicate vapour pressure to be a critical parameter in the partitioning and final aerosol yield. Current estimation methods are highly sensitive to boiling point temperature. An initial evaluation indicates that lowering the boiling point temperature for all species by ~3% (10 – 15 K) brings the predicted aerosol yield into closer agreement with the observations. Further evaluation of boiling point temperature and vapour pressure estimation techniques will be presented, highlighting the propagation of errors in the model. Of concern is the estimation of vapour pressure for compounds containing organic nitrates (major contributors to the aerosol speciation). Sensitivity runs were also conducted to characterize the nature of the wall reactions occurring in the chamber and their impact on the NOX budget in the model. The behavior and representation of the fraction of organic matter over the course of the experiments is examined in the model. The mass transfer treatment is currently in the kinetic regime but will be examined to ensure the appropriate representation of conditions in the chamber. Since the particles present in the chamber are sufficiently small, the importance of the Kelvin effect will be examined. The model will be further verified through application to an independent smog chamber data set.

1PA10

DIRECT NUMERICAL SIMULATION OF PARTICLE DEPOSITION IN TURBULENT CHANNEL FLOW.

HOJAT NASR, Goodarz Ahmadi, and John B. McLaughlin, Clarkson University, Potsdam, NY 13699.

Aerosol particle transport, dispersion and deposition in a turbulent channel flow are studied. The time history of the instantaneous turbulent velocity vector is generated by the direct numerical simulation (DNS) of the Navier-Stokes equation via a pseudospectral method. The particle equation of motion takes into account the Stokes drag, the Saffman lift, the Brownian motion, and the gravitational forces. Starting with an initially uniform concentration near the wall an ensemble of particle trajectories is generated and statistically analyzed. Several simulations for deposition and dispersion of aerosol particles of various sizes are performed and the corresponding deposition velocities are evaluated. It is also shown that the coherent vortical structure of near-wall turbulent flow plays an important role on the particle deposition process. It is also seen that some particles are removed from the wall region by being captured in the high speed streams moving away from the wall, which are formed by the flow structure. The simulated results under various conditions are compared with the available experimental data and earlier simulation results.

1PA11

THE ROLE OF ZETA POTENTIAL ON THE AUGMENTATION OF THERMAL CONDUCTIVITY IN NANOFLUID.

Jae-won Kim, DONGGEUN LEE,Boggi Kim, Pusan National University, Busan, Korea

Many mechanisms of thermal conductivity of nanofliuds have been issued in preceding treatises since U.S. Choi published a significant enhancement of thermal conductivity of nanofluids. One of the most significant factors has been widely believed without a quantitative evidence to be a suspension stability. In this study, we measured changes in zeta potential and hydrodynamic size with varying fluid conditions. Regarding the DLVO theory, we are able to control the zeta potential by changing surface charge state with varying PH of the solution, resulting in change of hydrodynamic size in the suspension. The thermal conductivity are obviously correlated only with zeta potential. Also effective thermal conductivity of nanofluids is enhanced to 15% with increse in volume addition of particle to liquid, but the change shows obvious nonlinear dependence on volume fraction of nanoparticles. We will explore the new findings with an fittable model and mechanism.

1PA12

ASSESSING THE PHYSICAL PROPERTIES OF POROUS PARTICLES FOR INHALATION. Vasu Sethuraman, Mark DeLong, Craig Dunbar, Alkermes, Inc, Cambridge, MA

The development of particles with low densities for pulmonary drug delivery has generated interest in accurate and precise porous particle density measurements. Porous particles typically have irregular morphologies, requiring definition of geometric and/or dynamic properties of an equivalent sphere to estimate the particle density. Geometric properties can be described in terms of diameter, area, volume, spherical envelope or mass. Dynamic properties are described in terms of the particle drag force or terminal velocity via Stokes' law. Approaches for estimation of the density of porous particles by measurement of the geometric and dynamic properties are described.

1PA13

CLUSTER STRUCTURE IN DENSELY AGGREGATING SYSTEMS. FLINT PIERCE, Amit Chakrabarti, Chris Sorensen, Kansas State University, Manhattan, KS

In dilute aggregating systems, where the motion of the particles and clusters is governed by brownian diffusion and clusters aggregate with unitary probability upon collision, the clusters formed exhibit fractal structure with the well known fractal dimension for Diffusion Limited Cluster Aggregation of approximately 1.8. For low nonzero value of initial monomer volume fraction the fractal clusters grow until the point that they begin to crowd, the system exhibiting a crossover from the dilute limit to dense. At this point, the clusters begin to aggregate with each other into a superaggregate structure characterized by an increased fractal dimension of ~ 2.6. This occurs at approximately the theoretical gel time of the system. The true gel time of the system occurs at a slightly increased time, due to the fact that the system exhibits some polydispersity. The evolution of systems at high monomer volume fraction is noticeably different, as the clusters formed never grow in the dilute limit and already exhibit correlations in their separation from one another. It is the study of these aggregating systems (from initially dilute to dense) that we wish to present. The geometric structure factor, correlation function, and a coordinate space study through the mass and perimeter fractal dimensions are used to analyze these systems. A comparison between our results and the works of other researchers is made. Gelation of the systems is also discussed, specifically through a comparison of the theoretical and measured values of gel times.

1PA14

PATTERNS IN MIE SCATTERING: EVOLUTION WHEN NORMALIZED BY THE RAYLEIGH CROSS SECTION.

MATTHEW BERG, Chris Sorensen, Amit Chakrabarti, Kansas State University, Manhattan, KS

Light scattering is an important unintrusive tool for studying the size, shape, structure and composition of particles and particle systems. It is also important for determining the effects of aerosol particles in the atmospheric environment and is the basis of many naturally occurring optical phenomena, (Mishchenko, 2002). Many particle systems contain spherical particles and spherical particles are frequently used for modeling more complex systems, (Mishchenko, 2002).

Light scattering measurements are traditionally interpreted as a distribution of light in terms of a scattering angle, theta. An alternative to using the scattering angle in describing light scattering from a uniform dielectric sphere is the dimensionless parameter qR, where R is the radius of the sphere, q=2ksin (theta/2) and k is the wave number of the incident light. Simple patterns appear in the scattered intensity if qR is used in place of the scattering angle, (Sorensen and Fischbach, 2000). These patterns are characterized by the envelopes approximating the scattered intensity distributions and are quantified by the phase shift parameter p=2kR|m-1| where m is the real refractive index of the sphere. Here we describe new patterns in these envelopes when the scattered intensity is normalized to the Rayleigh differential cross section. Mie scattering is found to be similar to Rayleigh scattering when p<1 and follows simple patterns for p>1 which evolve predictably as a function of p. These patterns allow us to present a unifying picture of the evolution of Mie scattering for changes in kR and m.

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C. M. Sorensen and D. J. Fischbach, ``Patterns in Mie Scattering, \ Opt. Commun. 173

1PA15

THEORETICAL ANALYSIS OF DATA FROM THE DMA-APM SYSTEM.

MARK EMERY, Peter McMurry (Particle Technology Laboratory, Minneapolis, MN, USA)

Rader and McMurry [1] describe a theoretical basis for evaluating data from the TDMA (i.e., DMA-DMA) instrument system. The TDMA has been used widely for studying processes that lead to changes in mobility size, such as water uptake, evaporation, or chemical reaction. In this paper we describe an analogous theoretical procedure for analyzing data from the DMA-APM (aerosol particle mass analyzer) instrument system. This analysis involves convoluting the transfer functions for the DMA [2] and the APM [3]. The DMA classifies particles according to electrical mobility, which depends on particle size and shape. The APM classifies particles according to mass-to-charge ratio, independent of shape or other particle properties. For singly charged particles, the APM classifies particles according to mass. The DMA-APM system has been used to measure particle density, shape factors, fractal dimensions, etc. It can also be used for first-principle measurements of aerosol mass distributions.

We studied the theoretical performance of the DMA-APM system to determine factors that determine measurement resolution. Resolution for the TDMA system is determined primarily by the ratio of sheath to aerosol flows. The resolution of the APM depends on a parameter that describes the ratio of axial to radial transport times for particles as they are transported through the annular classifying region of the APM. This parameter accounts for APM aerosol flowrate, angular velocity, and voltage. While the resolution of the TDMA is unaffected by the magnitude of the DMA2 voltage, the resolution of the DMA-APM system changes as the APM classifying voltage changes. We identify the dependence of system resolution on DMA and APM operating parameters, and determine the range of conditions that lead to acceptable system performance.

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1PA16

THE EFFECT OF MEAN FLOW ACCELERATION ON MICROPARTICLE DETACHMENT FROM SURFACES BY TURBULENT AIR FLOWS.

ABDELMAGED H. IBRAHIM and Patrick. F. Dunn Particle Dynamics Laboratory, Department of Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, IN, USA

Microparticles reside on surfaces and are subjected to a variety of flow conditions in different natural and industrial situations. In this work, stainless microspheres approximately 70 micrometer in diameter deposited on glass substrates were subjected to an accelerating air flow. The flow acceleration was controlled through a programmable controller and was varied from 0.014 m/s2 to 2.39 m/s2. Microvideographic images of the particles on the surfaces were acquired at different flow velocities. The detachment fraction of the particles was then determined versus the flow velocity at different mean flow acceleration. Two regimes of mean flow acceleration were identified: At relatively low mean flow accelerations, namely around 0.34 m/s2 or less, the data suggest that the detachment process is independent on the mean flow acceleration. However, at more rapid flow accelerations, namely from around 0.34 m/s2 to 2.39 m/s2, it was observed that the flow velocity required to detach 50% of the microparticles increases with the mean flow acceleration. Near-wall hot wire measurements suggest that this increase is due to non-equilibrium conditions in the boundary layer associated with rapid temporal mean flow accelerations.

1PA17

A COMPUTATIONALLY EFFICIENT METHOD FOR SOLVING DYNAMIC GAS-PARTICLE MASS TRANSFER DIFFERENTIAL EQUATIONS.

RAHUL ZAVERI, Richard Easter, Jerome Fast, Leonard Peters, Pacific Northwest National Laboratory, Richland, WA

Three-dimensional models of atmospheric inorganic aerosols need an accurate yet computationally efficient method for solving the gas-particle mass transfer equations. While H2SO4 is usually treated as a non-volatile species, the characteristic times for semi-volatile gases such as HNO3, HCl, and NH3 to reach equilibrium can vary widely between aerosol particles of different sizes, sometimes by several orders of magnitude. This makes the coupled system of ODEs extremely stiff, and hence computationally expensive to solve. In this paper, we describe the development and evaluation of a new algorithm called ASTEEM (Adaptive-step Species Time-split Explicit Euler Method) applied to a sectional aerosol framework. ASTEEM first solves the condensation of H2SO4 and NH3 for all the aerosol sections simultaneously over the host 3-D model time-step (usually ~5 min). It then solves the coupled condensation/ evaporation of HNO3, HCl, and NH3 gases for each section in a time-split fashion over a chosen time-splitting interval (TSI). The value of TSI is estimated such that the maximum overall change in the gas-phase concentrations of the semi-volatile species over the interval is less than ~10% (or a user-specified value). This approach significantly reduces the stiffness of the system, thus allowing the solver to take much longer time steps than are required when all the species in all the sections are integrated simultaneously. Accuracy and computational efficiency of ASTEEM is evaluated for several representative cases found in tropospheric aerosols. ASTEEM is part of the host model MOSAIC (Model for Simulating Aerosol Interactions and Chemistry), which includes a rigorous treatment of aerosol solid-liquid equilibrium, and a new, computationally efficient method for calculating activity coefficients. MOSAIC has been incorporated in PNNL’s 3-D chemical transport model PEGASUS and PNNL’s version of WRF-Chem. Performance statistics of ASTEEM/MOSAIC within these 3-D models for the SCAQS 1987 and TexAQS 2000 episodes will also be briefly discussed.

1PA18

REMOVE EFFICIENCIES OF PARTICLES FROM CLOTH AND PLANAR SURFACES BY AIR JET IMPINGEMENT. ROBERT FLETCHER, Nathanael Briggs, Jennifer Verkouteren, Allyson Fisher and Greg Gillen, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD

Particle removal from surfaces by pulsed air jets is an important process for industry, contamination control, forensics, and the identification of trace residues of explosives and narcotics for homeland security. Others have reported particle removal by air jets from clean surfaces (1-4). In our experiments, we utilize monodisperse fluorescent polymer spheres ranging from 1 µ;m to 45 µ;m in diameter distributed on polycarbonate surfaces and muslin cloth. Samples are prepared by wet and dry transfer as well as fingerprinting. Initial images of particle distributions are taken using a new automated fluorescence microscope system that locates a region of interest, auto focuses, irradiates with 488 nm radiation, captures an image, then challenges the region of interest with a pulsed air jet. After the sample is interrogated by the air jet, a subsequent fluorescence micrograph is acquired from the same region of the sample. This process is continued using automated sample stage control in order to examine a sufficient number of particles to produce statistically significant comparisons. Particle removal rates are determined by comparison of the before and after images using automated particle counting implemented by image processing. The auto focus feature enables us to examine samples on cloth substrates.

We found that the cloth surface has a particle release efficiency significantly higher than the polycarbonate wet transfer surface under similar jet conditions. However, the cloth surface releases particles at approximately the same rate as dry transferred spheres. As expected, there is a particle size dependence on removal rate. We are conducting a study to examine the release rates of agglomerated spheres that are preferentially removed from the surface and to learn the morphology of the released clumped particles. In the past, a conical jet with a 1 mm diameter opening has been employed. Other jet types are being explored such as an annular and a cylindrical jet. We are examining other substrates and particle materials that will realistically simulate explosive sampling media. One likely transfer method of particles is through fingerprints either onto cloth of flat surface. Tests on fingerprints will be reported.

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1PB1

ANALYSIS OF INDOOR PARTICLE SIZE DISTRIBUTIONS FROM AN OCCUPIED TOWNHOUSE USING POSITIVE MATRIX FACTORIZATION. DAVID OGULEI, Philip Hopke, Clarkson University; Lance Wallace, United States Environmental Protection Agency (Retired)

Human activity studies have shown that humans spend an average of at least 85% of their time inside buildings (66% in residential buildings) and another 5% inside vehicles (Klepeis et al., (2001), J. Expo. Anal. Environ. Epidemiol., 11(3), 231-252). While present indoors, personal exposure to airborne particles arises either from indoor sources or penetration of ambient particles present in outdoor air. For an occupied residential building, indoor particle sources such as cooking, sweeping, resuspension from clothes, etc, are often prevalent while outdoor particles are often from both mobile and stationary (natural or anthropogenic) sources. Each of these particle sources produce different size distributions that may be useful in studying the mortality and morbidity effects of airborne particulate matter since they will have different penetrability and deposition patterns. From 1999 through March 2001, measurements of particle number (10 nm - 20 µm in aerodynamic diameter), black carbon (BC) and particle-bound polycyclic aromatic hydrocarbons (PAHs) concentrations were made inside and outside of a townhouse occupied by two non-smoking adults and located in Reston, VA (approximately 25 miles northwest of Washington, D.C.). The particle size measurements were made using an SMPSTM and an APSTM (Models 3071 and 3320, TSI Inc., St. Paul, MN, respectively) as well as a Climet optical scattering instrument (Climet Instruments Co., Redlands, CA). The BC and PAH measurements were made using an aethalometer (Magee Scientific Co., Berkeley, CA) and a photoelectric aerosol sensor (PAS-1000 & 2000, EcoChem Analytics, League City, TX), respectively. Additional continuous monitors were employed to measure air change rates, wind speed and direction, temperature, and relative humidity (RH). In this study, Positive Matrix Factorization (PMF) is used to study the indoor particle size distributions. These size distributions or profiles are compared with profiles obtained from outdoor measurements in an attempt to apportion the relative contributions of indoor and outdoor sources to the observed particle concentrations inside of the townhouse. Since number concentrations tend to be very dynamic in the presence of indoor sources, such as cooking, PMF enables the individual down-weighting of some extreme data points that would otherwise distort the analysis. The results from this study will be presented.

1PB2

CHARACTERISATION OF ENVIRONMENTAL TOBACCO SMOKE (ETS) PARTICLES BY USING REAL-TIME MASS SPECTROMETRY. MANUEL DALL'OSTO, Roy M. Harrison, Division of Environmental Health and Risk Management, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K.; E. Charpantidou, G. Loupa and S. Rapsomanikis, Laboratory of Atmospheric Pollution and Control Engineering of Atmospheric Pollutants, Xanthi, Greece

An Aerosol Time-of-Flight Mass Spectrometer (ATOFMS; TSI 3800) was deployed at Athens (Greece) during August 2002. The ATOFMS provides information on a polydisperse aerosol, acquiring precise aerodynamic diameter (±1%) within the range 0.3 to 3 micrometers and individual particle positive and negative mass spectral data in real time. Sampling was carried out indoors and outdoors at an office in Athens. During this period, the ATOFMS was deployed under a broad range of different conditions i.e. different ventilation (natural and mechanically assisted ventilation). Different outdoor and indoor sources were apportioned. The smoke present in ambient air as a result of tobacco smoking (ETS) arises from a combination of sidestream smoke and exhaled mainstream smoke, both greatly diluted by the ambient air. Different classes of ETS particles were apportioned: ETS_tot1, ETS_tot2 and ETS_tot3 were potassium-rich particles (with different degrees of carbon) emitted directly from the exhaled mainstream smoke. ETS_smo1 and ETS_smo2 were instead detected when the cigarette was left smouldering on an ash-tray on the table. These particles were characterised by the presence of peaks at m/z -45, - 59 and -79, likely to be due to the formate [CHO2-], acetate [C2H3O2-] and [C3H3O2-] ions, respectively. ETS_84 presents a strong signal at m/z 84, most likely to be due to a nicotine fragment. This class is characterised by a very interesting temporal trend, showing how sorption of ETS compounds can greatly affect indoor particle concentrations. The results will be described and discussed in contrast to the ourdoor measurements.

1PB3

MICROPARTICLE MOTION RELEVANT TO HVAC SYSTEMS. ABDELMAGED H. IBRAHIM and Patrick. F. Dunn University of Notre Dame, Notre Dame, IN, USA

Microparticles reside in heating, ventilation and air conditioning (HVAC) ducts. Due to air flow inside the duct, the microparticles can detach from the duct surface and entrain into the air flow. In this work, different microparticles deposited on two different surfaces were studied over a series of flow velocities. The surfaces used were scanned with an atomic force microscope and a stylus profilometer to determine their roughness-height distributions at different length scales. The microparticle velocities during their motion along the surface were measured versus time using a high-speed camera. It was experimentally observed that the particle velocities exhibit large fluctuations in velocity. This causes the particle velocity to vary by approximately 50 % around the mean velocity at a free-stream velocity of 2 m/s and by approximately 5 % at a free-stream velocity of 6 m/s. This reduction in amplitude ratio is due to the combined effects of higher frequency components in the driving flow at higher flow velocities and the increase in microparticles rolling dissipation. The measured velocities of the particles will be presented, along with near-wall hot-wire flow velocity measurements. The resulting aerodynamic lift and drag forces on the microparticle will be estimated. The measurements will be compared to numerical simulations of the governing equations of motion.

1PB4

PERSONAL EXPOSURE TO AEROSOLS FOR WOMEN IN URBAN HOUSEHOLDS.

RASHMI S PATIL,Virendra Sethi, Suresh K Varghese and S Gangamma Centre for environmental Science and Engineering IIT,Bombay,India

It is being realized recently, that indoor sources are a greater threat to human health than outdoor sources, since people, especially women and children, spend larger percentage of their time inside homes. The most dominant source of indoor air pollution is domestic cooking. The aim of this study was to measure indoor exposure to aerosols in typical middle income urban households using LPG as cooking fuel in the city of Mumbai,India. Monitoring was done in three microenvironments viz. kitchen, living room and outdoors for cooking and non-cooking hours so that total personal exposure could be assessed. The purpose of the study was also to assess the effect of various control techniques to reduce exposure.Three cases were considered namely (i) natural ventilation (ii) a vented exhaust fan and (iii) a vented electric chimney. Sampling was done on a longitudinal basis that is with and without control techniques.

The results showed that the indoor concentration of particulate pollutant (PM5) was most of the times above the Indian regulatory standard. Particulates during non-cooking periods in the kitchen were mostly found in coarser mode with mass median aerodynamic diameter as 1.04µm and an average mass fraction of 0.69. Cooking generated very high concentration of particles, 4 to 5 times more than the non-cooking periods, with almost all of the particulate mass in the submicron size range. Particulate size distributions showed bimodal characteristics for both cooking and non-cooking periods. Accumulation mode (0.05-0.2µm) was found predominant during cooking. Taking into account the time activity pattern of the respondents, personal exposure was also estimated. It was found that cooking contributed upto 40% of the total exposure for women. There was considerable variation in exposure between houses due to factors like type of food cooked, placement of stove, size of kitchen and most prominently because of direction of air exchange rate.Results showed that considerable improvement in indoor air quality can be achieved by using mechanical facilities like exhaust fan and electric chimney.

The use of exhaust fan reduced the concentration of particulates during cooking and total exposure by 63 % and 73 % respectively.The study demonstrated that the most effective way to reduce exposure in developing countries is to ensure proper ventilation through appropriate building codes.

1PB5

EFFECTS OF COAGULATION ON AEROSOL DEPOSITION ONTO AN ISOTHERMAL VERTICAL FLAT PLATE.

C.B. Huang, C.S. Lin, Yuan Ze University, Taiwan, ROC

Deposition onto surfaces is a commonly observed phenomenon for particles in indoor air. Examples of this phenomenon include submicro and micro particles deposit onto wafers in the cleanroom, tobacco smoke or bioaerosol deposits in lungs, and paintings or other works of art soiled by dust and ash. To eliminate aerosol deposit onto surfaces, it is important to investigate both the distribution of aerosol concentration and aerosol dynamics within the boundary layer near surfaces. The aerosol dynamic behavior along an isothermal vertical flat plate is investigated in this study. The height of plate is 3 m, and maximum temperature difference between the plate and surrounding air is 20K so that the flow field along the plate transits from a laminar into a turbulent flow. The main computational scheme is based on a boundary layer type solution combining the flow field and sectional aerosol simulation. The SIMPLE method is adopted to solve the flow continuity, momentum, energy, and aerosol concentration equations. Various transport and removal mechanisms of aerosol dynamics, including fluid convection, Brownian motion, gravitational settling, thermophoretic drift, and coagulation of aerosols, are considered in the simulation model. The effects of aerosol coagulation on particle transport and deposition onto an isothermal vertical plate are addressed.

1PB6

AGEING OF SIDESTREAM & ENVIRONMENTAL TOBACCO SMOKE. JOHN McAUGHEY and Conor McGrath, British American Tobacco, Southampton, UK

Sidestream tobacco smoke (SS) is a complex, dynamic aerosol, generated at the tip of the cigarette during puff and smoulder phases. Environmental tobacco smoke (ETS) comprises SS and exhaled mainstream (MS) smoke, the latter contributing 15-43% of particulate matter to ETS (Baker and Proctor, 1990).

Various size data have been reported for SS and ETS with number median diameters from approximately 100–200 nm (Jenkins et al, 2000). The diameter reflects a combination of smoke age, composition, concentration, room ventilation, and continuing dynamic behaviour. Recent data published by Morawska et al, 1997 have indicated initial ETS peaks in the 60 to 90 nm range post-generation, with subsequent growth over the following 30-60 minutes.

In this work, an aged and diluted sidestream smoke was generated by machine smoking cigarettes in a sealed 20 m3 chamber. Environmental tobacco smoke was generated by 10 smokers, in a 120 m3 meeting room ventilated at 10 air changes per hour.

Particle concentration and diameter were measured by sequential 150s scans by a Scanning Mobility Particle Sizer (SMPS: TSI Model 3936L10) and at 1s intervals by a Condensation Particle Counter CPC: TSI Model 3022) and an Electrical Aerosol Detector (TSI Model 3070A). The combination of EAD and CPC will yield aerosol length (d1 diameter), particle concentration and a mean diameter (EAD/CPC). Additional measurements were conducted with fast electrical mobility spectrometers for comparison (DMS500, Cambustion UK and EEPS, TSI Model 3090). These measurements included ‘fresh’ mainstream and undiluted sidestream smoke.

Chamber data for SS & ETS both show a clear pattern of build-up and decay with particle half-times of 11.3 minutes (unventilated) and 3.9 minutes (ventilated) respectively. CO half-time in the unventilated room was 28 minutes. Increases in number median diameter over time through particle accumulation were observed for the unventilated chamber.

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1PB7

ON THE RESEARCH OF THE MICROENVIRONMENT BY USING OF CONTROLLABLE NUCLEAR EMULSION. A. B. Akopova, M.M.Manaseryan, A.A. Melkonyan, S.Sh. Tatikyan

This paper summarizes the results of the measurements of the microenvironments on the board and inside of the cabin of different cosmic apparatus and civil aviation planes, caused by flaxes of charged particles (nuclei with $z \geq 6$) and fast neutrons ($E=1\text{-}15MeV$). Nuclear photoemulsion with different sensitivity BR and BY types of layers were placed inside of the cabin of crews and at the different fixed locations on the board of many Kosmos-type satellites, space Shuttles, orbital stations MIR, ISS and on board of aircrafts as well. Nuclear emulsion plays an important role in space radiation dosimetry, which possesses the same combination of features - small size and mass, zero power and robust design.

Development and scanning of the emulsion layers have yielded data on the integral LET spectra of charged particles and on the differential spectra of fast neutrons. These data were used to calculate the absorbed and equivalent doses from the charged and neutral cosmic ray component. These results are important in order to minimize the risk due to radiation exposure.

1PC1

A NEW, LOW-COST BAM MONITOR FOR PM10, PM2.5 AND ULTRAFINE PM MASS DESIGNED FOR COMMUNITY-SCALE EXPOSURE MEASUREMENTS. SATYA SARDAR, Bhabesh Chakrabarti, Constantinos Sioutas, Philip M. Fine, University of Southern California, Los Angeles, CA; Brad Orton, David Gobeli, Met One Instruments, Grants Pass, OR

Using a single central monitoring site to assess human exposure to air pollution can miss some of the community-level variation found on smaller spatial scales. The problem is more pronounced for pollutants such as ultrafine particles, which can vary significantly with distance from their sources. Thus, accurate intra-community human exposure measurements are needed for epidemiological studies assessing the health impacts of such pollutants. Since these efforts will require many instruments located throughout the community of interest (saturation monitoring), there is need for accurate, lower-cost, low-maintenance, and user-friendly PM monitors. Continuous or semi-continuous data is also desirable to capture the daily temporal variation in PM levels. Beta-Attenuation Monitors (BAMs) have been shown to provide accurate PM mass measurements on 24-hour and hourly bases. But the current cost limits the number of monitors that can be deployed within a community of interest. In collaboration with Met One Instruments, Inc., a simplified low-cost BAM monitor was developed to address these community monitoring needs. The target cost is approximately $3000 per unit, allowing for deployment on finer spatial scales. The new instrument was tested for accuracy against commercially available BAM units, as well as an array of other filter-based samplers and continuous PM instruments. Low-cost size-selective impaction inlets were also developed to provide PM10, PM2.5 and PM0.18 (ultrafine) cut-points for the new monitor. Results include a full performance assessment of the new BAM monitor under various operating conditions such as the length of the sampling period and the different inlet configurations. Transmission efficiency curves for the new inlets are also reported.

1PC2

IMMUNOCHROMATOGRAPHIC METHOD OF REAL TIME DETECTION OF LEGIONELLA IN THE AIR. S.F.Biketov, V. D. Potapov, I.M. Baranov, E.V. Baranova, State Scientific Center of Applied Microbiology, Obolensk, Moscow region, Russia, V.I. SIGAEV, A.D. Tolchinsky, K.G. Soloviev, S.N. Uspenskaya, R.V. Borovick, N.R. Dyadishchev, Research Center for Toxicology, Hygienic Regulation of Biopreparations, Serpukhov, Moscow region, Russia

In 1976 the agent of legionella disease was identified. Since then it has been observed more frequently in the USA, Europe, Asia and Australia. This is connected with man-made transformation of the environment favorable for reproduction and spread of legionella in different water objects. Aerogenic contagion, difficulties of the disease and high death-rate justify considerable interest to this infectious agent and to the development of methods for its detection in the environment. Most attention is paid to detection of legionella in the air of the most probable industrial and residential area since fine aerosol is the main mechanism for legionella spread. Immune methods have recently become widely used for express-diagnostics of legionella.

The aim of the study was to develop immunochromatographic methods for legionella detection in air and to obtain results on-site. For air sampling we used liquid cyclone sampler designed earlier, with recirculating liquid film and volume airflow of 60 l/min (Proceedings of AAAR 2001, p.406). We used L.micdadei lipopolysacharide (LPS) as immunogen to obtain specific monoclonal antibodies. For visualization of “antigen-antibody” complexes collaurin particles (of 15 µm) were used as a tag. Membrane carriers were made by Schleicher&Schuell firm (FF 60/100 type). For easy and effective real-time detection of legionella we accomplished competitive immunochromatographic method of analysis. The volume of liquid under analysis made up 50 µl. On test-strips specific reactions in the form of two colored strips were revealed once no less than 104 cells/ml of L.micdadei were put into entry cells. Cross-reactions at other bacteria inoculation (up to 109 cells/ml of E.coli, S.pullorum et al.) were not revealed.

L.micdadei fine aerosol (D50-2.0µm) was created in aerosol dynamic chamber. The device developed before was connected with aerosol chamber (Proceedings of AAAR 2002, p. 270). The device included sampler with exhaust device and immunochromatographic unit. After air sampling during the specified time aliquot of sorbent liquid from the sampler went automatically into entry cell of the plate with chromatographic strip zonally covered by immune reagents. After dyed control and analytical zones were formed they were scanned using laser (680nm) and photodiode matrix. Matrix signal was digitized and processed by special computer program. Total detection time made up 30 minutes (15 minutes – air sampling, 15 minutes – analysis). Detection sensitivity achieved in chamber experiments made up 5x104 cells of L. micdadei/ml.

Therefore fine L.micdadei aerosol cited as an example proved to have potential for real-time detection of legionella by immunochromatographic method. In further studies specific monoclonal antibodies with fluorescent tag will be used, what will ensure considerable improvement of detection sensitivity.

The study was conducted under financial support of US DTRA in the framework of the #1487p project of the International Science and Technology Center (ISTC), Moscow.

1PC3

CHARACTERISTICS OF SILVER NANOPARTICLE GENERATION BY SPARK DISCHARGE USING AIR AS A CARRIER GAS. HYUNCHEOL OH, Hyungho Park, Sangsoo Kim, KAIST, KOREA; Junho Ji, SAMSUNG ELECTRONICS CO., KOREA.

A pulsed spark discharge aerosol generator using air as a carrier gas has successfully been applied to silver nanoparticle production in connection with an evaluation of by-product gases such as ozone and NOx. The spark discharge between two silver electrodes, which was periodically obtained by discharging the capacitor, produced sufficient high temperatures to evaporate a small fraction of the silver electrodes. The silver vapor was subsequently supersaturated by raid cooling and condensed to silver nanoparticles by nucleation and condensation.

Gap distance of two silver electrodes of 3 mm diameter was precisely adjusted by micrometer. Experiments were conducted for spark electrode gap distance from 0.3 to 0.7 mm, and air flow rates for 2 to 10 lpm, repetition frequency from 20 to 120 Hz, capacitance for 5 to 12.5 nF. The particle size distribution was measured using a SMPS system and some fraction of spark-generated particles was sampled on TEM grids or glass fiber filters for further particle characterization.

The particle mode diameter and the particle concentration increased as capacitance, frequency, gap distance increased and flow rate decreased. This implies that silver evaporation rate is increases with increasing spark energy, which is function of capacitance, frequency, gap distance. The morphology of the generated particles observed by transmission electron microscope was spherical and the element composition of the nanoparticles was silver, which was determined by energy dispersive spectrometer (EDS).

The crystal phase of the particles spark-generated under air atmosphere was composed of silver and silver oxides phase, which was determined by X-ray diffraction (XRD) analysis. While the nanoparticles generated under nitrogen atmosphere had only silver phase. This indicates that some fraction of the evaporated silver vapor could be oxidized in air atmosphere by the reaction with oxygen.NOx production rate of spark discharge in air atmosphere was increased monotonously with spark energy. While, ozone production rate shows complex features. For example, Ozone concentration decreased with increasing spark energy or decreasing flow rates for some experimental conditions. This may be due to effects of ozone reduction by oxidation and decomposition of silver nanoparticles.

A stable operation of the spark discharge generator has been achieved, and the size and concentration of the particles can be easily controlled by altering the repetition frequency, capacitance, gap distance and flow rate of the spark discharge system.

1PC4

FIELD EVALUATION OF A HIGH-VOLUME DICHOTOMOUS SAMPLER. SATYA BRATA SARDAR, Bhabesh Chakrabarti, Michael D.Geller, Constantinos Sioutas, Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA; Paul Solomon, US EPA, Las Vegas, NV

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 1000 lpm with major and minor flows of 900 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 160 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 = 11) of high-volume to MOUDI measured coarse PM concentration being 0.89 ± 0.06. 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 0.93 ± 0.08). 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 are 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.

1PC5

NUCLEATION SENSOR COMBINED WITH GAS CHROMATOGRAPHY. VLADIMIR B MIKHEEV, InnovaTek, Inc, Richland, WA; Richard Lee, Oleg Egorov, Nels Laulainen, Stephan Barlow, Kenneth Swanson, Pacific Northwest National Laboratory, Richland, WA

Nucleation Sensor based on Laminar Flow Tube Reactor (LFTR) has been combined with Gas Chromatography (GC) in order to develop new technology for the ultra-sensitive detection of chemical weapons (CW) and compounds associated with nuclear material production (NMP).

After passing through the GC-column, trace amounts of the analyte molecules (normally irradiated by UV-light) are injected into the condenser part of the LFTR, causing nucleation (new particle formation) of the supersaturated host vapor (dibutylphthalate or ethylene glycol). Freshly formed (nucleated) aerosol particles are detected by an optical counter.

Preliminary tests were run with mixture of the CW-surrogates (2-chloroethyl ethylsulfide, dimethylmethyphosphonate, diethylmethylphosphonate, diisopropylmethylphosphonate) and with mixture of the compounds associated with NMP (n-butanol, n-amylnitrate, tributylphosphate).

Although during these preliminary tests LFTR-GC interface was not optimized (wall losses of the analyte molecules can be estimated at the level of several orders of magnitude), ~0.2 ng of the analyte compounds were detected.

Different sensitivity of the host vapors (dibutylphthalate and ethylene glycol) to the analyte molecules (nucleation rate of the host vapor on the analyte molecules) has been observed.

1PC6

THE EFFECT OF WIND SPEED AND ORIENTATION ON SAMPLER PENETRATION CURVES. PATRICK O'SHAUGHNESSY, Vijay Golla, University of Iowa, Iowa City, IA Jason Nakatsu, Stephen Reynolds, Colorado State University, Fort Collins, CO

Aerosol sampler penetration curves were determined using a novel method in both still-air (down-flow 1 cubic meter chamber) and moving-air environments (wind tunnel at 0.2 and 1.0 m/s). Specially formed cylinders with a conical inlet were fabricated to hold the inlet portion of personal samplers in order to sample particles penetrating the inlet directly with a multi-channel particle counter while holding the samplers in their proper orientation on a human torso mannequin. ISO test dust was generated in both environments. Particle counts in each of 15 size channels were compared when the sampler configuration was attached versus detached from the counter. When detached, a straight smooth tube was used to sample air by the counter. Likewise, a second counter placed in the same environment was used to normalize the temporal variation in aerosol concentrations. Results obtained from IOM and Button inhalable samplers, an SKC respirable cyclone, and three-piece closed-face cassette were compared over a particle size range of 0.3 to 15 microns. Results indicated that the size-selective samplers (IOM, Button, and cyclone) matched their respective ideal definition curve best when sampling in the 0.2 m/s environment with oversampling relative to the definition in still-air and undersampling at 1.0 m/s air. The curves for the IOM and Button were well matched except at 1.0 m/s where the IOM oversampled relative to the Button. As expected, the closed-face cassette undersampled relative to the inhalable samplers. During the wind-tunnel tests, the mannequin was held in one of 3 positions relative to the wind direction (facing, side, and downwind). An average effect was calculated from the data obtained from all positions. Likewise, curves were generated for each position. Results showed a large discrepancy in the curves between positions. These results demonstrate significant differences in the penetration curve of samplers when sampling in varying wind environments and orientations to the wind. However, the results are to be interpreted relative to one another and cannot be taken as absolute measures of penetration because they are based on the unknown penetration of the straight smooth tube.

1PC7

DESIGNING AERODYNAMIC LENSES FOR NANOPARTICLES.

XIAOLIANG WANG, Peter H. McMurry, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN; Frank Einar Kruis, Process and Aerosol Measurement Technology, University Duisburg-Essen

Narrow particle beams with small divergence angles are used in many applications to enhance transport efficiency, improve measurement resolution or deposit micropatterns precisely on substrates. Aerodynamic lens systems (Liu, et al., 1995a, b) have been widely used to produce such collimated particle beams. Conventional designs for aerodynamic lenses effectively collimate particles as small as 30 nm. However, the focusing performance degrades dramatically for particles smaller than 20 nm. The major challenges in focusing sub-20 nm particles arise from their low inertia and high diffusivity. Because of their low inertia, nanoparticles tend to follow the gas streamlines very closely and only minor focusing can be achieved. The focusing of nanoparticles is further degraded by their high diffusivities, which lead to particle loss and beam broadening.

We focus on designing aerodynamic lens systems to focus nanoparticles in this presentation (Wang, et al., 2005a). A simple viscous flow model is used to estimate the flowrate and pressure drop through orifices with reasonable accuracy. We first determine the minimum particle size that can be focused exactly onto the axis with a single lens provided diffusion is absent. We then describe a systematic procedure to find proper lens geometries and operating conditions for nanoparticle focusing. Special attention was directed to increase the inertia and limit the diffusion of nanoparticles. Finally, we provide a case study that illustrates the use of this procedure for designing an aerodynamic lens to focus 5 nm spherical particles of unit density using helium as the carrier gas. We prove the validity of the design procedure by comparison with the detailed flow simulation using computational fluid dynamics (CFD) and particle trajectory simulation by solving the Langevin equations (Wang, et al., 2005b).

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1PC8

NANOPARTICLE SURFACE AREA MONITOR FOR OCCUPATIONAL HEALTH EFFECTS STUDIES.

MANISHA SINGH, Brian L. Osmondson, TSI Incorporated, Shoreview, MN

There is ever increasing interest to commercially develop nano-scale materials, structures and devices to take full advantage of the unique properties affecting physical, chemical and biological behavior that result. However, occupational health risks associated with manufacturing and use of nanoparticles are not clearly understood. Subsequently, workers may be exposed to these nanoparticles through means of inhalation, at levels that greatly exceed ambient concentrations.

Current workplace exposure limits are based on particle mass. However, a growing number of experts contend that the surface area, rather than mass, should be measured because nanoparticles have far more surface area for the same amount of mass of larger particles, which increases the chance they may react with the body (Shanbhag et al., 1994; Oberdöster, 1996; Donaldson et al., 1998). As a result, the need has arisen to assess workplace conditions and personal exposure to engineered-nanoparticles based on the measurement of particle surface area.

The Electrical Aerosol Detector (EAD, TSI model 3070A) measures particle current following unipolar diffusion charging. Wilson et al. (2004) reported that the EAD signal is highly correlated (R2 ranging from 0.82 to 0.87) to the calculated amount of surface area deposited in the lung; the absolute relationship between the EAD signal and the surface area deposited being a function of breathing rate and tidal volume as determined by the level of exertion.

Recently, a Nanoparticle Surface Area Monitor (NSAM, TSI model 3550) has been developed. The instrument is based on EAD technology but features an improved design that brings the instrument response even closer to the surface area dose. The NSAM measures the surface area of particles deposited in different areas of the lung corresponding to specific breathing patterns (eg. resting and nose breathing, light exercise and mouth breathing etc.). This technique provides a simple and fast solution for measuring the surface area dose. Applications of the instrument in the area of occupational health and exposure are discussed.

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1PC9

DEVELOPMENT OF DIGITAL MICRO FLUIDIC IMPACTOR FOR REAL-TIME MEASUREMENT OF THE AEROSOL CHEMICAL COMPOSITION. ANDREY KHLYSTOV, Yilin Ma, Dept. of Civil and Environmental Engineering, Duke University, Durham, NC; Vladislav Ivanov, Richard Fair, Dept. of Electrical and Computer Engineering, Duke University, Durham, NC

Knowledge of chemical composition of ambient aerosol is of critical importance for understanding a multitude of environmental problems. Knowledge of aerosol chemical composition at different particle sizes is required for prediction of light scattering by the aerosol as well as its effect on clouds. Cascade impactors are the most widely used instruments for measurements of aerosol size-segregated composition. However, impactors require a large amount of manual handling to obtain one sample, which makes their application for long term monitoring extremely expensive. Impactors also have a low time resolution (several hours) which hampers their use on aircraft.

The rapid development of micro-fluidic techniques (or Laboratory-on-Chip - LoC) for determination of inorganic and organic substances allows us to develop micro fluidic substrates integrated with cascade impactors for automated measurements of major inorganic ions in ambient aerosol. Micro-fluidic impaction substrates offer fast analysis and small reagent consumption. Due to the small quantities of analyte needed for detection, these systems have the potential to offer lower limits of detection and/or faster analysis times (of the order of a minute) for determination of size segregated chemical composition of the ambient aerosol when integrated with cascade impactors, such as the Micro-Orifice Uniform Deposit Impactors (MOUDI).

We describe the development of a prototype system that integrates a single stage impactor with a digital micro-fluidic substrate for determination of sulfate in aerosol. The aerosol is impacted directly onto the surface of a Teflon-coated micro-fluidic chip. After a brief collection phase, the collection surface is extracted with a micro-liter droplet of ultra pure water that is digitally directed across the surface dissolving collected aerosol constituents. The extraction droplet is then mixed with sulfate-specific reagents that produce a colored reaction. The concentration of the analyte is determined by measuring absorption at a specific wavelength using an on-chip light-emitting diode and a photodiode detector.

1PC10

ESTIMATION OF PARTICLE DENSITY USING A CPC AND ELECTRICAL LOW PRESSURE IMPACTOR. HENNA TUOMENOJA, Ari Ukkonen, Erkki Lamminen, Ville Niemelä, Pirita Mikkanen, Dekati Ltd, Tampere, FINLAND

Measurement of aerosol particle density is of general interest in both scientific and industry aerosol applications. The most common way to do this is to match aerodynamic and electrical mobility classified particle number distributions to find the effective density of the particles. This technique has been widely used by measuring the particle size distributions with an Electrical Low Pressure Impactor (ELPI, Keskinen et al 1992) and a Scanning Mobility Particle Sizer (SMPS). In this work a more simplified method for aerosol particle density estimation is discussed.

ELPI is a real-time particle size distribution measurement instrument combining a cascade low-pressure impactor with a diffusion charger and electrical detection. ELPI measures particle number size distribution divided in 12 size fractions from 7 nanometers to 10 micrometers. Because particle size classification is carried out according to particle inertia, aerodynamic particle size distribution is acquired. However, the particle charging process is dependent on the particle stokes diameter, and therefore the resulting particle number concentration is dependent on the used particle density in the calculation.

Dekati Condensation Particle Counter (CPC-1500) counts single particles from 4 nm to 3 μm with a maximum concentration of 100000 part./cm3. The particle number concentration measured with the CPC is independent of particle density. If aerosol particles with unknown density are measured with the ELPI and CPC, the two measured number concentrations may differ because of different effect of density on the results. The effective aerosol particle density can now be found by re-calculating the ELPI result with different densities until the ELPI and CPC number concentrations match.

The method was first verified by measuring particles of known density (DEHS, r = 0.91 g/cm3) with an ELPI and CPC-1500. The ELPI results were found to match the CPC with density of 0.82 g/cm3 and the used method was found to be effective for estimating particle density. The error of 10% in the result is caused by different measurement ranges of the two instruments and measurement accuracies of the devices and the setup.

After the verification, the described method was used in estimating the density of ambient air particles in different conditions. Measurements were conducted in urban and rural conditions. The method, and the results from these measurement are presented in more detail in this work.

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1PC11

REAL TIME MEASUREMENT OF FUGITIVE NANOPARTICLE EMISSION.

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The characterization of the particles produced by interactions between laser and material is faced with the measurement of fugitive emission of nanoparticles, for which real time data acquisition is mandatory. Real time analysis of fugitive nanoparticle emission is now possible thanks to two kinds of aerosol measurement devices, such as the Electrical Low Pressure Impactor (ELPI) and the Engine Exhaust Particle Sizer (EEPS).
In the frame of the study of the aerosol produced by laser ablation of paints from concrete surfaces, we have developed an experimental set-up based on a pulsed Nd:YAG laser. The concrete target sample is mounted in a ventilated cell of 100 cm3; the ventilation flow rate is fixed at 20 l/min. The experiments consist in carrying out single laser shootings on the target. The particles produced by ablation are directly sampled at the cell exhaust and measured simultaneously with an ELPI working in the range 7 nm - 10 µm and an EEPS working in the range 6 nm - 560 nm. For these two particle sizers, the complete size distributions is achieved in 1 s.

The concentration of the nanoparticles is determined below 560 nm on a common size range to the ELPI and the EEPS; one can observe a time evolution with a rapid increase of particle concentration followed by a decrease corresponding to the cell ventilation. However, we observe a peak of concentration during 4 s for the EEPS measurements, but in the case of ELPI measurements, the peak is broadened and remains during 12 s. For ELPI, we note that 52 % of the number of particles have an aerodynamic diameter below 29 nm (Dae) corresponding to the cut off diameter of the first impaction stage and for EEPS the median mobility diameter (Dm) is 41 nm. These results show that Dm is greater than Dae; if we assume that these nanoparticles are spherical, the particle density has to be smaller than 1.

In conclusion the measurements performed with ELPI and EEPS show that real time determination of the nanoparticle size distribution is possible. However, attention has to be paid on the fact that the concentration time evolution given by ELPI is broadened in respect with the one determined by EEPS. One explanation of this result could be derived from some different plug volumes at the entry of each measurement device.

1PC12

A NEW THERMOPHORETIC SAMPLING DEVICE FOR COLLECTION OF ULTRAFINE PARTICLES.

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Ultrafine particles (diameter < 100nm) are suspected to have an adverse effect on the human health. To understand the mechanism by which these effects are triggered and why some particles are worse than others, it is essential to determine parameters such as chemical composition, shape, internal structure and composition of the particles. All these parameters can be determined using a transmission electron microscope (TEM). To exclude artefacts related to the sample preparation, particles are best collected directly onto TEM grids. This can be achieved by using a thermophoretic sampling device as described in this study.

Since the thermophoretic effect is independent of particle size or composition, a homogeneous distribution of particles on TEM grids can be realized. Our device is based on a prototype described by Maynard (1995) and is designed for field use. A pump is combined with two mass flow controllers which allows an independent adjustment of the sample flow (2l/min) and the main air flow (3l/min) to the sampler. The temperature gradient can be varied between 2.5e5 K/m and 5.5e5 K/m by individually controlling the temperature for the hot (100 - 160°C) and cold pole (0 - 20°C) which are 0.3mm apart. Thus, the sampler can be adjusted to various conditions. By restricting the size of the hot and cold area to the size of a TEM grid and magnetically attaching the grid to the cold pole, particles will be collected directly onto the grid.
All adjustable parameters can be set on a LabView interface and are continuously logged and displayed in real time. Changing conditions are easily detected and can be compensated.

Prior to the calibration of the device, a numerical evaluation of the key parameters such as flow rate and temperature gradient was performed. These calculations were used to optimize the settings of the device regarding short sampling times and minimal size fractionation of particles. Using these settings, sampling times for urban background particle concentrations will be less than an hour for 0.1% coverage of a TEM grid, which is enough for TEM work. Calibration experiments with synthetic polydisperse aerosols will be used to validate our calculations.

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1PC13

SHROUDED INLET FOR AIRBORNE MULTI-ANGLE-LIGHT-SCATTERING SPECTROMETER.

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The multi-angle-light-scattering spectrometer (MLS) is an airborne instrument designed to measure phase function, sphericity, and size of individual particles for a wide range of particles in different atmospheric conditions. These measured particle properties will be used to provide real aerosol characteristics needed to interpret remote sensing observations.

To ensure representative aerosol sampling with respect to number concentration and size distribution we designed a shrouded inlet to be used for aircraft sampling. The shrouded inlet has two main functions: to achieve isokinetic sampling conditions at the aerosol inlet and to straighten the aerosol trajectories for small aircraft pitch angles.

Using a computational fluid dynamics program, the design of the shroud was optimized to satisfy several requirements for sampling. The flow computation takes into account not only the shrouded inlet but also the entire instrument pod behind the inlet. The shroud is mounted coaxially with the inlet, and has two cylindrical sections connected by a conical section. The air enters the smaller cylinder and exits through the annular space between the larger cylinder and the aerosol inlet. By controlling the exit area of the shroud it is possible to maintain nearly isokinetic conditions at the aerosol inlet. The shrouded inlet has been designed for a cruising velocity of 50 m/s, so the flow has been modeled as turbulent, incompressible flow. The aerosol inlet has two conical diffusers to reduce the velocity from 50 to 5 m/s, which is a requirement for the optical sensor. The flow field was also calculated inside the sampling tube to ensure that flow separation does not occur inside the diffusers.

Once the airflow pattern was determined and optimized, aerosol particles trajectories from the shroud to the aerosol inlet were calculated numerically. The particle trajectory calculations were used to estimate the particle transmission efficiency from the shroud to the end of the sampling inlet as a function of particle diameter (0.5 to 15 micrometers) and pitch angle (0 to 5 degrees). The particle trajectories took into account aerodynamic drag, gravity and inertial effects.

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1PC14

INTERCOMPARISON OF THREE TECHNIQUES TO MEASURE AEROSOL CONCENTRATION FOR NIST TRACEABLE METROLOGY.

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Accurate aerosol concentration measurements are important in many applications of aerosol science and technology. This work compares the measurement results of three independent techniques for measuring number concentration: continuous flow condensation particle counter (CPC); aerosol electrometer (AE) and the aerosol concentration derived from microscopic particle counting. Because of the transient nature of aerosol, there are no concentration artifact standards such as exist for particle diameter standards. We follow the approach of Liu and Pui (1) by employing a mobility classifier to produce ideally a nearly monodisperse, 80 nm, polystyrene latex, singly charged aerosol. The test aerosol is used as a challenge for the CPC and the AE, and is subsequently filter-sampled for electron microscopy. Our test stand design incorporates a continuous CPC aerosol concentration monitor to verify the aerosol stability and the continuous measurement of pressure, temperature and flow rate. The CPC determines particle concentration by single particle optical counting at a constant sample flow rate. The AE has been calibrated to a NIST traceable current standard and the subsequent aerosol concentration measurement is obtained by determining the electrical current at a controlled aerosol flow rate. In the past, there has been a persistent bias in the AE-CPC comparison resulting from multi-charged particles. We were able to overcome the charge induced bias by using an electrospray aerosol generator to produce the challenge particles. This generator was able to produce aerosol concentrations over the range of 100 to 15,000 particles/cm3 with particle double production rates at approximately 0.5%. In our work, independent measurement of aerosol concentration is obtained by quantitatively collecting samples of the airborne polystyrene latex spheres on a small pore filter material and determining the number of particles collected by electron microscopy. Electron micrograph images obtained using a field-emission scanning electron microscope are analyzed using particle analysis software. We have NIST traceability for flow rates for all methods and a methodology to calibrate the AE to NIST traceable electrical standards. The latter provides a calibration and a determination of the uncertainty in the aerosol derived current measurement. Results of the comparisons and estimates of the uncertainties associated with the measurements will be presented.

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1PC15

FIELD EVALUATION OF P-TRAK ULTRAFINE PARTICLE COUNTERS.

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Ultrafine particles have been suggested as a possible causative agent for the increase in mortality and morbidity associated with increases in particulate matter concentration. The P-trak Ultrafine Particle Counter is a portable version of a condensation particle counter (CPC). Both instruments detect particle number concentrations in real time but have different detection limits. P-trak has been widely used for indoor air quality evaluation and aerosol research. However, there is very limited information about the reliability and precision of this instrument and its comparability with other similar instruments. The purpose of this study was to compare the P-trak ultrafine particle counters with a standard CPC and evaluate its applicability to ambient air monitoring.

This study was carried out near the I-405 freeway where the concentration of ultrafine particles is much higher than other areas away from sources. Measurements were made at increasing downwind distances from the freeway as well as in two 2-bedroom apartments near the freeway. A CPC and a Scanning Mobility Particle Sizer (SMPS) were used to sample side by side with two P-traks and the results compared.

In general, for outdoor measurements, the P-trak and CPC instruments showed better agreement with increasing distance from the freeway. Higher correlations were observed between P-trak and CPC data for indoor measurements than outdoor. The highest P-trak and CPC correlation (r^2=0.9385) was detected inside Apartment 2, which is located farther away from the freeway than Apartment 1. The poorest correlation occurred at 30 m downwind from the freeway. In that case, the P-trak reported about 25% of ultrafine particle concentration that CPC did. Based on collected SMPS data, we identified two types of ultrafine particle size distributions, one with the dominant mode diameter at 15 nm and the other at 30 nm. Correlations between the P-trak and the CPC were better for the latter case.

Overall, we concluded P-trak worked reasonably well when sampled indoor air. However, it has significant limitations in detecting freshly emitted ultrafine particles from vehicles. The P-traks underestimated ultrafine particles especially for particles smaller than 30 nm. Caution must be given in interpreting data collected by P-traks near sources.

1PC16

COMPARISON OF MEASUREMENT INSTRUMENTATION UNDER VARIOUS TEST CONDITIONS.

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For the last four years, Diagnostic Instrumentation and Analysis Laboratories (DIAL) has undertaken a HEPA filter monitoring study establishing the failure signatures and source term responses of industry-standard HEPA filters. The technical challenge has been to provide accurate particle size distributions and number density data up and downstream of a HEPA filter and to correlate these values with data gathered by EPA Reference Method 5 (RM5) or 5i (RM5i). Tests have been conducted over a broad range of filter challenge conditions: RH levels between 15% and 95%; particulate materials including KCl, NaCl, sugar, and DOP; and particle size distributions with count median diameters from 100 nm to 400 nm. The need to measure both upstream and downstream of a high-efficiency filter has produced characterizations at extremes of particle concentration. Typically, upstream concentration levels were around 30 mg/m3 or 200,000 particles/cm3; concentrations downstream of partially loaded filters dropped below 0.001 particles/cm3.

Throughout the testing, RM5i samples have provided benchmark measurements of the aerosol mass concentration upstream of the filter, and a Pilat cascade impactor has supplied a gravimetrically-determined mass distribution. Additionally, DIAL has employed several instruments to continuously monitor the upstream aerosol, including a Scanning Mobility Particle Sizer (SMPS), an Aerodynamic Particle Sizer (APS), and an Electrical Low Pressure Impactor (ELPI). Data from these instruments have been compared to RM5i and impactor samples collected concurrently, and correlations have been determined for the several aerosols encountered during conduct of the testing. RM5i and an impactor are robust enough to produce valid results under most test conditions; however, the least-optimal test conditions (such as elevated relative humidity or high particle concentrations) often require the SMPS, APS, and ELPI to operate outside customary bounds, producing less accurate results and limiting the correlation to the direct mass-reading techniques. The differences among the methodologies of these instruments produces disparities under most conditions, and uncertainty is introduced because particle density and shape are required to calculate aerosol mass and, for the APS and ELPI, number concentration as well.

Mass measurement techniques are generally not suitable for the low concentration levels encountered downstream of high-efficiency filters. The downstream concentration levels were continuously monitored by two instruments: a Condensation Particle Counter (CPC) and a Laser Particle Counter (LPC). The correlation between the data collected concurrently by the two instruments were examined for each aerosol used.

1PC17

CHARACTERIZATION OF TWO NEW BUTANOL-BASED CONDENSATION PARTICLE COUNTERS (TSI MODEL 3776 UCPC AND 3775 CPC). QIAN SHI, Hee-Siew Han, Steve Kerrigan, Ed Johnson, TSI Incorporated, Shoreview, MN

Condensation particle counters (CPCs) are widely used airborne particle detectors in scientific aerosol research and other particle related applications. This paper presents design and performance characteristics of two new TSI CPCs, the model 3776 Ultrafine CPC (UCPC) and model 3775 CPC, which are the upgraded replacements of the TSI 3025A UCPC and 3022A CPC respectively.

The new 3776 UCPC and 3775 CPC have improved features including higher detection efficiencies, better flow control, removable saturator, and water removal system to extract condensate from the saturator. The 3776 UCPC has a higher aerosol flow rate (50 instead of 30 cm3/min) and measures concentrations of ultrafine particles with higher efficiencies. The 3775 CPC uses both live-time corrected single-count and calibrated photometric modes to provide highly accurate concentration measurements up to 107 particles/cm3 and extends the single-count mode from 104 (3022A) to 105 particles/cm3. The 3775 CPC also features faster response time and higher particle detection efficiencies. Both models offer greater resistance to “flooding” of the optics due to tilting or aerosol inlet restrictions.

In this study, the performances of three 3776 UCPCs and three 3775 CPCs were characterised for background counts, detection efficiency, response time, concentration linearity and other important specifications. Detection efficiency measurements were made with different aerosol sources (sucrose and NaCl) using an aerosol electrometer (AE TSI 3068A) as the reference. D50 (i.e., the size with 50% detection efficiency) is estimated as 2.4 nm for the 3776 UCPC and about 5 nm for the 3775 CPC. To establish the linearity, the CPCs were challenged with particle concentrations from < 103 to 107 particles/cm3. 3776 UCPCs show excellent correlation with the AE up to 3×105 particles/cm3 (< 5% error), where coincidence effects begin to become pronounced; concentrations continue to be displayed up to 106 particles/cm3. The 3775 CPC shows good correlations with the AE (< 5% error), counting single particles at concentrations from 0 to 105 particles/cm3. The response time for the 3776 UCPC is < 1 sec at high-flow mode and ~ 5 sec at low-flow mode. For the 3775 CPC, the improved saturator-condenser flow path enables a much faster response time (~ 5 sec) at both high and low flow modes compared with nearly 13 sec at low-flow mode and nearly 20 sec at high-flow mode in the 3022A CPC. Results from other tests will be discussed including background counts test, high temperature and high humidity test, pressure test, etc.

1PC18

MATRIX EFFECTS IN THE MEASUREMENT OF FINE PARTICULATE MATTER NITRATE BY FLASH VOLATILIZATION. Catherine Reid, JAY TURNER, Washington University, St. Louis, MO; Susanne Hering, Aerosol Dynamics, Inc., Berkeley, CA

A flash volatilization method for quantifying ambient fine particulate nitrate has been developed by Aerosol Dynamics, Inc. (ADI) and commercialized by Rupprecht and Patashnick (R&P 8400N). Previously published results by various investigators indicate excellent regression slopes (e.g., 1.06) with respect to filter nitrate for the ADI prototype unit deployed in California. However, other studies report relatively low regression slopes for 8400N deployments in the eastern United States (e.g., 0.83 in Pittsburgh and 0.65 in New York City; regression intercepts less than 0.2 µg/m3). The St. Louis – Midwest Supersite has deployed at least one R&P 8400N monitor periodically since December 2001 – including continuous operation of at least one unit since February 2003 – at its core monitoring location in East St. Louis (IL). This presentation summarizes key findings, including flash volatilization nitrate recoveries relative to both filter measurements and Particle-into-Liquid-Sampler (PILS) measurements. With respect to filter nitrate, 8400N recoveries were excellent below ~2 µg/m3 nitrate but decreased – and exhibited more variability – with increasing nitrate. A detailed analysis of hourly data for the 8400N nitrate, PILS nitrate, and Sunset carbon reveals a matrix effect for 8400N nitrate recovery with aerosol composition. At low carbon concentration there appears to be a deficiency of electron donors (for which carbon is the most likely source) for promoting the reduction of nitrate to NO/NO2; for these conditions the 8400N nitrate recovery with respect to PILS nitrate is low and variable. As the aerosol total carbon concentration increases, the 8400N nitrate recoveries increase and become less variable. Nitrate concentrations are highest in the springtime throughout the Midwest; these conditions provide a wonderful natural laboratory for investigating nitrate recoveries. During spring 2005, the hypothesis of an electron donor deficiency was tested by doping the 8400N nitrogen purge gas with 10 ppmv carbon monoxide. For two collocated 8400N units, the instrument with the CO-doped purged gas exhibited an immediate and sustained 20% increase in reported nitrate concentration. This purge gas doping experiment confirms that there can be an electron donor deficiency for the 8400N in some environments; more work is needed to optimize a scheme for adding electron donors to the flash zone towards improving overall instrument performance.

1PC19

FIELD EVALUATION OF THE EFFECTS OF SAMPLING ARTIFACTS AND OPERATING PARAMETERS ON THE PERFORMANCE OF A SEMI-CONTINUOUS EC/OC MONITOR. MOHAMMAD ARHAMI, Thomas Kuhn, Philip M. Fine, Constantinos Sioutas, Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA

The carbonaceous component of PM is suspected of being very relevant with respect to observed health responses. Elemental carbon (EC) is emitted from incomplete combustion occurring in sources such as diesel engines and biomass burning. Organic carbon (OC) is a component of particles emitted from almost every primary particle source. Some particulate organic carbon can also be secondary organic aerosol (SOA), formed by atmospheric photochemical reactions of organic precursors. The OC and EC components of PM have traditionally been measured off-line subsequent to time-integrated daily particle collection on filters. Useful information on the sub-daily or hourly variability of EC and OC is thereby lost. Such data provided on finer temporal scales can help to assess the variability of sources, ambient levels and human exposure to EC and OC.

In this study, the performance of the Sunset Laboratory, Inc. semi-continuous EC/OC monitor was assessed in a field setting. Two collocated instruments were run concurrently on a cycle consisting of 45 minutes of sampling and a 15 minute analysis. The monitors were deployed near downtown Los Angeles, about 80 m downwind of a major freeway, surrounded by multi-story buildings and near a construction area, thus representing a good urban pollution mix. An inter-monitor comparison showed high precision and allowed for the evaluation of the effects of monitor maintenance such as filter changes. By changing the inlet configurations of one of the monitors (adding a denuder, a Teflon filter, or both), the influences of positive and negative sampling artifacts were investigated. The positive artifact was found to be relatively large (~5 µg/m3), but it was practically eliminated with a denuder. The negative artifact was small and may be neglected in most cases.

With the same denuder inlet configuration, the temperature profiles were varied between the instruments, including a fast 3-minute analysis using an optical EC correction rather than the thermal EC measurement. Finally, a novel configuration using a size selective inlet impactor removing particles greater than 250 nm in diameter allowed for semi-continuous size-fractionated EC/OC measurements over an extended period of time. It was observed that EC in PM2.5 is found mainly in the ultrafine mode (particle diameters less than 250 nm), whereas OC is found in about equal parts in both ultrafine and accumulation modes. Evolution of OC at different temperatures of the thermal analysis also provided data on the relative volatility of OC in different size ranges.

1PC20

TANIC: TANDEM INTEGRATING CAVITY ABSORPTION METER FOR FILTER-BASED MEASUREMENTS ON AEROSOL DEPOSITS. KIRK FULLER, Venkataramanan Krishnaswamy, David Bowdle, University of Alabama in Huntsville, Huntsville, AL

Absorption coefficients of atmospheric particles are frequently inferred from transmission and/or reflection measurements made on quartz, nuclepore, or Teflon filters. A proper accounting of scattering in the radiative transfer is a requirement in all measurements of absorption by particulate matter. Also of relevance to filter samples, but much less understood, are the alterations of a particle's absorption (and scattering) spectrum by its close proximity to other particles and by its attachment to substrate surfaces.

An absorption meter (absorptometer) has been assembled from a pair of integrating cavities, coupled at their sample ports, which greatly reduces uncertainties in accounting for photons scattered by particle deposits. In addition to absorption, this instrument is capable of determining the hemispheric transmittance and reflectance of the filter deposits. The measurement of direct backscatter and direct transmittance (extinction) may also be provided by this apparatus to aid in the full articulation of the optical properties of the filter samples. The design of the instrument is such that its scope of application may extend well beyond that of atmospheric radiation, and its utility for research in areas such as biomedical optics will be discussed. The absorptometer will accommodate various filter substrates, allowing its use in the analysis of aerosol deposits collected from a variety of sampling instruments.

A study has also been made of important aspects of microparticle optics that have not been adequately addressed in previous absorption measurements on particle-laden air filters. These include coherent scattering and electrodynamic coupling of particles to nearby structures. This latter effort involves both rigorous theoretical analysis and controlled laboratory experiments, and provides a means of more accurately relating the optical properties of the filter deposits to those of the original in situ aerosol.

1PC21

USING THE FAST MOBILITY PARTICLE SIZER™ SPECTROMETER FOR AIR QUALITY MEASUREMENTS. TIM JOHNSON, Robert Caldow, TSI Incorporated, Shoreview, MN;

The Fast Mobility Particle Sizer™ (FMPS™) spectrometer was designed specifically to measure rapidly changing submicrometer particle size distributions. The spectrometer is based on licensed Electrical Aerosol Spectrometer (EAS) technology from the University of Tartu, Estonia. It measures particle size distributions in the 5.6 to 560nm range at a rate of once per second. The distributions are reported as 16 channels per decade based on a real-time data inversion from 22 individual low-noise electrometers. The measurement is based on the same electrical measurement as the industry-standard SMPS measurement. While the size and concentration resolution of the FMPS is less than the SMPS, the speed of the measurement makes it possible to make a variety of new measurements that were not possible with the SMPS which typically takes several minutes for a single size distribution.
A test was made of the lower noise level of the instrument. The noise level is dependent on size and averaging time. The test was made by recording the RMS noise level for HEPA filtered air. For one second time resolution the noise level is approximately a straight line on a log-log plot of particle size and concentration with a point at 100 particles/cm3 for 6nm and 1 particles/cm3 for 520nm. Longer averaging times give better noise results. The upper concentration limit is also dependent on particle size but not on averaging time. This limit is about 100,000 times higher than the 1 second noise level.

Data was taken using variety of aerosol generation methods on stable aerosols to compare the size distributions measurements from a FMPS and a SMPS. Concentration comparisons were also done between the FMPS and a CPC. Results show that the FMPS compared well in both tests.

The FMPS was used for a variety of air quality measurements where fast changing aerosols can be encountered. Examples of tests done are aerosols generated during cooking (on both gas and electric stoves) as well as charcoal grills. Roadside measurements were done and the plumes from high emitting vehicles can be clearly seen above background levels. Measurements were done on road to measure the levels that exist there and comparisons were done between inside the passenger compartment and outside the vehicle.

1PC22

DESIGN AND PERFORMANCE OF AN OPTICAL PARTICLE COUNTER USING A WHITE LED LIGHT SOURCE. ADAM G. WOLLNY, Craig Simons, Charles A. Brock, NOAA Aeronomy Laboratory, Boulder, CO and University of Colorado, CIRES, Boulder, CO

White light scattering particle counters have advantages over single wavelength detection techniques for measuring the size distribution of coarse particles since they reduce the uncertainties for particle size calibration caused by Mie oscillations of the response function and by dependence upon chemical composition and refractive index. Despite these benefits, laser-based single wavelength instrument are more common due in part to engineering benefits like intensity and stability of the emitted light and size, and the weight and cost of the light source and its cooling system. Recently, high intensity white light emitting diodes (LEDs) have become available. If their temperature and electric current are controlled, they provide an extremely stable light, bright enough for detecting and sizing particles larger than about 0.5 µm in diameter. Using a 3 W white LED stabilized with a thermoelectric cooler, a white-light optical particle counter (WLOPC) was developed for aircraft based measurements. Particles with different refractive indices ($1.47 < n < 1.59$) were used to calibrate the detectable size range of ~0.6 µm to ~8 µm in diameter. The response function was modelled and the design optimized to improve the performance. First atmospheric measurements were performed with the WLOPC onboard the NOAA WP-3D during NEAQS-ITCT project in 2004. The instrument was highly reliable, and particle size distributions were taken with a 1 second resolution in a large variety of conditions including marine, free tropospheric, and urban airmasses and in the plumes from power plants and forest fires.

1PC23

EVALUATION OF AN INLET CONDITIONER FOR PARTICULATE MATTER MEASUREMENT. THOMAS PETERS, Adam Riss, University of Iowa, Iowa City, IA; Manisha Singh, TSI Incorporated, Shoreview, MN

Field studies have shown that coarse particulate matter (PM10-2.5) estimated with data from the Aerodynamic Particle Sizer (APS Model 3321) agrees with that measured with filter-based, Federal Reference Method (FRM) sampler when conditions are dry (average daily relative humidity < 60%). In contrast, when conditions are wet (average daily relative humidity > 60%), PM10-2.5 estimated with data from the APS is substantially lower than measured with filter-based samplers. This work evaluated the performance of an inlet conditioner to remove particle-bound water from ambient aerosol prior to measurement with the APS. The inlet conditioner, referred to as a smart heater, is composed of a standard FRM downtube surrounded by a heating element, a sensor that measures the relative humidity of the APS outlet air, and an electronics control box. The control box gradually increases the power to the heater as the relative humidity of the air that exits the APS rises above 45%. The rise in air temperature maintains the air stream entering the APS to below 60% relative humidity.

Lab tests were conducted to evaluate the performance of the inlet conditioner. A vibrating orifice aerosol generator (VOAG) was used to generate monodisperse ammonium salts tagged with 5% fluorescein. After being diluted and neutralized, the aerosol was either humidified to 90% or dried to 20%. This aerosol was passed through an inlet conditioner and then sampled simultaneously with the APS and a filter sampler. The mass concentration on the filter was measured fluorometrically. The mass concentration estimated with data from the APS was compared to that measured with the filter sampler. The particle size of the aerosol measured with the APS was compared to that estimated from theory. Ammonium sulfate aerosol was used to test the ability of the heater to sufficiently dry the aerosol. Ammonium nitrate aerosol was to investigate the effect of evaporation due to increasing temperature. For each aerosol type, 1-µm and 5-µm aerosols were tested to estimate the effect of inlet conditioning with a smart heater on PM2.5 and PM10-2.5.

1PC24

FIELD RESULTS WITH A WIDE RANGE AEROSOL SPECTROMETER COMBINED WITH A PAH SENSOR. T. RETTENMOSER 1), C. Gerhart 1), M. Richter 2) and H. Grimm 1) 1) GRIMM AEROSOL Technik GmbH, Dorfstrasse 9, D-83404 Ainring, Germany. 2) G.I.P GmbH, Research Department, Mühlbecker Weg 38, 0671 Pouch, Germany.

Gravimetric measurements have shown, that the fine dust below 0,5 µm makes not even 1% of the entire aerosol mass. But, if the particles are counted, 80% of all particles are in the size range below 0,5 µm. It is not obvious if the particle number or the particle mass has a greater effect on the human health. However an outdoor wide range measurement system able to detect the size distribution from a few nanometre to 30 micrometer in many different size Ranges on a portable or stationary base is a desirable, new technique. Only a combination of high an efficient Aerosol Spectrometer in combination with a Differential Mobility Analyser (DMA) and Condensation Particle Counter (CPC) is capable to count particles from the coarse fraction down to the nucleation mode.

In the recent years it became more and more obvious that polycyclic aromatic hydrocarbons (PAHs) play an important role for human health effects. The formation of PAH compounds principally occurs during incomplete combustion through oligomerisation and cyclisation of acetylenes (mostly during the incomplete burning of fuels, such as oil, wood, gasoline, diesel and jet fuel, and garbage). So it seemed to be a very important and challenging option to measure particles from the ultra fine up to the coarse fraction and the PAHs, simultaneously. GRIMM has developed this system. An outdoor measurement campaign is carried out in an alpine valley in central Europe.

The GRIMM Portable Aerosol Spectrometer 1.109 provides single particle count and size classification in real time. The sample air is drawn through a flat light beam, produced by a focused laser diode. Each scattered signal from a single particle is detected by 90 degree by a high-speed photo diode and is then counted and classified in 31 size channels in the range from 0,25 to 32 µm by an integrated pulse height analyzer. The GRIMM M-DMA 5.500 (a Vienna type DMA) cuts out mono-disperse particle size fractions of the poly-disperse aerosol sample, according to the electrical mobility of the particles. 44 size channels in the range of 5,5 to 350 nm are detected by scanning/stepping. The size-classified particles are increased by a condensation process and counted in the GRIMM CPC 5.400 by crossing a laser beam. These counts are then stored as data and also transmitted via the RS-232 to an external data acquisition device. The data from the CPC and the spectrometer then are combined with a special software. The complete WRAS (Wide Range Aerosol Spectrometer) system (shown in figure 1) covers the range from 5 to 30000 nm. The GRIMM Particle Bound PAH Detector 1.300 qualitatively measures the concentration of particle-bound PAHs. The sensor uses an excimer lamp to photo- electrically charge the particulate matter. The particles are then collected on a filter in an electrometer, which measures the charge flow in the range of 5 to 5000 fA. This gives a relative measure of particle-bound PAH concentration.

Reischl, G.P., (1991), Measurement of Ambient Aerosols by the Differential Mobility Analyzer Method: Concepts and Realization Criteria for the Size Range Between 2 and 500 nm, Aerosol Sci. Tech. 14, 5-24

1PD1

MERCURY CAPTURE WITH IN-SITU GENERATED TIO2 PARTICLES BY ELECTROSTATIC PRECIPITATION.

Tai Gyu Lee, Jae Young Park, Deptment of Chemical Engineering in Yonsei University

Mercury has been known a focus of extensive research by many toxicologists and environmental experts due to its high toxicity and a tendency to bio-accumulate, which are very threatening to both human and the ecosystem. Due to toxicity of mercury, recently the regulation of mercury has been strengthened. In this study, the elemental mercury is removed by in situ generated titanium dioxide. However, titanium dioxide has several merits in mercury removal, in view of low cost, no desorption and high removal efficiencies.

We have been investigated the mercury removal using corona light source as a solution for the problems of activated carbon. The corona light source from ultraviolet wavelength in ESP was obtained by the formation of titanium dioxide. TiO2 particles were produced by tube electronic furnace. During the oxidization of TTIP (titanium tetra-isopropoxide) and air by heats of furnace, nucleation leads formation of primary particles. The following coagulation and condensation form nano-sized coagulation, TiO2 particles. Consequently the TiO2 particles produced react with Hg. The mercury reduction does not occur without UV irradiation. TiO2 is activated and has electrons and electron holes on its surface only by irradiation of UV irradiation. The UV irradiation, which photoactivate TiO2, comes from corona in ESP. Hole is generated by OH radical formation according to the adsorption of O2 or H2O. Thereafter adsorbs on the surface of TiO2 as a form of HgO which oxidants element Hg with less volatility.

1PD2

CHARACTERISTICS OF REDUCTION REACTION OF METAL OXIDE NANOPARTICLES ACCOMPANIED BY MORPHOLOGY CHANGE DURING SPRAY PYROLYSIS.

Tae Il Kim, Sung Min Choi, DONGGEUN LEE, Pusan National Univerisity

Nano metal particles are of considerable interest for a variety of applications. High temperature heating or the reducing gas such as hydrogen or carbon mono oxide has been widely used to reduce late transition metal oxide to metals. Recently, Kim and Ehrman reported that some additions of alcohol could also act as a safe reducing agent. While producing copper nanoparticles employing their method, we found that Cu nanoparticles experienced at all the time the morphological change from shell-like to near solid, which was confirmed by Energy Dispersive Spectroscopy (EDS) measurement with Transmission Electron Microscopy (TEM). Raising the reaction temperature results in a transition of crystalline phase accompanied by the morphology change. X-Ray Diffraction (XRD) analysis revealed the shift of lattice constant of Cu to the direction to decreasing lattice constant. with raising the temperature. This may imply that the Cu nano crystallite are bonded to oxide at atomic scale or exist together with copper oxide as a solid solution. Possible reduction mechanism will be suggested with the measurement of kinetic parameters.

1PD3

ION-INDUCED NUCLEATION: DIPOLE-CHARGE ORIENTATION, SIGN PREFERENCE AND CHEMISTRY EFFECT. ALEXEY NADYKTO, Fangqun Yu, Atmospheric Sciences Research Center, State University of New York at Albany, Albany, USA

We investigate the uptake of common precursors by ion clusters using seven different approaches including Nadykto-Yu model (NY), effective polarizability model (EP), Barker-Ridge (BR) model, the average dipole orientation theory (ADO), the angular momentum conservation ADO (AADO), refined ADO theory (ADO`), and refined AADO theory (AADO’). We found that the enhancement factor due to the dipole-charge interaction predicted by different uptake/capture models can deviate by a factor of more than 5. At ambient temperature of 300 K the enhancement factor for the uptake of water, sulfuric acid and ammonia molecules by 0.5 nm singly charged molecular cluster is in the range of 2.3–12, 2.5–20 and 1.75–9.8 respectively. In addition to the uncertainties in absolute values of the enhancement factor, there is a considerable difference in its temperature dependence. The temperature dependence of EP, and ADO is typically weaker than that of the other theories. BR, ADO’, AADO’ and NY, which are derived using different capture/uptake conditions and similar dipole orientation models, are in quite a good agreement in most cases, while ADO and ADO’ and AADO and AADO’ models obtained using identical capture/uptake conditions and different orientation models deviate dramatically. Present analysis shows that uncertainties in the enhancement factor are largely arise from the difference in how the relative dipole orientation of the polar molecule in an ion field is expressed. This means that the average dipole orientation in the ion field is an important parameter controlling gas-to-charged particle/cluster conversion and needs to be investigated further.

1PD4

THE EFFECT OF DILUTION ON ORGANIC COMPOSITION OF DIESEL PARTICULATE MATTER (DPM). Fuyan Liang, MINGMING LU, Tim. C. Keener, Zifei Liu, University of Cincinnati, Cincinnati, OH

In current decades, there has been a growing interest in quantifying and reducing the amount of diesel particulate emissions from non-road diesel powered engines. Studies have indicated that diesel particulate matter (DPM) can be hazardous to human health since DPM is mainly in the respirable range (< 1 μm) and many organic species in DPM, such as polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs, are considered as potential occupational carcinogens.

DPM concentration and composition are significantly affected by dilution factors due to the condensation of some organic compounds which constitute approximately 20%-60% of DPM. In order to provide more accuracy in addressing health risks associated with DPM exposure, it is important to be able to individual species in the organic compounds. High volume sampling with dilution is often required to collect sufficient mass for the above purpose. The comparison of DPM composition under dilution conditions and non-dilution conditions will help to understand the condensation mechanism of different kinds of organic compounds in DPM, as well as to estimate the actual concentration and components of DPM in ambient air.

The main objective of this study is to investigate the effects of dilution factors on the distribution of organic species in DPM. The study was performed on a Generac diesel generator which serves as a DPM emission source. High volume sampling system (for source influenced atmospheres or with dilution for source) and EPA method 5 sampling train (Determination of Particulate Matter Emissions from Stationary Sources) were used to collect DPM. DPM mass concentrations, organic carbon and elemental carbon (OC/EC), and organic compositions were compared for dilution, source and ambient samples. DPM mass concentration was gravimetrically measured. The distributions of OC and EC loadings on the filters were determined by NIOSH Method 5040, a thermal-optical (transmission) method commonly used in OC/EC measurements. The organic compounds were identified and quantified with GC/MS and classified as n-alkanes, branched alkanes, cycloalkanes, PAHs and alkylated PAHs, alkylbenzenes, and organic acids.

1PD5

OXIDANT UPTAKE BY MODEL ORGANIC AEROSOL MIXTURES. AMY M. SAGE, Kara E. Huff Hartz, Emily A Weitkamp, Allen L. Robinson, Neil M. Donahue, Carnegie Mellon University, Pittsburgh, PA

The rate of oxidant uptake by organic aerosol partially dictates the rate at which it ages. Oxidant uptake rates are needed in order to understand the changes in the physical and chemical properties of the aerosol that take place in the atmosphere and to account for aging processes accurately in source-receptor models. In response to this need, oxidant uptake rates for atmospherically-relevant model aerosol mixtures have been measured in smog chamber experiments. Four-component mixtures composed of an alkane, an alkanoic and an alkenoic acid, and a sterol, each in approximate proportion to relevant ambient samples, were exposed to ozone. The ozone loss rate and changes in aerosol composition were measured continuously, providing total-aerosol and species-specific oxidant uptake rates, respectively. Agreement between the sum of the species-specific rates and the measured total rate provides valuable mass-balance information. Additionally, the use of the ratio of the AMS signal at mass 44 to that at mass 57 as a marker of aerosol aging was investigated as a potential surrogate measure of the ozone loss rate.

1PD6

METHODS FOR SPECIATION OF METALS IN ATMOSPHERIC AEROSOLS USING X-RAY ABSORPTION NEAR EDGE STRUCTURE (XANES) SPECTROSCOPY. Brian J. Majestic, Martin M. Shafer, and James J. Schauer, Environmental Chemsitry and Technology Program, University of Wisconsin-Madison, Madison, WI

X-ray absorption near edge structure (XANES) spectroscopy uses a synchrotron electron ring to create a focused X-ray beam which can excite the core electrons in an atom. This method is sensitive to oxidation state and bonding environments. XANES spectroscopy has long been used to measure the oxidation states of transition metals in minerals and soils. This technique also has the potential to study the atmospheric processing of particulate matter where red-ox chemistry is important. At this time, however, XANES spectroscopy studies on atmospheric aerosols have yet to be performed. With this technique, oxidation state ratios (e.g. [Fe(II)] / [Fe(III)]) can be determined directly from the particulate matter, requiring no wet chemical extraction steps. This presentation will focus on key parameters that we have found to be critical to successful implementation of XANES spectroscopy on atmospheric particulate matter. The optimal air sampler and collection substrates will be presented here, as well as potential limits to this technique such as detection limits, spectra analysis, and lack of synchrotron facilities. In this study, the iron L2 and L3 edges were analyzed using an X-ray absorption chamber on the TGM 10 meter and the HERMON beam lines at the Synchrotron Radiation Center (SRC) in Stoughton, WI. Iron (II) and iron (III) ammonium sulfate salts were used as calibration standards for Fe(II) / Fe(III) determinations. Aerosol samples were initially collected on Teflon substrates and then coated with 15 Angstroms of platinum metal in order to form a conductive surface. Other samples were collected using high-purity aluminum foil substrates. It was found that Teflon filters cannot readily be used for XANES analysis without a high degree of preparation, whereas aluminum foil substrates require no additional preparation. Further, XANES spectroscopy analysis was performed on aerosols sampled using a standard ambient sampler (a URG PM10 inlet with a cow udder) and a personal cascade impactor sampler (PCIS). It was found that, because of its ability to concentrate the aerosol to a small section of the filter, the PCIS was far superior for XANES spectroscopy analysis when compared to the ‘standard’ ambient sampler

1PD7

EFFECT OF NH3 ON THE ION-INDUCED NUCLEATION IN SO2/H2O/AIR MIXTURES. KENKICHI NAGATO, Tohru Kawabuchi, Kochi National College of Technology, Nankoku, Japan; Chan S. Kim, Kikuo Okuyama, Hiroshima University, Higashi-Hiroshima, Japan; Motoaki Adachi, Osaka Prefecture University, Sakai, Japan

The ternary nucleation of H2O-H2SO4-NH3 has been considered as the key mechanism of new particle formation in the lower atmosphere. However, the roles of NH3 molecules in the formation and the growth of nanometer-sized molecular clusters have not been well understood. To investigate how NH3 molecules participate in the formation and the growth of nano-particles, we made an experimental study on ion-induced nucleation in SO2/H2O/Air mixtures. The size distribution as well as the composition of cluster ions was measured using the cluster-differential mobility analyzer combined with Faraday cup electrometer (C-DMA/FCE) and the drift tube ion mobility spectrometer/mass spectrometer (DT-IMS/MS).
The ionization of H2O/Air mixtures by radioactive source (241Am) usually led to the formation of negative cluster ion of approximately 1nm in diameter. When SO2 was introduced to the gas mixture (H2O:4900ppm, SO2:50ppm), another ion peak appeared at about 1.9 nm. The abundance of these larger ions significantly increased by the addition of NH3 (1ppm), indicating that NH3 enhances the growth of negative cluster ions. Initially formed cluster ions were mass-analyzed using DT-IMS/MS. In the condition of SO2/H2O/Air mixtures, cluster ions of SO4-(H2O)n were found as major negative ions. Sulfuric acid cluster ions of HSO4-(H2O)n were also detected. On the contrary to the DMA measurements, no significant changes were observed in the negative ion mass spectra by the addition of NH3. These results shows that NH3 does not play important role in the initial negative ion formation, but contributes to the growth of negative cluster ions of SO4-(H2O)n and/or HSO4-(H2O)n.

1PE1

PREDICTION OF VENTURI SCRUBBER PERFORMANCE USING LIQUID ATOMIZATION MODEL. Sun-Il Pak, KEUN-SHIK CHANG, Korea Advanced Institute of Science and Technology, Daejeon, Korea

Venturi scrubbers are highly efficient gas cleaning equipments which use a liquid for removing particulate matters from an exhaust gas stream. Liquid is transversally injected into the gas stream from the orifices and breaks up into small droplets by aerodynamic force. In order to predict the performance of this device such as pressure drop and overall collection efficiency, the three-phase interaction caused by gas flow, liquid droplet and dust particles must be properly treated. Here the atomization of the liquid jet in crossflow and particle capturing by the droplet were modeled and included in the Eulerain-Lagrangian numerical simulation. For the various gas velocities and liquid-to-gas loading ratios, we preformed the numerical analysis and comparison with the experimental data turned out pretty reasonable in this numerical modeling.

1PE2

NANOPARTICLES IN THE RESULT OF POLITETRAFLUOROETHILEN THERMAL DECOMPOSITION.

M.P. Anisimov, A.M. BAKLANOV, I.A. Zayko, and A.A. Onischuk

Politetrafluoroethilen (Teflon-4)-polymer $(C_2F_2)_n$, n = 50-200. Nanoparticles of Teflon-4 have a wide distribution in chemical and atomic industry, mechanical engineering, transport etc. as a chemically inert material. The good adhesive behavior and low friction coefficient of Teflon - 4 make it a profitable as the machine oil additive.

Study of kinetics and mechanism of nanoparticle formation in a result of thermal decomposition of a polymer, for example politetrafluoroethilen, is an important problem of nucleation. The aim of the present research is an investigation of nanoparticle generation from the residue of politetrafluoroethilen thermal destruction.

For generation of politetrafluoroethilen nanoaerosol the thermal decomposition is used. Flow reactor was composed of heated quartz tubing with inside diameter 12mm. A sample was placed inside of the tubing. Nitrogen gas with flow rate 1 l/s was used. The temperature of reactor was controlled by chromel-alumel thermocouple. Efficient length of hot zone was 350mm. A thermoprecipitator was applied for nanoparticles collection on formvar film . Concentration and particle size distributions are measured by screen diffusion battery. Resulting mean diameter was 20-100nm for particles which are generated from the politetrafluoroethilen thermal decomposition residue.

Morphology and size of nanoparticles was determined using TEM and discussed in the present research. In many cases one can see dark and relatively transparent areas for the same particle. We think that the different transparency within one particle is associated with the polymerized and nonpolymerized parts of single particle. The overview of the total results gives to us the ability to conclude that possible initial monomers can produce particles of polymerized and nonpolymerized tetrafluoroethilen and their mixtures with nanosize dimensions. Measurements of the particle size distributions shows the time dependent mean mode value. The measured in the present experiments the nanoparticle diameter time trends are varied from 0.07 nm/min to 0.25 nm/min. That trend is temperature dependend, i.e. growth of the trend rate is $3.6.10^{-3}$ nm/min. degree.

Grant RFBR 05-03-32208 is acknowledged.

1PE3

A NEW FRICTION FACTOR FOR LAMINAR, SINGLE-PHASE FLOW THROUGH FRACTURES.

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Single- and multi-phase flows through fractures occur in various situations, such as transport processes in cracks across building envelops, sequestration of carbon dioxide in brine-saturated reservoirs, transport of dissolved contaminants through geological strata, and in enhanced oil recovery from depleted field. In the present study fluid flows through individual fractures were simulated. A post-processing code was developed and used to digitally generate a three-dimensional fracture using a CAD package from the CT scan data of a natural rock fracture. Several sections along the fracture were considered and GambitTM code was used to generate unstructured grids for flow simulation. Single-phase flows through the fracture section with different flow rates were studied. It was shown that the pressure drop was dominated by the lowest height passages of the fracture. The accuracy of parallel plate models for estimating the pressure drops through fractures was studied. It was shown that the parallel plate flow model with inclusion of the tortuosity factor and appropriate effective fracture aperture could provide reasonable estimate for the fracture pressure drops. Based on the CFD simulation data, a new expression for the friction factor for flows through fractures was developed and the model predictions were compared with the simulation results and favorable agreement was found.

1PE4

UNIPOLAR CHARGING OF SUBMICRON PARTICLES USING CONDENSATION-EVAPORATION METHOD. Y. J. CHOI, S. S. Kim and J. B. Choo, Department of Mechanical Engineering, KAIST, Daejeon, Republic of Korea

We applied a new unipolar charging technique using condensation-evaporation method to charge submicron particles. Submicron particles are saturated by n-butanol, flow through a condenser and then grow to about 3~5 μm in diameter regardless of their initial size as the temperature of a saturator increases from 35 °C; to 45°C. These grown particles are charged by a corona based charger and dried to shrink their initial size through a evaporater. Results show that average particle charges are similar, regardless of their initial size.

1PE5

SIMULTANEOUS CLEANUP OF PARTICLES AND HYDROGEN SULFIDE. KYOUNG SOO LIM, Young Ok Park, Jung Hwan Lim, Fossil Energy & Environment Department, Korea Institute of Energy Research, Daejeon, South Korea

The filter system was designed in order to remove dusts and hydrogen sulfide simultaneously, and a series of experiments on an sorbent for hydrogen sulfide were conducted to examine the effects of dusts on the removing efficiency of the sorbent hydrogen sulfide.

Numerical computations have been performed for the optimal design of a cleanup filter system, and numerical prediction of fluid field and dust transport for filter system with a tangential and conventional inlet have been simulated and compared, which may be used as basic data for seeking the characterization of a pore size and surface area for dust cake. In the experiment on a sorbent for sulfur oxides, removing efficiency hydrogen sulfide was evaluated to characterize the absorbent properties such as surface area and porosity

1PE6

THE ROLE OF SALT IN SALT-ASSISTED AEROSOL-GEL AND SPRAY PYROLYSIS SYNTHESIS OF NANOPOROUS PARTICLES. Sung Min Choi, Seung Geun Lee, DONGGEUN LEE, Pusan National University

Kim and Zachariah recently proposed that an inert inorganic salt can be used to avoid inter-particle growth of sols or nuclei during aerosol-gel or spray pyrolysis reaction and reported the structure of the resultant particles are highly micro porous. Based on their method, we demonstrate the role of the salt as a reinforcing agent of gelling structure, resulting in collapsing hollow structure to sphere-like in spray pyrolysis reaction. Also the co-precipitated salt during drying and pyrolyzing droplets changes crystallite size and often reduces. Apparently the salt is likely to inhibit the coalescence between metal oxide primaries in a collapsed sphere, but not completely. Similar action of the salt was expected in aerosol-gel reaction and confirmed by TEM and BET. The salt in the latter case freeze the further coalescence by preventing significant linking between the silica matrixes. But, at the beginning of sol-gel reaction in a droplet, the ultrafine sols are isolated each other by pre-precipitated salt, therefore unagglomerated very fine particles are produced after washing out the salt with water. Comparisons with TEM photos before and after nebulizing droplets at different hydrolysis time will support again the role of salt.

1PE7

PORTABLE ION GENERATORS AS PARTICLE REMOVAL DEVICES. XIAORUI YU, Nasim Mullen, Ping Zhao, Richard Corsi, Jeffrey Siegel, Department of Civil, Architectural and Environmental Engineering, The University of Texas at Austin, Austin, TX

A conservative assessment suggests that over 1% of homes in the U.S. use ionizing air cleaners. They work by charging incoming particles with a corona and removing them to oppositely charged electrodes. In the present investigation, five ionizing air cleaners from different manufacturers were evaluated. Size resolved (0.1 - 10 μm) particle removal efficiency and clean air delivery rate (CADR) were measured in a well-mixed stainless steel test chamber for each cleaner. Two different test aerosols were used for the experiments: a combustion aerosol from incense and KCl particles from a large particle generator. The results suggest that the ionizing air cleaners are effective at removing supermicron particles with efficiencies that ranged from 20 – 100%, but that CADRs were relatively low (5 – 60 m3/hr), considerably lower than most HEPA air filters. Applying these CADRs to a model of a typical residence suggests that most portable ion generators will not cause a large decrease in indoor particle concentrations. Furthermore, most ionizers generate ozone as a byproduct of their operation. Ozone emission rates were comparable to those from photocopiers and laser printers (1 - 4 mg/hr). Although the ozone emission rates are not as high as a dedicated ozone generator, they can raise indoor ozone levels enough to cause concern about potential human exposure. These results allow for a more complete analysis of the positive and negative indoor air quality impacts of portable ion generators and suggest caution in using them as air cleaners in indoor environments.

1PE8

AEROSOL PENETRATION THROUGH THE POLYSULFONE MEMBRANE FILTERS.

Hsiao-Lin Huang, Department of Occupational Safety and Hygiene, Chia Nan University of Pharmacy & Science Yi-Chin Huang, Department of Land Management and Development, Chang Jung Christian University Pei-Chun Chuang, Graduate Institute of Public Health, National Yang Ming University Shinhao Yang, Graduate Institute of Environmental Engineering, National Taiwan University

Generally, polysulfone (PSF) membrane filters are used as an engineering thermoplastic material to fabricate membranes for applications in water ultrafiltration system and gas separations such as carbon dioxide stripping from natural gas streams and the production of high purity nitrogen from air. However, the PSF membrane filters rarely been applied to aerosol filtration, such as aerosol sampling. Therefore, this objective of this work was to generate the PSF membrane filters in different PSF concentrations and examine the aerosol penetration through the PSF membrane filters. A Collison atomizer was used to generate monodisperse PSL aerosols. The aerosol concentrations upstream and downstream of the tested filters were measured using a condensation particle counter (CPC). Two PSF membrane filters created by two different concentrations (15% and 20%) were examined for the aerosol penetration in this study. The pressure drop across the filter was measured by a pressure gauge. Face velocities of 5, 10 and 20 cm/s were considered to elucidate the effect on aerosol penetration. The experimental results show that the most penetrating size of both PSF membrane filters is approximately 0.05 µm. The 0.05 µm-size aerosol penetrations through the 15% and 20% PSF membrane filters at a face velocity of 10 cm/s are 9.7% and 3.8 %, respectively. The results also imply that the aerosol penetration through the 15% and 20% PSF membrane filters increases with face velocity increasing by diffusion mechanism.

1PE9

CHALLENGE AND REGENERATION PROCEDURE FOR REGENERABLE FILTERS.

R. Arunkumar, John A. Etheridge, John C. Luthe, Brian A. Nagel, Olin P. Norton, Michael S. Parsons, Donna M. Rogers, Kristina U. Hogancamp, and CHARLES A. WAGGONER, Diagnostic Instrumentation and Analysis Laboratory, Starkville, MS

High efficiency particulate air (HEPA) filters employing fibrous glass filtering media are used extensively throughout the DOE complex and are a critical element in treating off gases from waste treatment processes. These filters are capable of lowering particulate matter (PM) emission rates to levels much lower than regulatory thresholds, however, they have definite limits with regard to mass loading capacity and ability to withstand certain upset conditions. The most commonly identified threats to HEPA filter performance are moisture and rapid blinding of filters by smoke. Filtering media of sintered metal or ceramic has been suggested as an alternative for fibrous glass, yet unit cost and operational parameters such as differential pressure across the filters have reduced their deployment as alternatives to HEPA filters. There does seem to be great potential for using these types of filters, however, as protective pre-filters for nuclear grade HEPAs. Regenerable pre-filters do not have to achieve HEPA performance levels and so lower pressure drop units can be developed. Additionally, these filter media have much greater strength and can withstand the rapid blinding of a process upset without failing structurally. Finally, these filters will not be adversely affected by moisture and can serve to protect the conventional HEPA from becoming wet.

A procedure for loading and washing regenerable filters has been developed and employed in a series of tests to evaluate the performance of regenerable media after repeated loading and washing cycles. Three media types have been challenged: sintered metal fiber (Porvair and Mott), sintered metal powder (Mott), and ceramic (CeraMem). Filter media have been challenged with both wet and dry aerosols followed by cleaning cycles using a variety of wash solutions. Media were evaluated for pressure drop and filtering efficiency changes from one cleaning cycle to the next. Filter media were examined under a scanning electron microscope to determine the extent to which residues remain after cleaning.

1PF1

REDOX ACTIVITY OF AIRBORNE PARTICULATE MATTER (PM) AT DIFFERENT SITES IN THE LOS ANGELES BASIN. Arthur K. Cho, Debra A. Schmitz, John R. Froines, UCLA, Los Angeles, CA: Bhabesh Chakrabarti, CONSTANTINOS SIOUTAS, University of Southern California, Los Angeles, CA

Epidemiologic studies have shown associations between ambient particulate matter (PM) and adverse health outcomes including increased mortality, emergency room visits, and time lost from school and work. The mechanisms of PM related health effects are still incompletely understood, but a hypothesis under investigation is that many of the adverse health effects may derive from oxidative stress, initiated by the formation of reactive oxygen species (ROS) within affected cells. While the adverse effects from PM have historically been associated with the airborne concentration of PM and more recently fine particle PM, we considered it relevant to develop an assay to quantitatively measure the formation of ROS from PM as the initial step in the induction of oxidative stress. PM redox activity could then be related to different sources, chemical composition, physical and spatial/temporal characteristics in the ambient environment. The measurement of ROS formation in relation to sources and other factors will have potential relevance to control of redox active PM. If oxidative stress represents a relevant mechanism of toxicity from PM, the measurement of redox activity represents a first step in better understanding the subsequent downstream processes.

We have developed an assay for redox activity utilizing the reduction of oxygen by dithiothreitol (DTT) which serves as an electron source for PM. We have found that PM will catalyze the reduction of oxygen and have examined the distribution and chemical characteristics of the redox activity of PM fractions collected in different sites in the Los Angeles Basin (LAB). Samples of concentrated coarse, fine and ultrafine PM, obtained with aerosol concentrators, were studied in terms of their chemical properties and redox activity. Redox activity was highest in the ultrafine fraction, in agreement with results indicating ultrafines were the most potent toward inducing heme oxygenase expression and depleting intracellular glutathione, which has relevance to induction of oxidative stress. Comparison of the redox activity with chemical composition showed a reasonable correlation of redox activity with elemental carbon (r2 = 0.79), organic carbon (r2 = 0.53) and with benzo [ghi]perylene (r2 = 0.82), consistent with species typically found in mobile emission sources.

1PF2

FIBROUS PARTICLE DEPOSITION ON HUMAN NASAL PASSAGE. ZUOCHENG WANG, Philip K. Hopke, Goodarz Ahmadi, Center for Air Resources Engineering and Science, Clarkson University, Potsdam , NY; Paul A. Baron, Gregory Deye, National Institute for Occupational Safety and Health, Cincinnati , OH; Yung-Sung Cheng, Wei-Chung Su, Lovelace Respiratory Research Institute, Albuquerque, NM.

The filtration efficiency of the nose during nose inhalation determines the fraction of aerosol particles reaching the lung. Information on regional deposition can also be used to evaluate the toxic potentials caused by inhaled fibrous particles. In this research, monodisperse glass fibers with a diameter of 1.0 micrometer and aspect ratios of 5, 10 and 30, were generated by a dielectrophoretic fiber classifier and then used as test aerosols in a human nasal airway model. The geometrical data of the human nasal airway was obtained by using magnetic resonance imaging (MRI) of a human subject. Stereolithography was used to construct the nasal airway models at Clarkson. Both total and regional deposition efficiencies in nose were measured. We found that deposition fractions vary with the fiber length and flow rate.

1PF3

PARTICLE DEPOSITION IN HIGHLY IDEALIZED MOUTH-THROATS. YU ZHANG, Tze Luck Chia, Warren H. Finlay Department of Mechanical Engineering Aerosol Research Laboratory of Alberta University of Alberta Edmonton, Alberta, Canada

Particle deposition in the human mouth-throat is a key factor in evaluating the loss of drug delivered by inhalation devices, such as pMDIs or DPIs. Currently, the USP standard mouth-throat has been shown to drastically underpredict mouth-throat deposition. However, the prototype geometry of a highly idealized mouth-throat has been proposed as a promising replacement of the USP mouth-throat (J. Aerosol Sci., 35, 2004, 789-803).

In this study, partial optimization of the highly idealized mouth-throat is performed using computational fluid dynamics simulations. The performance of these highly idealized mouth-throat geometries, using a straight tube of inner diameter 17.3 mm as the inlet to the models, is evaluated experimentally by measuring particle deposition efficiency as a function of inertial parameter. Gravimetry is used to determine particle deposition fractions in these geometries. Monodisperse particles (DEHS) with mass median diameter of approximately 2.5 - 6.0 micron are used at two steady inhalation flow rates of 30 and 90 l/min. The results show that, at the higher flow rate of 90 l/min, a mouth-throat with a bend diameter of 8.5 mm and curvature radius of 50 mm follows in vivo average (J. Aerosol Med. 2(3), 1989, 285 -308) most closely. In contrast, at the lower flow rate of 30 l/min, a mouth-throat with a bend much smaller than 8 mm in diameter is required to mimic the above in vivo curve. A significant Reynolds number effect on particle deposition is observed in all geometries studied.

1PF4

SPATIAL AND TEMPORAL VARIABILITY OF BLACK CARBON IN NEW YORK CITY IN WINTER 2004. PRASANNA VENKATACHARI, Liming Zhou, Philip K. Hopke, Clarkson University, Potsdam, NY; Dirk Felton, Oliver V. Rattigan, NYS Department of Environmental Conservation, NY; James J. Schwab, Kenneth L. Demerjian, State University of New York, Albany, NY.

Measurements of black carbon made at two sites in New York City during the winter of 2004 are compared. Spatial and temporal variability in the black carbon concentrations were explored by examining the diurnal, weekday/weekend, and day-of-week trends in black carbon concentrations at these two sites. Associations of black carbon with gaseous copollutants such as CO, NOx, and non-methane hydrocarbons are also explored in an attempt to identify temporal variations in their emissions. It was found that the concentrations of black carbon vary in response to the interplay of source activities, meteorological conditions, and spatial factors. BC contributed 8 % and 11 % to the total fine particle mass at these two sites, respectively. The BC measured at these two sites was only weakly correlated, suggesting that the daily/diurnal fluctuations of the sources represented by BC cannot be precisely estimated for exposure assessment for larger spatial scales based on a single site. Diurnal BC behavior was observed on weekdays as well as weekends consistent with traffic patterns and mixing conditions. However, a clear day-of-week dependence of BC concentrations was not observed. The diurnal variations in BC as well as the gaseous copollutants indicate that local mobile sources are the dominant sources of BC. The high time resolution measurements were found to yield insights into the spatial scales of emissions that are not possible with longer time scale measurements such as 24 hour averages.

1PF5

THE EFFECT OF BODY ORIENTATION ON DEPOSITION OF PARTICLES IN THE HUMAN LUNG. BAHMAN ASGHARIAN, Owen Price, CIIT Centers for Health Research, Research Triangle Park, NC

Studies on health effects of inhaled particles, whether conducted in laboratory settings or by theoretical modeling, implicitly use a standing or sitting upright position of the body. The influence of body position on particle deposition is assumed negligible. But the existence of a pressure gradient in the pleural cavity causes airflow distribution in the lung to be nonuniform. This in turn causes particle deposition to vary with body position. In addition, sedimentation losses of particles to the airway walls will change with body position. Using a model of lung ventilation based on lung compliance and airway resistance, airflow distribution throughout the lung was obtained and used in a particle deposition model (MPPD or Multiple-Path Particle Dosimetry, CIIT Centers for Health Research, Durham, NC) to investigate variation of regional and lobar deposition with change in lung orientation. Predicted results indicated that for a given exposure and breathing scenario, total deposition of particles in the lung remained the same and independent of body orientation. This was true for all particle sizes considered in this study. However, lobar distribution of deposited particles for standing and supine positions differed slightly. The difference in deposition between upper and lower lobes decreased for supine position when compared to standing position because of more uniform lung ventilation in the absence of pressure variation in the pleural cavity. Furthermore, a noticeable variation was observed when lying on one’s side. Particle deposition increased in the right lobes when lying on the right side and vice versa. Increase in deposition in right lobes comes with decrease in deposition in the left lobes and vice versa. The trend was more significant in the upper lobes for small particles in the diffusion range and large particles in the impaction range, indicating the influence of lung ventilation with body position. The findings in this study have implications in health risk assessment and beyond. Therapeutic drug delivery can be improved by finding optimal body position for maximum dose to target sites in the lung.

1PF6

EFFECT OF PARTICLE SIZE ON RATES OF PHOTODEGRADATION OF ATMOSPHERIC TOXINS ADSORBED ON SOOT AEROSOL PARTICLES. XIANG PAN, Ao Lin, Sergey Nizkorodov Department of Chemistry, University of California at Irvine, Irvine, CA

Polycyclic Aromatic Hydrocarbons (PAHs) and their derivatives found in atmospheric particulate matter are well known for their high toxicity and carcinogenicity. This work focuses on the mechanisms and rates of oxidation of selected PAHs on model discharge-generated soot particles as a function of the particle aerodynamic size. The following results are reported: i) construction of a CI APMS (chemical ionization aerosol particle mass spectrometer); ii) use of CI APMS for detection of PAHs on soot particles; iii) kinetic and mechanistic study of ozonolysis of pyrene on soot particles. The data will potentially be useful for assessing the health impact of anthropogenic sources of air-borne PAH/soot particulate matter.

1PF7

DEPOSITION OF POLYDISPERSE AEROSOLS IN THE HUMAN LUNG. JUNG-IL CHOI, North Carolina State University, Raleigh, NC; Chong S. Kim, National Health and Environmental Effects Research Laboratory, US EPA, Research Triangle Park, NC

The deposition of polydisperse aerosols in the human lung is important for health risk assessment of inhaled particles because aerosols in the natural environment are mostly polydispersed. Particle size distribution of urban aerosols is typically bi-modal with local maxima at around dp=0.3 and 5 micron. In the present study, total and regional deposition of both unimodal and bimodal aerosols were calculated using Weibel’s symmetric lung model. For unimodal aerosols a log-normal distribution was used with varying geometric standard deviation (1.5-4.0). For bimodal aerosols the mass ratio between the two modes was varied from 0-1. Results show that the polydispersity (sigma-g) has a varying effect on deposition depending on particle size. Total lung deposition increases in the fine particle size range, but decreases in the coarse and ultrafine size range with increasing sigma-g. The trend is similar for tracheobronchail (TB) and alveolar deposition for fine and coarse range particles. However, polydispersity has an opposite effect between TB and alveolar deposition for ultrafine particles. TB deposition increases but alveolar deposition decreases with increasing sigma-g for dp = 0.02-0.1 micron. The effects are reversed for dp < 0.01 micron. Deposition of bimodal aerosols varies widely depending on the position and sigma-g of each mode and mass ratios of the two modes. In general, bimodal aerosols have a greater effect on deposition than unimodal polydisperse aerosols, particularly in the TB region. This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

1PF8

TECHNOLOGY FOR EFFECTIVE AEROSOL VACCINATION. K. G. Soloviev*, E. Kurbatova**, N.B. Egorova**, A.D. Tolchinsky*, V.I. Sigaev*, S.N. Uspenskaya*, R.V. Borovick,* Semenov B.F. ** * Research Centre for Toxicology and Hygienic Regulation of Biopreparations, Bld.102A, Lenin Str., Serpukhov, Moscow Region, 142283 Russia ** Mechnikov Research Institute of Vaccines and Sera at the RAMS; 5 Maliy Kazenniy pereulok, Moscow, Russia.

Preventive measures (i.e. immunization of humans and animals with vaccine preparation) play an important role in disease control. Effectiveness of immunization depends not only on the quality of vaccine preparations but also on routes of administration. Currently experimental studies on design of aerosol immunization for humans and animals are carried out worldwide. For this purpose investigations have been initiated worldwide on novel vaccines for aerosol application and on schemes and devices ensuring aerosol delivery into respiratory system. We carried out the series of studies on aerosol delivery of VP-4 vaccine into respiratory tract of small lab animals. The previous experiments (Efremova, 1996 r.) showed that mice were not a good model for aerosol immunization since they have small volume of lung ventilation and narrow airways. Therefore we conducted studies on distribution of aerosol particles (5 μm and less) in respiratory tract (nasopharynx, trachea and lung) of white mice using model of liquid preparation [physiological solution with 10 % of glycerin; spores of Bacillus thuringiensis in concentration of 1.2 – 1.6) x 108 spores/cm3 and 2.6 and 4.8 μm average particle size]. Experiments showed that 74% of aerosol with dm50 = 2.6 μm settled in deep portions of respiratory tract (lung). 85% of aerosol with dm50= 4.8 μm settled in nasopharynx. We analyzed the data and concluded that mice could be used as models for evaluation of immunological activity with aerosol dm50= 3-5 μm, settled in respiratory tract. To generate aerosol vaccine we used aerosol chamber with outer frames for 40 small lab and pneumatic generator. We selected optimal regime for generator operation to convert vaccine preparations into aerosol: 1.5 kg/cm2 compressed air pressure, volume flow 40 – 50 dm3/min., volume flow of liquid suspension 2.0 cm3/min. Conditions were specified and mass concentration of the vaccine in aerosol was 7100 mg/m3, dm50 – 4.6 μm, particle-size distribution was up to 5 μm in 60 %, 5 μm and more – in 40%. Dose of antigens per mouse was 140 μg/ mouse. At 5-fold immunization with 3-day interval and intraperitoneal challenge by Klebsiella pneumoniae virulent strain we obtained protective activity (60-80)% after 7 days of vaccination.
Conclusion:

1. Mice could be used as models for evaluation of immunological activity of aerosol vaccines.
2. Polycomponent vaccine VP-4 could be used effectively for prophylaxis and treatment of respiratory diseases at aerosol introduction.

1PF9

ACTIVATION OF INNATE AND ADAPTIVE IMMUNITY AT AEROSOL INTRODUCTION OF VACCINE «IMMUNOVAC-VP-4». E.Kurbatova**, N.B.Egorova** K.G. Soloviev *, S.N.Uspenskaya*, A.V.Tretiakova*, A.N. Varfolomeev*, I.M. Gruber**, V.N. Efremova**, N.K. Akhmatova**, N.R. Dyadishchev*, I.B. Semenova**, F.B. Donenko***, B.F. Semenov**, R.V. Borovick* * Research Centre for Toxicology and Hygienic Regulation of Biopreparations, Bld.102A, Lenin Str., Serpukhov, Moscow Region, 142283 Russia ** Mechnikov Research Institute of Vaccines and Sera at the RAMS; Maliy Kazenniy pereulok, Moscow, Russia *** Russian Research Center of Oncology named by N.N. Blokhin at the RAMS

Polycomponent vaccine "Immunovac-VP-4" consisting of antigens Klebsiella pneumoniae, Staphylococcus aureus, Proteus vulgaris and Escherichia coli contains pathogen-associated molecular patterns (lipopolysaccharide, peptidoglycan, teichoic acid and others) , which are activators of innate immunity. Mucous membrane of respiratory tract contains cells-effectors of innate immunity. Therefore goal of the study was to evaluate efficacy of aerosol introduction of the preparation to ensure protection against infection.

Four schemes of aerosol mice immunization with "Immunovac-4" at different time of exposure in aerosol chamber with following intraperitoneal challenge with Klebsiella pneumoniae K16 virulent strain were tested. Daily immunization or immunization with 1-day interval did not provide protective effect. Only inconsiderable delay of mortality of the vaccinated animals was observed. Once interval between immunization sessions was increased up to 3 days protective effect was obtained and survival of mice made up 65-80%, what was considerably different from the control ($p<0,05$). Protective effect of aerosol immunization could be compared to effectiveness of single subcutaneous immunization. But entire inhalation dose was considerably lower than doses introduced subcutaneously. Aerosol immunization stimulated proliferation activity of spleen lymphocytes, cytokine production (IL-10, IL-12) and specific antibodies synthesis. Some considerable changes were observed in system of mucosal immunity characterized by considerable increase of IgG and IgA synthesis in lavage liquid from deeper portions of respiratory tract."Immunovac-VP-4" stimulation of innate immunity effector cells caused high cytotoxic and anti-tumor activity. Subcutaneous vaccination of mice facilitated increase of proliferation and cytotoxic activity (up to 85.0±2.1) % of splenocytes in mice with suppressed immunity caused by cytostatics. Intraperitoneal introduction of vaccine into mice with B16 implanted melanoma caused inhibition of tumor growth by 69.3%. Anti-tumor effect might be expressed stronger at aerosol route of vaccine administration since faster activation of innate immunity effectors will occur in mucous system and bronchus-associated lymphoid tissure.

Conclusions: 1. Mice could be used as models in studies of protective activity of vaccine preparations at aerosol introduction;

2. Intervals between immunizations must be no less than 3 days to obtain protective effect;

3. Aerosol immunization brings to stimulation of innate and adaptive immunity;

4. Study on anti-tumor activity of "Immunovac-4" is reasonable at aerosol method of application;

5. Perspective development of "Immunovac-4" form for aerosol application.

The work was accomplished in the framework of the ISTC # 1438 project.

1PF10

TOXICOLOGICAL EVALUATION OF REALISTIC EMISSIONS OF SOURCE AEROSOLS (TERESA) STUDY: RESULTS OF FIELD EXPERIMENTS (EXPOSURE CHARACTERIZATION) CONDUCTED AT TWO POWER PLANTS. Pablo A. Ruiz, TARUN GUPTA, Choong-Min Kang, Joy E. Lawrence, Stephen T. Ferguson, Jack M. Wolfson, Annette C. Rohr and Petros Koutrakis. Department of Environmental Health. Harvard School of Public Health, Boston, MA.

This is one of a series of posters describing the TERESA study, whose objective is to evaluate the toxicity of coal-fired power plant emissions. Our approach involves: in-situ sampling and dilution of emissions; simulation of plume reactions for several possible atmospheric scenarios, and; animal exposures to the reacted aerosol. We included the following typical atmospheric scenarios: a) oxidation of SO_2 in a plume to form H_2SO_4; b) the oxidized plume mixes with background air containing ammonia which neutralizes acid particles; and, c) the plume mixes with background VOCs from biogenic sources yielding secondary organic aerosol (SOA). In the past, a few toxicological laboratory studies using primary coal combustion emissions have been conducted. However, TERESA study is the first of its kind to involve toxicological assessment of actual power plant emissions, including atmospheric transformations, in a real field setting.

Sampling and dilution of the emissions were conducted using an aspirator. Sampling rate (as well as dilution ratio) was controlled using either an orifice or a restriction tube. In a mobile reaction lab, diluted stack emissions, containing primary particles, NO and SO_2, were fed continuously through a first reaction chamber where O_3 was added. In this chamber H_2SO_4 was formed through photochemical reaction initiated by UV lamps (see accompanying poster). A second reaction chamber was used to neutralize the acidic aerosol with ammonia and to form SOA by reacting α-pinene (a representative biogenic VOC) with ozone. A novel diffusion denuder was used to remove non-selectively ~80% of all pollutant gases (see accompanying poster) after each chamber. The aerosol was further diluted before being transported to animal exposure chambers in a mobile toxicological lab. Here, the aerosol was characterized extensively using continuous monitors for $PM_{2.5}$ mass, particle number, SO_2, NO_x, O_3, T and RH; and for $PM_{2.5}$ mass, sulfate, nitrate, pH/acidity, ammonium, EC/OC, ammonia, and organic speciation (SOA, ketones, aldehydes and α-pinene) using integrated samples.

Several rounds of exposures of 3-4 days each were attempted in two power plants. Each round simulated a specific atmospheric scenario. These scenarios ranged from un-reacted primary emissions to most complex transformation including oxidation, neutralization and formation of SOA. In this poster, we present the design and implementation of the complete toxicological

1PF11

POWDER DEPOSITION IN ORO-PHARYNGAL CAST OF HUMAN UNDER REALISTIC INSPIRATORY CONDITIONS.

TOMASZ R. SOSNOWSKI, Arkadiusz Moskal, Leon Gradon Warsaw University of Technology, Warsaw, Poland

The study was focused on measurements of powdered drug deposition in the oro-pharyngeal silicone cast during non-steady flows corresponding to the real inhalation. The cast was prepared according to CT scans obtained for an adult male while using an inhaler. The same powder inhaler (Cyclohaler-type, single-capsule DPI) was then used for aerosol emission in experimental studies. The air was drawn through the cast and inhaler by the system constructed at the Warsaw University of Technology, consisted of programmed piston pump driven via the electrocylinder (Parker Hannifin) with the stepper motor. The motor was controlled by the computer program. Three types of inhalatory patterns were studied: (A) PIF = 94 LPM, inspiration time = 2.8 s, and (B) PIF = 76 LPM, inspiration time = 3.4 s, and (C) PIF = 39 LPM, inspiration time = 6.2 s. Particle size distribution of aerosol emitted from the inhaler and the aerosol penetrating the cast was measured with the white-light spectrometer WELAS 2100 (Palas GmbH) in the range 0.2-40 micrometer.

Particle size distribution in aerosol emitted from the inhaler at all airflow patterns (A, B, C) was characterized by the mass median diameter (MMD) of 6.1 micrometer and fine particles fraction (FPF - the relative mass of particles below 5 micrometer) of 33%. After penetrating the oro-pharyngeal cast for at flow patterns (A) and (B), the MMD was reduced to 5.3 micrometer and FPF raised to 44%. For weak inspirations (flow pattern C), the MMD = 6.5 and FPF = 27%. The results suggested that for high inspiratory flowrates powder particles larger than 10 micrometer were almost completely collected in the cast. At lower inspiration rates, a longer residence time allows smaller particles to be deposited, slightly increasing the outflow MMD and decreasing the FPF value. Regional deposition within the cast was not studied at this stage of the research but it is planned as the next step in order to find the relationships between the non-steady flow conditions and local deposition efficiency as a function of particle size.

In the view of aerosol therapy, these results demonstrated that particles larger than 8-10 micrometer are effectively captured in the oro-pharyngeal region during simulated inspiration, so they will not be able to penetrate to deeper lung regions.

1PF12

IDENTIFICATION OF THE TOXICOLOGICAL EFFECTS OF REACTIVE OXIDATIVE SPECIES.

PRASANNA VENKATACHARI, Nupur Dutta, Pavithra Rao, Philip K. Hopke, Centre for Air Resources Engineering and Science, Clarkson University, Potsdam, NY

Identifying the most important sources and variability of source impact for particulate matter is essential to assessing their health impacts. A central hypothetical mechanism of how particles affect human health involves the generation of reactive oxygen radicals at target sites. These could be generated via activation of cells by cell-particle interactions and by oxidative species present in particulate matter. Prior studies indicate that there are reactive oxidative species associated with ambient respirable particles. In order to test whether or not particle-bound ROS can induce effects in test animals, an aerosol generator was developed to produce ultrafine ROS-containing particles.   A nebulizer was used to generate an α-pinene aerosol. The α-pinene was the reacted with ozone in a flow reactor. The size distributions of the resulting aerosol was characterized and its oxidative capacity was assessed in terms of an equivalent H2O2 concentration. The aerosol exiting the flow reactor was then passed through a charcoal denuder to remove the unreacted ozone before being used in controlled exposure experiments on test animals. The details of the aerosol generation and characterization study will be discussed.

1PF13

BIOAEROSOL PROPAGATION CAUSED BY LETTER OPENING.

Igor E. Agranovski, Oleg V. Pyankov, Igor S. ALTMAN, School of Environmental Engineering, Griffith University, Brisbane, QLD, Australia

Mailing envelopes containing pathogenic spores of bacillus anthraxes recently used by terrorists to infect humans calls for a new investigation to identify a level of possible contamination of ambient air as the result of opening such envelopes. Here we show that opening an envelope and unfolding a letter aerosolize microbial particles located inside and create their cloud with the diameter equivalent to the length of the letter side along which it was folded. With no motion of an envelope recipient (first case study presented in this work), the front of the cloud moves due to forced convection caused by the impulse at opening and reaches a human face (approximately 50 cm from the opening zone) in about 6 sec. The concentration of particles at that distance is about three times lower compared to the concentration in the source. Further spread of the cloud brings its front to the distances of 1 and 1.5 meters within 25 and 55 seconds with the corresponding concentrations of around 10 and 5 % compared to the source respectively. The second case study presents the results for a more realistic scenario when an envelope recipient, after observing a dust cloud, appearing as the result of the opening of the envelope, recoils in fright creating additional air flows significantly disturbing the aerosol propagation described in the former study. It was found theoretically and verified by experiments that the amount of particles captured by the letter recipient varies significantly depending on the geometrical characteristics of the human, distance to the opening zone, reaction time and recoil velocity.

1PF14

PASTEURIZATION OF METALWORKING FLUIDS FOR CONTROL OF MICROORGANISMS.

AL ARMENDARIZ, Southern Methodist University, Dallas, TX; Nancy Dorsey, Environmental Protection Agency, Dallas, TX; John Wandryk, Crouch Engineering, Fort Worth, TX.

Metalworking fluids (MWFs) perform a variety of tasks in metal machining industries, including removal of metal chips, lubrication, and heat removal from workpieces and tools. Over time, the fluids become contaminated with populations of bacteria, fungi, and microbiological products like endotoxins. Exposure to liquid and aerosol MWF has been linked to a variety of adverse health effects. Advanced technologies for the control of microbes in liquid environments are used in many industrial sectors, including wastewater treatment, drinking water preparation, pharmaceutical production, and food processing. The objectives of this research were to: (1) assess the potential effectiveness of pasteurization to control microbe growth in large industrial MWF systems, and (2) and to perform an analysis of the cost to implement pasteurization on large MWF systems. A small number of laboratory and pilot-scale trials of MWF pasteurization have been performed since the 1960's. The results of these tests suggest that pasteurization can reduce microbial concentrations in industrial MWF systems by approximately 90%. The data from the small-scale trials was combined with the machinery and processes used in large-scale dairy and juice pasteurization to design a series of industrial MWF pasteurizers. An economic analysis of the capital and operating costs indicates that integrating pasteurization to a 30,000 gallon MWF system would cost approximately $250,000 per year. This cost is reduced when offset by savings from reductions in waste disposal, fluid purchase, and machinery maintenance. Overall, a metal working facility looking to improve the usable life of its fluids and reduce the potential health impacts from exposure to MWF aerosol and liquid could consider pasteurization for a cost of $250,000 per year or less.

1PF15

COMPARISON OF METHODS FOR CASCADE IMPACTOR DATA ANALYSIS TO PREDICT AEROSOL DEPOSITION INTO PATIENT AIRWAYS. CAROLINE MAJORAL, Alain Le Pape, Patrice Diot, Laurent Vecellio, INSERM U618, Tours, F-37000 France ; IFR135, Tours, F-37000 France ; Université François Rabelais, Tours, F-37000 France

This work compares the usual method of aerosol particle size data processing to an approach which is not based on a specific hypothesis. Particles were sized using an Andersen cascade impactor (8 stages). The way experimental data are treated can influence the interpretation of particle size and result in different predictions of deposition site in the respiratory tract.
The usual method consists in plotting the mass fraction (Fj) deposited on each stage vs. the cut-off diameter (Dcj) corresponding to the stage. According to the European Standard (EN13544-1), a best-fit curve links the points Dcj, Fj. One can as well link the points (Dcj + Dcj+1)/2 (middle of cut-off diameters), Fj+1. The distribution can also be fitted by a log-normal mathematical model.
The usual method assumes that each stage has ideal collection efficiency. This work develops another method of particle size data processing based on cascade impactor calibration, which takes into account imperfect stage collection efficiency. Impactor calibration provides the actual size distribution of particles deposited on each stage. To calibrate the cascade impactor, monodisperse aerosols of diameter Dcali (i = 1 to m) were generated, and the mass fraction deposited on each stage was measured. The mass fraction of monodisperse aerosols of diameter Dcali deposited on impactor stage Dcj is fi,j. Values of Fj and fi,j can be represented by mathematical matrix. To obtain the corrected distribution of aerosol, the particle size distribution of each stage (fi,j) is multiplied by the mass fraction deposited on each stage (Fj), which gives a third matrix.
Results obtained with the usual method were 3.5µm to 6µm for MMAD and 40% to 82% for respiratory fraction (particles between 1µm and 5 µm). The calibration method gave a MMAD between 3µm and 4 µm and a respiratory fraction between 77% and 88%.
Thus the utilization of impactor calibration data facilitated more precise calculation of MMAD and respiratory fraction.
Impactor calibration must be done with many monodisperse aerosols to obtain an accurate estimate of particle size distribution analysis.

1PF16

CFD INVESTIGATION OF PARTICLE INHALABILITY. T. RENEE ANTHONY, Michael Flynn, The University of North Carolina, Chapel Hill, NC

This study uses computational fluid dynamics to investigate particle aspiration at the low air velocities typical of occupational settings. A realistic representation of a human head on a simpler geometric torso was positioned facing the wind (0.2, 0.4 m/s), and breathing was simulated using constant inhalation (1.8, 4.3 m/s). Particles ranging from 0.3 to 116 um were released from fixed positions, and laminar particle transport was simulated to locate the critical area upstream of the mannequin where particles were inhaled. Results from the 0.4 m/s freestream and 4.3 m/s inhalation rate compared well with results from the literature for smaller particles. For particles 68 um and larger, simulations yielded smaller aspiration efficiencies than reported in experiments, and for all velocity conditions studied the aspiration efficiency curve dropped well below the 50% recommended by the ACGIH inhalability curve. While not simulating particle bounce directly, this study also provides an upper limit to particle inhalation due to secondary aspiration. Although an investigation at other orientations is needed to fully define an inhalable curve, a recommendation to reconsider the inhalable particulate mass criterion for large particles is warranted as the facing-the-wind condition reflects the highest anticipated aspiration efficiency.

1PF17

ANOMALOUS RESPONSES (ARCING, ELECTRICAL DISCHARGE) IN A DIFFERENTIAL MOBILITY ANALYZER CAUSED BY ULTRAFINE FIBROUS CARBON AEROSOLS. BON KI KU, Andrew D. Maynard, Paul A. Baron and Greg J. Deye, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH, USA

From a health perspective, there is growing concern about the potential toxic effects of carbon nanotubes/nanofiber [1]. Past industrial experience with asbestos has called attention to the potential hazards associated with small diameter fibers [2]. In order to understand the properties of airborne particles containing these different types of fibers, there is a need to characterize airborne carbon nanotubes in the submicrometer size range using the DMA. In this study, we measured size distributions of as-produced carbon nanotubes from two different production sources using a scanning mobility particle sizer and discovered an anomalous behavior in the DMA that occurred only with these materials. This peculiar behavior, which produced highly skewed distributions, has not been reported for other nanoparticles. These are associated with sudden increases in measured number concentration, fluctuations in DMA voltage and audible high frequency sounds from the DMA column. Three different kinds of unprocessed carbon-based ultrafine fibrous powders– High Pressure Carbon Monoxide (HiPCO) carbon nanotubes and Pyrograf III – were used to generate aerosols through agitation in a laboratory vortex shaker [3]. Onset of the anomalies (arcing/electrical discharge) depended on the material forming the aerosol, sampling flow rate and prior contamination of the DMA column. Several mechanisms are suggested to explain the observations. The results indicate that measurement of nanometer-diameter conducting fibrous material by electrical mobility analysis present a unique challenge. It may be possible to reduce these anomalous results by removing large particles from the measured aerosol by impaction or settling.

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1PF18

DEVELOPMENT OF A SMALL ANIMAL WHOLE BODY INHALATION FACILITY FOR DIESEL PARTICLES. CHARLES STANLEY, Joseph K. H. Ma , Rakesh Nandivada, West Virginia University, Morgantown, WV

In recent years, the health community has focused its attention on the health effects of diesel exhaust. This is due in part to the increased use of diesels in cars, trucks, and other applications. This has lead to attempts to identify additional mechanisms for diesel particulate interactionn with the lungs, for example increased attention is being given to very small particles with diameters below 0.1 microns.

The purpose of this paper is to describe the modifications to the existing Inhalation Facility at West Virginia University to investigate the effects of diesel particles on lung diseases in rat lung models.The older facility was constructed in 1983 as part of the U.S. Bureau of Mines to study the effects of coal dust on rat models.

Whole body inhalation testing is more rigorous than other means of inhalation but is more realistic than nose only or tracheal instillation systems. The 500 square feet facility contains two Hazelton 2000 chambers. Each can house up to 144 rats. One chamber is fitted with a jet-mill to break up the particles.

Instrumentation was selected to control the relative humidity in each chamber to about 50% and the temperature to about 70 degrees. Additional instrumentation was selected to interface the chambers with the internet to allow monitoring conditions during night time hours. To monitor dust concentration, a tapered element oscillation microbalance (TEOM) was chosen.

NIST 2975 diesel exhaust dust was chosen to limit dust cost and still provide a consistent supply of dust. Operation of the chambers has proven to be successful at conditions of 20 mg / cu m dust concentration for four hours per day for two weeks.

1PF19

PARTICLE CHARGE EFFECT ON DOSE DETERMINATION WITH IMPACTORS. PIRITA MIKKANEN, Henna Tuomenoja, Ari Ukkonen, Dekati Ltd., Tampere, Finland

Particle size distributions for pulmonary drug studies are carried out with cascade impactors. These studies determine repeatability of a dose of an inhaler discharge. Commonly applied cascade impactors are Andersen (ACI) and New Generation Impactor (NGI), where the dose is determined by High Performance Liquid Chromatography (HPLC) analyses of the collected particles of ca. ten discharges. Recent studies suggest, that there might be significant losses for fine particles on upper stages of impactors. These losses may be enhanced by static charges carried by particles smaller than 1 mm. We have studied the effect of particle charge with Electrical Low Pressure Impactor (ELPI, Keskinen et al. 1992).

ELPI is a real-time particle size distribution measurement instrument combining a cascade low-pressure impactor with a diffusion charger and electrical detection. ELPI measures particle number size distribution divided in 12 size fractions from 7 nm to 10 mm with 5 size fractions below 0.5 mm. The particle charge distribution is measured by disabling the diffusion charger. Combining this result with a number size distribution, a charge per particle distribution is achieved.

Losses for fine particles on upper stages of impactor were studied with high accuracy electrometers. In this method, an impactor stage was insulated and current was measured while charged fine particles were depositing. The impactor stage geometry was recorded in order to estimate volumes and residence times within each stage.

In this study, impactor characteristics and data available for particle charge levels was utilised to estimate particle losses within an impactor stage. Consequently, this data with available analyses results were applied to estimate variation of dose measurement due to charge effects. The effect of the bipolar particle charge on the repeatability of the inhaler discharge measurements is discussed.

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1PF20

FLUOROCHROME IN MONITORING INDOOR BIOAEROSOLS. Chih-Shan Li, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University Tzu-Yi Huang, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University

Total concentration, viability, and culturability of indoor and outdoor bioaerosols in ten residential environments were monitored by using epifluorescence microscopy with fluorochrome (EFM/FL) with four fluorescent dyes (AO, DAPI, PI, and YOPRO-1). Results from the non-culture-based method were then compared with those using a commonly used culture method. The total indoor cell concentrations measured using the non-culture-based methods was 600-5,000 times higher than that using the culture method; from 1.38x106 to 4.48x106 cells/m3 with AO staining, and from 7.84x105 to 2.75x106 cells/m3 with DAPI staining, compared with the average concentration of 721 CFU/m3 CFU/m3 for bacteria and 587 CFU/m3 for fungi by the culture method. Regarding Indoor/outdoor ratios of concentrations, the ratios were found to be in the range of 0.61 -1.68 by AO, 0.75-2.27 by DAPI, 0.64- 2.33 for bacteria, and 0.60-1.94 for fungi. The viability ranged from 0.69 to 0.90 with PI staining, from 0.19 to 0.72 with YOPRO-1 staining, and from 0.0002 to 0.0015 by the culture method. The viability by EFM/FL was much higher than the culturability. In summary, the total concentration and viability were highly underestimated by the culture method. In conclusion, EFM/FL method can effectively assess the total concentration and viability of bioaerosols in indoor samples.

1PF21

FLUOROCHROME AND FLUORESCENT IN SITU HYBRIDIZATION TO MONITOR BIOAEROSOLS IN SWINE HOUSES. Chih-Shan Li, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University Miao-Ching Chi, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University

Total concentration, viability, and culturability of bioaerosols in swine houses were monitored by using epifluorescence microscopy with fluorochrome (EFM/FL) with four fluorescent dyes (AO, DAPI, PI, and YOPRO-1) and by using fluorescent in situ hybridization (FISH) with five oligonucleotide probes (fl-Univ, fl-EUB, cy-EUK, fl-PSMg, and fl-NotEUB) probes. Results from these two non-culture-based methods were then compared with those using a commonly used culture method. The total cell concentration measured using the non-culture-based methods was 10 to 200 times higher than that using the culture method; from 6.05 x 106 to 2.18 x 107 cells/m3 by EFM/FL with AO staining and from 5.03 x 106 to 2.13 x 107 cells/m3 with DAPI staining, compared with the average concentration of 1.02 x 105 CFU/m3 for bacteria and 1.3 x 103 CFU/m3 for fungi by the culture method. The viability ranged from 0.27 to 0.76 by EFM/FL with PI staining, from 0.02 to 0.60 with YOPRO-1 staining, from 0.53 to 0.79 by FISH, and from 0.002 to 0.033 by the culture method. The viability by EFM/FL and FISH were much higher than the culturability. In summary, the total concentration and viability were highly underestimated by the culture method. Based on the FISH results, eubacteria and eucarya were the dominant components of the bioaerosols. In conclusion, EFM/FL and FISH methods can effectively assess the total concentration and viability of bioaerosols in environmental samples.

1PF22

ANTIVIRAL ACTIVITY OF THE INFLUENZA VIRUS INHIBITOR MEASURED IN VITRO AND IN VIVO FOR DIFFERENT INFLUENZA VIRUS STRAINS. LEONID BULYCHEV, Svetlana Rack, Olga Pyankova, Elena Goncharova, Alexandr Salnikov, Sergey Shepelenko, Vasiliy Poryvaev, Alexandr Ryzhikov. State Research Center of Virology and Biotechnology “Vector”, Koltsovo, Novosibirsk reg., Russia

Efficacy trials of the influenza virus inhibitors were investigated in an in vitro, in vivo and biokinetics models. The main attention was attracted to the compliance between the data on virus inhibition obtained in cell culture and in animal model.

In vitro model. Several influenza virus strains adapted and non-adapted for mice were cultured in MDCK cells. Different polymer sialosides were studied as viral hemagglitinin inhibitors. Antiviral activity of the influenza virus inhibitor was measured as fifty percent inhibition concentration (EC50) determined in MDCK cells by three different assays. These include the plaque forming unit (PFU, virus yield in cell culture (CCID50) and infected focuses forming unit (FFU) reduction assays.

In vivo model. To characterize efficacy of drugs for different influenza virus strains we have investigated a non-pathological mouse model, which is based on measuring the value of respiratory RID50 for mice. A mouse was counted as infected if the virus was detected in the lungs 3 days after aerosol challenge with influenza virus.

Biokinetic modeling. Virus-cell interaction was studied experimentally in MDCK cells to estimate biokinetic constants for virus, cellular receptors and polymer syalosides. The data obtained allowed predicting the therapeutic regimen for respiratory application of virus inhibitor in mice from in vitro experiments.
Aerosol experimental plant. Whole body aerosol exposure of mice was produced in small dynamic aerosol chamber (SDAC). Aerosol dose was estimated using the aerosol concentration experimentally measured and mouse minute breath volume.

Results. Preliminary experiments on mouse breathing showed that mice retard their breathing during 10 seconds when aerosol flow enters SDAC that influences the total respiratory dose. The value EC50 was significantly different when measured by three different in vitro assays. Minimal EC50 value for different influenza virus inhibitors was shown in PFU reduction assay whereas virus yield in CCID50 reduction assay indicated 40-fold greater value. This value obtained in vitro correlates well with therapeutic EC50 in mice, which were challenged by influenza virus aerosol at the dose 7-10 RID50. The non-pathological animal model allowed us to investigate a wide strain specificity of virus inhibitor without preliminary influenza virus strain adaptation for mice.

1PG1

THE USE OF LASER-INDUCED IONIZATION TO DETECT SOOT INCEPTION IN A WELL-STIRRED REACTOR/PLUG-FLOW REACTOR.

DAVID B. LENHERT, Samuel L. Manzello, George W. Mulholland, Building and Fire Research Laboratory, National Institute of Standards and Technology (NIST), Gaithersburg, MD

Soot formation from hydrocarbon fuels involves complex chemical and physical processes including fuel pyrolysis, polycyclic aromatic hydrocarbon (PAH) formation and particle inception, coagulation, surface growth, carbonization, agglomeration, and oxidation. Although the soot evolution process has been investigated and modeled in many studies, the soot inception process is not well understood. Understanding the chemistry of particle formation in laminar flames is difficult due to large concentration and thermal gradients and poor spatial resolution. To mitigate these problems, a well-stirred reactor (WSR) coupled with a plug-flow reactor (PFR) has been built at NIST to investigate PAH growth and soot inception. A laser-based diagnostic is desired for implementation within the WSR to quantitatively determine the soot inception point and for maintaining the reactor close to the soot inception point during reactor operation. Laser-induced ionization is an attractive diagnostic to probe the inception point since it has been successfully used to detect small soot particles (≈ 2 nm) and atomic ions in premixed flames [1-3].

The goal of this study was to implement and perform laser-induced ionization measurements in the PFR section of the WSR using a dual electrode configuration. The configuration consisted of two electrodes (each 1.0 mm in diameter) horizontally spaced 1.0 mm to 5.0 mm apart using a ceramic thermocouple insulator. A Nd:YAG system operating at a 532 nm was used to ionize the incipient soot particles. The laser beam was aligned perpendicular to the electrodes and focused 1.0 mm to 1.0 cm below the midpoint between the electrodes using a 200 mm convex lens. Laser-induced ionization in the WSR showed clear evidence of soot inception at an equivalence ratio of 1.85, while filter collection, Nano-DMA, and TEM sampling did not detect the presence of incipient sooting until an equivalence ratio of 1.9 was reached. In addition, results are presented on the: (1) efficacy of the laser-induced ionization diagnostic to detect soot inception in a WSR/PFR, (2) effect of electrode configuration and excitation on signal intensity/stability, and (3) effect of laser power on signal intensity. These results show promise for being able to control a WSR/PFR at the soot inception point.

[1] K.C. Smyth and W.G. Mallard, Combust. Sci. Tech., 26:35 (1981)
[2] W.G. Mallard and K.C. Smyth, Combust. Flame, 44:61 (1981)
[3] S.L. Manzello, E.J. Lee, and G.W. Mulholland, Applied Optics, in press (2005)

1PG2

EXPERIMENTAL STUDIES AND MODELING OF THIN-WALLED HOLLOW PARTICLE FORMATION BY SPRAY PYROLYSIS OF GEL-FORMING PRECURSORS.

Wenping Guo, TIMOTHY WARD, University of New Mexico, Albuquerque, NM

Spray pyrolysis is a well-known approach to produce spherical particles of a wide variety of inorganic materials. Because of the inherent development of internal solvent concentration gradients, hollow particles are formed under appropriate conditions with some precursors. We have explored the intentional synthesis of very thin-walled hollow particles using precursors that gel at the droplet surface (in contrast to precursors that precipitate). In the synthesis of iron oxide and barium titanate, we have produced thin-walled nanocrystalline particles using citrate precursors, as well as polymer complexation chemistry. Experimental evidence shows that the thin wall forms at relatively low temperature and is retained through calcinations to the final hollow oxide particle. Normal multicomponent solution evaporation modeling cannot predict the steep concentration gradients that are likely to lead to such particles; however modeling that allows for a concentration-dependent diffusion coefficient, as would be expected with polymer or gel formation, can predict very steep surface gradients that are consistent with thin walled particle formation. A summary of our experimental and modeling results will be presented.

1PG3

VARIABILITY IN ON-BOARD MEASUREMENTS OF LIGHT-DUTY VEHICLE PARTICLE NUMBER EMISSIONS.

YINGGE QU, Eric Jackson, Britt A. Holmén, Lisa Aultman-Hall, University of Connecticut, Storrs, CT

Abstract

This study investigated the tailpipe particle number emissions of a light-duty vehicle during on-road real-world operation on a freeway, a two-lane highway and a downtown grid network with traffic signals. All data were collected, on a one-second basis, from one vehicle driven by twenty different drivers along the same 30-mile route. A TSI model 3025 ultrafine condensation particle counter (UCPC) operating at 1.5 liters per minute recorded the total particle (Dp = 3nm - 3,000nm) number concentration (#/cm3) in the vehicle exhaust after being diluted by the MD19-2E mini-diluter at a dilution ratio of at least 300. Simultaneously, vehicle operating data were obtained from an on-board diagnostics (OBDII) Scan Tool, a GARMIN GPS receiver and a 3-axis accelerometer.

Initially, the total particle number emitted by each driver and along each road type was considered in aggregate. Differences between drivers were significant, but the reason for these differences was not apparent. Based on visual inspection of time series plots, total particle number emissions had patterns that related to the engine RPM, load and vehicle speed. This relationship to vehicle operation was more evident than any aggregate pattern between road types. Both transient operating events (short time intervals of very high acceleration or engine load) and transient particle emissions (short durations of high outliers in particle counts) were noted in the data stream. Both temporal and spatial analysis were conducted using Geographic Information Systems (GIS) to determine if operating transients and emissions transients were associated with each other.

Other recent research has explained some of the overall variance in emissions by defining vehicle operating mode in small time increments. In this case, we used 5-second increments and defined four vehicle operating mode bins based on engine conditions and vehicle acceleration. Significant differences in average particle number emissions were found between operating modes but the data suggest further refinement of operating mode characterization is warranted to predict particle emissions within the transportation network. However, current vehicle and emissions data collection temporal resolution issues may limit the ability to accurately develop mode-based vehicle emissions at temporal resolutions lower than 5 seconds.

1PG4

PARTICLE FORMATION IN GASES FROM TOTALLY FILTERED MAINSTREAM CIGARETTE SMOKE.

JOHN McAUGHEY and Conor McGrath, British American Tobacco, Southampton, UK

Aerosol particle formation and growth has been observed in ageing, initially particle-free gases obtained from filtered mainstream cigarette smoke. A similar particle mode has also been observed in mainstream cigarette smoke, on ageing of a smoke bolus.

Observation of fresh particle formation and growth in filtered mainstream cigarette smoke was observed initially by Ingebrethsen and Lyman (2002). Measurements by light scattering techniques described particle formation and growth over the order of minutes, in the size range of approximately 100 nm, with a dependency on cigarette tobacco type. The rate of particle size increase observed agreed best with that predicted for growth controlled by condensable species formation.

In this work, measurements were conducted using a similar smoke generation technique but with measurement by electrical mobility. Cigarettes were smoked to a regime of a 35 ml puff of 2 seconds duration with an inter-puff interval of 60 seconds and measurements of totally filtered smoke conducted behind a Cambridge filter pad. Particle diameter was measured using a fast electrical mobility spectrometer (Model DMS500, Cambustion, UK) with particle concentration measured using a condensation particle counter (Model 3022, TSI, MN).

Particles of 30–40 nm diameter were observed within seconds behind the particle filter at particle number concentrations of up to 1E12 particles per cubic metre. It should be noted that this represents less than 0.1% of the particle mass collected on the pre-filter.

Similar particle modes in the 30-40 nm region were later observed in the presence of unfiltered mainstream cigarette smoke (primary mode = 150-200 nm diameter) on ageing within a glass bulb.

These data will be discussed in the context of the relative sensitivity of the electrical mobility and light scattering measurement techniques, and in the context of the hypothesis of particle growth from condensable species suggested by Ingebrethsen and Lyman

Ingebrethsen, B.J. and Lyman, C.S., Particle Formation and Growth in Gases from Totally Filtered Mainstream Cigarette Smoke. Aerosol Science and Technology 36: 267–276 (2002).

1PG5

MEASUREMENT AND ANALYSIS OF SOOT INCEPTION LIMITS IN OXYGEN-ENRICHED NORMAL AND INVERTED COFLOW FLAMES. Ben Kumfer, Richard Axelbaum, ERIK PITONIAK, Washington University, Saint Louis, MO

Oxygen enrichment of air combined with fuel dilution has been demonstrated to be an effective tool in inhibiting soot inception in diffusion flames. Studies suggest that soot inception is not only governed by temperature and residence time, but also by flame structure. The focus of this study is to measure and interpret soot inception limits in normal and inverted coflow flames as a function of the amount of oxygen enrichment and fuel dilution, which together are quantified by the stoichiometric mixture fraction adiabatic flame temperature, and characteristic residence time.

In this work, an axial height in the flame was selected at which to identify the sooting limit. The limit is obtained by varying the amount of inert until luminous soot first appears at this predefined height. The results show that the sooting limit flame temperature increases linearly with stoichiometric mixture fraction, regardless of fuel type or orientation (normal or inverted). To understand these results, the relationships between flame structure, temperature, and local C/O ratio were explored through the use of conserved scalar relationships. Comparisons of these relationships with the experimental data indicate that the local C/O ratio is a controlling parameter for soot inception in normal coflow diffusion flames, as the global C/O ratio is in premixed flames. Gas temperature and fluorescence of PAH were also measured, and results indicate that the peak PAH concentration lies along a specific iso-C/O contour, a result supporting the critical role of the local C/O ratio on soot inception. Local axial velocities and radial velocities in the flame were measured using LDV (Laser Doppler Velocimetry) to determine a characteristic soot formation time. The effects of residence time were explored experimentally using LDV, and analytically using a Burke-Schumann model to estimate the local scalar dissipation rate. In inverted coflow flames, soot formation begins to occur at lower temperatures than in normal coflow flames due to increased residence time. A simple theory, which is supported by the experiments, suggests that the inception of soot particles first occurs where the local C/O ratio is above a certain critical value, and a temperature/residence time requirement is met.

1PG6

SIZE AND MORPHOLOGY OF PARTICULATES EMITTED FROM A SPARK-IGNITION ENGINE. Matthew F. Chandler, UMIT O. KOYLU, James A. Drallmeier, Department of Mechanical and Aerospace Engineering, University of Missouri-Rolla, Rolla, MO

Sub-micron particulates generated during the combustion of fossil-based fuels have significant negative impact on both environment and human health. Transportation vehicles involving internal combustion engines are major sources of ambient particulate matter. Accurate measurements of such particulates, including concentration, size, and morphology, are essential for developing emission reduction strategies and atmospheric air quality analysis.

Compression-ignition (diesel) engines produce relatively high amounts of soot while spark-ignition (gasoline) engines may be responsible for a substantial portion of the total particulate matter in the atmosphere with the high number of gasoline engines on the roads. Recently, physical properties of carbonaceous particles emitted from a diesel engine had been characterized using sampling and electron microscopy analysis in this laboratory. Here, this study is extended to consider a gasoline engine in order to investigate the differences and similarities between particulate emissions from different types of engines. Particles were collected onto a probe carrying a microscope grid that is quickly inserted into the exhaust stream of a single-cylinder, spark-ignition research engine fueled by isooctane. Direct visual observations under a transmission electron microscope together with advanced image analysis yielded the size distributions of spherules and aggregates as well as their morphologies. The engine was mounted on an electric dynamometer and utilized separate fuel, air and spark control systems to explore the effects of engine operating conditions on the particulate properties. The results were compared to those obtained from the diesel engine using the identical sampling technique.

1PG7

EMISSION CHARACTERISTICS OF SIDESTREAM CIGARETTE SMOKES. FENG-YU CHIANG, Kuan-Ting Hou, Tzu-Ting Yang, Chih-Chieh Chen, College of Public Health, National Taiwan University, Taiepi, Taiwan; Yu-Mei Kuo, Chung Hwa College of Medical Technology, Tainan, Taiwan.

Tobacco smoke is formed by a complex series of processes, including combustion, pyrolysis, evaporation, distillation and condensation. This complex matrix is composed of several thousand constituents. Numerous studies have been conducted to investigate the health effect. Historically, smoking-control efforts have focused on smoking prevention and cessation through individual and group counseling efforts, reflecting a reliance on the individual-based medical model. Compared to the policy-oriented control, the technology-oriented control measures do not receive as much attention as it deserves. Therefore, the ultimate goal of this work was to develop or improve the currently commercially air cleaners designed for removing sidestream cigarette smokes.

An experimental system, composed of a sidestream cigarette smoke generator, a mixing and test chamber, and a sampling train, was set up to investigate the chemical and physical characteristics of the sidestream cigarette smokes. Real time instruments (response time in seconds) were used to monitor the concentrations of CO and CO2; PID was used to measure the concentration of VOCs. Filter samples were collected for estimating the mass concentration. We also measured the particle size distribution (by using a scanning mobility particle sizer) and temperature of cigarette burning tip, by using a homemade thermocouple with 79 micron nickel-aluminum and chrome wires.

The results showed that cigarette combustion rate increased with decreasing packing density of cigarette due to less mass and therefore relatively higher oxygen transfer. The emission factors and emission rates of CO, CO2, aerosol mass concentration, VOCs, and the surface temperature of the smoldering cone all increased with increasing passing air flow. The thermal conductivity of the ashtray played an important role in both aerosol and gas emission. The design of the trench holding the cigarette was particularly critical. The cigarette smoldering rate decreased with increasing contact area, until the combustion ceased due to not enough heat generation.

1PG8

POLYMETHYL METHACRYLATE THERMAL DECOMPOSITION UNDER LASER RADIATION. A.M. BAKLANOV, A. A. Onischuk, M.P. Anisimov

It follows from the common consideration that light absorption ability has impact on laser ablation efficiency of solids. To test that effect experimentally the sample of Polymethyl Methacrylate (Acrylic Resin) has been taken. The CO2 laser is used as powerful light beam source. Polymethyl Methacrylate laser ablation in the nitrogen gas flow under two light absorption conditions is studied experimentally in the present research. Sample was placed in the box having the nitrogen gas flow rate about several cc per second. The sodium chloride window was used for the Acrylic Resin sample illumination by laser beam. Resulting aerosol was analyzed by Chromatograph, Transmission Electron Microscope, and Diffusion Aerosol Spectrometer. It is a great interest to measure the laser ablation efficiency at different light absorption which is associated with the wave lengths, for example, 981 and 1031 cm-1. One can easely find that bigger light absorption leads smaller efficiency of aerosol formation. The dipper penetration of the laser beam at lower absorbtion (1031 cm-1) produces bigger number of aerosol particles. It is reasonable to think that we have the considerable impact of mechanically generated aerosols in the last case. Grant RFBR 05-03-32208 is acknowledged.

1PG9

THE FATE OF FINE PARTICLE EMISSIONS FROM VARIOUS COMBUSTION PROCESSES. JORMA JOKINIEMI Jarkko Tissari Olli Sippula Terttaliisa Lind Jouni Hokkinen

We have measured several different combustion processes, where significant amounts of fine particles are formed. The mass and number size distributions have been determined as well as the particle composition and morphology. Roughly speaking the processes can be divided into two categories: carbonous and non-carbonous. In processes with good mixing, high combustion temperatures, high air/fuel ratio and long residence times non-carbonous inorganic fine parti-cles are formed. These processes include large boilers for heat and power production and some industrial processes. Carbonous particles are formed from incomplete combustion with short residence times at high temperatures. The particles are composed of soot and organic carbon. The ratio of soot and organic carbon varies with the type of fuel and process. Here we consider the formation mechanisms, measured properties and modelling the dynamics of carbonous and non-carbonous fine particles from various sources

The Processes studied were: pulverised coal combustion, fluidised bed combustion and grate boiler combustion with various fuels, heavy and light oil burners and small scale biomass com-bustion. Main emphasis was placed for fine particle emissions, here defined as PM1. For sampling and dilution a VTT based porous tube system was used (i) to avoid artifacts in sampling and (ii) to minimise deposition on sampling lines. ICP-MS and ICP were used for inorganic species chemical characterisation and thermal-optical methods for inorcanic/organic (IC/OC) carbon analyses. For mass and elemental size distribution low presuure impactors (LPI) were used and for number size distributions ELPI. Electron microscopy was used for size, morphol-ogy and chemical composition analysis.

From the obtained results it can be concluded that for large power plants Electrostatic Precipi-tators (ESP) and bag houses are efficient ways to remove TSP and for PM1 the bag house seems to be most efficient. For small scale combustion of biomass, oil burners, small grate boilers and heavy fuel oil marine and land based applications particle removal devices are not usually applied and thus the PM1 emissions are larger as compared to large power plants. These emissions can be reduced by two ways: (a) improving the combustion efficiency to reduce soot and hydrocarbons on fine particles (fuel additives or improved combustion efficiency) or (b) developing efficient and economically viable particle removals devices for these processes. In the first option also the energy efficiency is increased thus decreasing the green house gas emissions.

1PG10

DESIGN AND CHARACTERIZATION OF AN ULTRAFINE COAL ASH AEROSOL GENERATOR FOR DIRECT ANIMAL EXPOSURE STUDIES. Jong-Ik Yoo, WILLIAM P. LINAK, C. Andrew Miller, Takuya Shinagawa, Ha-Na Jang, M. Ian Gilmour, U.S. Environmental Protection Agency, Research Triangle Park, NC; Jost O.L. Wendt, University of Arizona, Tucson, AZ

Primary ultrafine particulate matter (PM) is produced during pulverized coal combustion by the nucleation and heterogeneous condensation of vapor-phase species. This differs from the mechanisms that control the formation of the supermicron fly ash that is heavily influenced by the fragmentation and coalescence of aluminosilicate phases derived from clay minerals in the coal. Although the ultrafine fraction typically represents much less than 5% of the total fly ash mass, this fraction dominates the particle number concentrations and exhibits reduced collection efficiency through particulate control systems. Recently published results from our group indicate that the ultrafine fraction of coal fly ash (operationally defined as PM<0.2 µm diameter) exhibits enhanced pulmonary toxicity compared to both PM fractions less than and greater than 2.5µm. However, these exposures were performed by intratracheal instillation of collected particles that does not necessarily simulate actual mechanisms of pulmonary exposure. This paper describes the design and characterization of an ultrafine coal ash generator that can be used for direct animal inhalation exposure studies. The system consists of a pulverized coal feeder, an externally heated three-zone (1350 °C) drop tube furnace, a cyclone particle separator, and an exposure chamber. System air and coal feed rates are 12 L/min and approximately 1 g/h, respectively. From the furnace, the emissions are passed through a five-stage cyclone designed to aerodynamically classify the primary fly ash particles into size fractions ranging from greater than 5 to approximately 0.5 µm (diameter) with minimal pressure drop. Particles less than approximately 0.5 µm are further diluted (23 L/min) and introduced to a 134 L exposure chamber (0.26 volume exchanges per min). To-date, Utah bituminous and Illinois bituminous coals have been characterized in preparation for animal exposure studies. In addition to temperature, pressure, humidity, noise level, and gas concentrations (O2, CO2, CO, NO, and SO2), the chamber environment has been characterized for ultrafine particle mass (TEOM, M-29), particle number, and size distribution. Extracted PM samples have been characterized by scanning electron microscopy and x-ray fluorescence spectroscopy. The system as currently configured is capable of conducting acute and chronic studies and is able to operate continuously up to 12 hours with minimal supervision.

1PG11

IN SITU DETECTION AND SIZE DETERMINATION OF CARBON NANOTUBES. CHAD UNRAU, Richard Axelbaum, Pratim Biswas, Washington University in St. Louis, St. Louis, MO

A method of in situ detection of carbon nanotubes in the aerosol phase is described. A differential mobility analyzer (DMA) is employed to identify carbon nanotubes (CNTs) and to estimate the dimensions of CNTs produced in an aerosol. This is achieved by determining the electrical mobility of a nanotube. If the dynamic shape factor and the slip correction factor are known, the electrical mobility is determined as a function of the CNT dimensions within the uncertainty of the number of charges carried by a nanotube. A charging theory was developed to determine the number of charges carried by a nanotube based on its dimensions and on the effective separation distance between charges. Using this calculation of mobility and the size distribution given by the DMA, the relative size and number concentration of the nanotubes can be determined. To test this theory, multiwall carbon nanotubes (MWNTs) ranging from 10 to 100 nanometers in diameter and 0.5 to 40 micrometers in length with a purity of 95% were aerosolized and the resulting size distribution was measured using a DMA. The DMA was then used to size select CNTs and these were collected directly onto a TEM grid. Scanning electron microscopy was used to determine the dimensions of the carbon nanotubes collected. These dimensions were then used to validate the theory wherein.

1PG12

MULTI-COMPONENT AEROSOL DYNAMICS IN A SPHERICAL MICROGRAVITY FLAME. B. M. Kumfer, Z. Sun, R. L. AXELBAUM Washington Univerisity, Dept. Mech. Engr., St. Louis, MO

Microgravity provides a unique environment for the flame synthesis of aerosols, due to the absence of buoyancy and long residence time. In addition, microgravity allows for the creation of a spherical diffusion flame in which the flow field is uniform and thus the particle history is easily ascertained. In this study a spherical sodium/carbon tetrafluoride flame was produced in microgravity in which carbon nanoparticles were synthesized. In this system the carbon particles become encapsulated within the flame due to heterogeneous condensation of sodium fluoride. Salt encapsulation of nanoparticles is desirable for the synthesis of nonoxide nanoparticles, since the coating protects the particles from contamination or oxidation during subsequent handling and post-processing. Experimental results suggest that in this system, the combination of long residence time and fast condensation can lead to the formation of large salt-coated particles having sizes of approx. 500 microns. This occurs as a consequence of the Kelvin effect, whereas only a small number fraction of the larger particles grow via condensation, and thus these few particles consume all of the condensable mass available. In order to verify these results, the system was numerically modeled using a spherical diffusion flame model coupled to a sectional model for multi-component aerosol dynamics. Discrepancies between the experimental and numerical results highlight the restrictions of the sectional method as it applies to modeling growth via condensation and predicting the size distribution of particles in this system.

1PH1

THE ALTITUDE PROFILES OF BIOAEROSOL CONCENTRATION IN THE TROPOSPHERE. ALEXANDER BORODULIN, Alexander Safatov, SRC VB "Vector", Koltsovo Novosibirsk region, Russia; Boris Belan, Mikhail Panchenko, Institute of Atmospheric Optics of the SB RAS, Tomsk, Russia; Vladimir Penenko, Elena Tsvetova, Institute of Computational Mathematics and Mathematical Geophysics of the SB RAS, Novosibirsk, Russia

Research Institute of Aerobiology SRC VB Vector and the Institute of Atmospheric Optics SB RAS have been conducting systematic monitoring of tropospheric bioaerosols in South-western Siberia. Atmospheric air samples are collected, and the concentrations of the total protein and culturable microorganisms in them are determined on one of the last 10 days of each month in the daytime in the point with the coordinates 54o23’ North, 82o09’ West at eight heights 0.5; 1; 1.5; 2; 3; 4; 5.5 and 7 km using an airplane laboratory.

Altitude profiles of the concentrations of the bioaerosols were obtained in the work using the procedure of averaging of the array of data on the concentration of tropospheric bioaerosols for 1999-2003, and the determined properties are discussed.

The obtained data array allowed us to reveal seasonal fluctuations of bioaerosol concentration in the troposphere. But obtained variations does not correspond to the maximal activities of the plant and animal kingdoms in the given region falling on May-August. The prevalence of south-western winds in our region confirms the hypothesis about a considerable influence of remote sources of atmospheric bioaerosols. Really, if we follow the wind rose, then such sources must be located in the region of Middle Asia where the plant and animals kingdoms are maximally active for a greater part of the year. To provide the quantitative justification of these conclusions, we calculated the reverse Lagrangian trajectories of the motion of air masses, from which air samples were collected in the point of measurements. The calculations demonstrate that aerosols originating not only from Middle Asia, but also from Africa and the American continent can get into the region of observations.

Bioaerosol sources are in a rather thin near-surface atmospheric layer and are mainly associated with the activities of the plant and animal kingdoms. If the circulation of the atmosphere were not so complex, the profiles of bioaerosol concentration would present functions monotonously decreasing with the height of the observation. The results show that individual local concentration maximums associated with complex trajectories of air masses motion in the atmosphere are superimposed on the obtained profiles.

Thus, each of the obtained altitude profiles of bioaerosol concentration presents a unique reflection of the state of the atmosphere of the Northern hemisphere, which gives the

1PH2

DATA ON CULTURABLE MICROORGANISMS VARIABILITY IN ATMOSPHERIC AEROSOL IN THE SOUTH OF WESTERN SIBERIA. ALEXANDER S. SAFATOV, Irina S. Andreeva, Alexander I. Borodulin, Galina A. Buryak, Yurii V. Marchenko, Victor V. Marchenko, Sergei E. Olkin, Valentina A. Petrishchenko, Oleg V. P’yankov, Vladimir E. Repin, Irina K. Reznikova, Alexander N. Sergeev, State Research Center of Virology and Biotechnology “Vector”, Koltsovo, Novosibirsk Region, Russia; Alexander N. Ankilov, Aantoli M. Baklanov, Konstantin P. Koutsenogii, Valeriy I. Makarov, Svetlana A. Popova, Institute of Chemical Kinetics and Combustion, SB RAS, Novosibirsk, Russia; Mikhail Yu. Arshinov, Boris D. Belan, Mikhail V. Panchenko, Gennadiy N. Tolmachev, Institute of Atmospheric Optics SB RAS, Tomsk, Russia; Vladimir V. Penenko, Vladimir F. Raputa, Elena A. Tsvetova, Institute of Computation Mathematics and Mathematical Geophysics, SB RAS, Novosibirsk, Russia

It is well known that there are a great number of live microorganisms in the atmosphere at the altitudes up to many kilometres. Numeric estimates show that microorganisms as part of aerosol particles may be in the atmosphere for a long time (about a month). During their wandering, these microorganisms are subjected to the effects of different adverse factors, which kill them or change their characteristics. Probably, it is long-term stay in atmospheric aerosol that is one of the reasons of the variability remained insufficiently investigated till recently, first of all, because there was no detailed information about long-term changes in the number and representation of live microorganisms in the atmosphere.

Monitoring of the number and composition of culturable microorganisms in atmospheric aerosol at the altitudes up to 7 km has been performed for more than 6 years. More than 500 samples were collected and analyzed. Microorganisms of widespread genera such as Micrococcus, Staphylococcus, Bacillus, etc., yeast and mould fungi were detected in the tested samples. It was shown that at the altitudes up to 7 km no changes in the concentration of culturable microorganisms with the altitude were revealed, while the seasonal variations of this concentration are well expressed. There is no enough data to reveal such dependencies for different microorganism species at present.

It was shown that some microorganisms strains isolated from air aerosols did not correspond to any of known taxons by their phenotypical characteristics. In a number of cases, the plasmacoagulation and hemolytic activities of detected microorganism cultures were determined for the direct evaluation of their pathogenicity in experiments in vitro. This result is indicative of high potential pathogenicity of microorganisms in the atmosphere and their possible effect on the morbidity of the region’s population.

1PH3

LASER STRATEGIC AEROSOL DATA COLLECTED IN FEEDYARDS OF THE HIGH PLAINS. CHARLES W. PURDY, USDA-ARS, Bushland, TX; David C. Straus, Texas Tech University Health Sciences Center, Lubbock, TX.

LASER STRATEGIC AEROSOL DATA COLLECTED IN FEEDYARDS OF THE HIGH PLAINS. Charles W. Purdy, USDA-ARS, Bushland, Tx; David C. Straus, Texas Tech University Health Sciences Center, Lubbock, Tx.

Aerosolized particulates caused by farming, including concentrated animal feeding operations (CAFO's), have come under increasing regulatory scrutiny. The concentration, size, and chemical composition of the dust particles need to be determined in open feedyards. Concentrations of aerosolized particulates that are 10 µm (PM10) or less in diameter are mandated not to exceed 150µg/m3 of air/24 hours, or exceed 50µg/m3 annually; the PM2.5 standard is not to exceed 65 µg/m3 in 24 hours or 15 µg/m3 annually. Recently the PM2.5 standard was modified by the Environmental Protection Agency (EPA) to include determining a temporal three-year and spatial averaging of concentrations. Four feedyards were examined using two Laser Strategic Aerosol monitors (SAM), one upwind and one downwind, over 8 days in the winter and summer. The SAM monitors sampled the air every 3 minutes at 1 m height and had a flow rate of 15L/min, and dust was weighed electro-optically. Particle size in µm was separated into nine classes (1.25, 3.00, 4.25, 6.00, 8.50, 12, 17, 24, and > 24). The overall statistical model statement showed a significant difference ($P \leq 0.0001$) between dust concentration downwind, 339 (±26) µg/m3 and upwind, 143 (±10) µg/m3. There was a significant difference in the mean overall emission data (µg/m3) for seasons [$P \leq 0.0001$; summer 428 (±47) and winter 234 (±25)], and feedyards (FY) [$P \leq 0.001$; FY1 192 (±25), FY2 460 (±53), FY3 341 (±48), and FY5 372 (±97)]. Highest dust concentrations occurred between 1800 and 2300 hours. The four feedyards exceeded the EPA PM10 standard.

1PH4

THE COMPARISON BETWEEN IMPROVE AND STN SOURCE IDENTIFICATION AT SEATTLE. EUGENE KIM, Philip Hopke, Clarkson University, Potsdam, NY; Timothy Larson, Joellen Lewtas, University of Washington, Seattle, WA

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 in urban area, to estimate long-term trends in constituents of PM2.5, and to support source apportionment for identification and quantification of sources impacting areas out of attainment of the new national ambient air quality standards for PM2.5. Source apportionment of STN measurements are needed for developing effective State Implementation Plans (SIP) for PM2.5. In a recent study, Positive Matrix Factorization (PMF) was successfully used to assess the STN PM2.5 data measured at Mid-Atlantic US area using the estimated error structures. PMF has been also used to apportion PM2.5 sources in several Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring site across US. The objective of this study is to examine the impact to PMF results of analyzing STN data versus IMPROVE data measured at co-located monitoring sites in Seattle, WA. The comparisons between the source compositions as well as contributions have been made. The results of this study provide insights into the differences between the data from the two networks and whether one network data appears to provide better source apportionments.

1PH5

COMPARISON OF ELEMENTAL COMPOSITION OF SPRINGTIME AEROSOL, BETWEEN URBAN CITY OF CHILLÁN AND A RURAL AREA, SAN CARLOS, CHILE.

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An aerosol monitoring study was established to measure ambient aerosol composition at the University of Concepción campus Chillán and San Carlos Agricultural Experimental Field Station (AEFS) located in the southern Biobío Region of Chile. This was the first attempt to classify air pollution during springtime in the urban city of Chillán and rural area of San Carlos, which are located about 400 km and 375 km south of Santiago, Chile, respectively. The Chillán campus is located about 2.0 km from downtown and San Carlos AEFS is located approximately 25 km north of the major city Chillán. The study employed an Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler with a PM10 Anderson inlet at 3 meters above ground collecting PM10 for 24 hours every two to three days on Teflon membrane filters at a flow rate of 16.7 L/min. The aerosol monitor operated at both sites from October 9th to December 9th, 1998.

The aerosol mass concentration was calculated using the gravimetric method. PIXE was used for elements with atomic mass less than Fe, XRF was used for elements Fe and higher atomic mass, and PESA was used for hydrogen. Further details on these techniques are described elsewhere (Cahill et al., 1984; Morales et al., 1995; Rojas et al., 1990). The measured aerosol mass concentrations and the quantitative aerosol source contributions for individual measurement of PM10 components were investigated. Moderate PM10 aerosol concentration was observed in San Carlos, ranging from 12.6 to 108.1 µg/m³, and in Chillán, ranging from 25.7 to 115 µg/m³. The mean composition of the PM10 particulate matter and heavy metals were also quantified.

1PH6

COMPUTATIONAL METHODS FOR MULTI-PHASE MULTI-REACTION THERMODYNAMICAL EQUILIBRIUM PROBLEMS.

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The computation of phase and chemical equilibria of aqueous organic electrolytes mixtures is of significant interest in atmospheric aerosol modeling. The presence of organic species in solution may substantially influence the phase transitions of the deliquescence and efflorescence of salts with changes in relative humidity. Dissolved electrolytes can have appreciable effects on the solubility of organic components in solution. We present here some computational methods for the prediction of the physical state of atmospheric particles.

In the case of inorganic aerosols, an Extended UNIQUAC model is used to compute the excess of Gibbs Free energy. Our method is derived from the minimization of the total Gibbs energy. The computational difficulty is to identify the solid phases existing at the equilibrium. Our algorithm is based on a primal-dual active sets-Newton method for the solution of the Karush-Kuhn-Tucker (KKT) conditions. The inequality constraints are tracked at each iteration so that possible solid salts remain sub-saturated. The corresponding inequality constraint becomes active when the saturation is reached. In the case of organic aerosols, liquid-liquid and liquid-solid equilibria as well as phase stability and separation are considered. The UNIFAC model is used for the calculation of activity coefficients for aqueous organic mixtures. We propose a primal-dual interior-point Newton method to solve the KKT conditions of a relaxed minimization problem.

We present numerical results for both inorganic and organic problems to show the ability of our approach, in the prediction of aerosol phases in the atmospheric particles.

1PH7

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

Manisha Singh, HARISH 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 co-pollutants (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, e.g. 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.

1PH8

BIOLOGICAL AND CHEMICAL POLLUTION OF FRESH SNOW (WHICH FELL DOWN ON FEBRUARY 18, 2005) IN NOVOSIBIRSK ENVIRON.

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Snow cover accumulates all atmospheric impurities from atmosphere during wintertime. There are two ways of impurities deposition: atmospheric aerosol (and dust) dry deposition and fallout of impurities inside snowflakes. Early we repored data on study of biogenis impurities of snow samples taken in the vicinity of different aerosol sources for full depth of snow cover in the end of winter. Different chemical impurities included total protein and wide variety of culturable microorganisms was found in these samples. To find out what impurities enter snow cover inside snowflakes we studied fresh snow samples. These samples were studied for the presence of culturable microorganisms and total protein, composition of some ions and elements, conductivity, ect.

The following agarized media were used to detect culturable microorganisms: LB and depleted LB medium (diluted 1:10) – to detect saprophyte bacteria; starch-ammoniac medium - to detect actinomyces; soil agar and Saburo's media - to detect lower fungi and yeast. Taxonomic groups the detected microorganisms referred to were determined up to the genus. Microorganisms of widespread genera such as Micrococcus, Staphylococcus, Bacillus, Nocardia, Arthrobacter, Rhodococcus, actinomyces, yeasts and mould fungi were detected in tested samples. Besides, estimation of plasmocoagulating, fibrinolytic hemolytic and some kinds of enzymatic (based on different carbohydrates utilization) activities were made.

It is known that some microorganisms can act as ice nucleation agents in atmosphere. Study of fresh snow saples will allow to expand our knowledge on ice nucleationg microorganisms. Ang gathering information on fresh snow chemical characteristics (including composition of elements ions and molecules) will allow to estimate possible sources of microorganisms found in atmospheric aerosols.

To determine ion composition each sample was divided in two parts: one for determination of NH4+, Na+, K+, F- + HCOO-, Cl-, NO3-, SO42 ions by means of high-performance liquid chromatography, and second for determination of pH and specific conductivity. Than concentration of HCO3-and sum of Ca2+ & Mg2+ was determined by means of conduct metric titration. Concentration of Mg, Pb, Mn, Sn, Zn, and Cu was determined by means of atomic emission spectroscopy with electric arc excitation of spectra using diffraction spectrometer PGS-2 (Germany). Total protein concentration in samples was determined by means of fluorescent method.

The work presents results of biological and chemical analysis of fresh snow samples obtained. The conclusion is made that such works should be continued with involving fresh snow samples from different regions and winter weather conditions analysis.

1PH9

PARTICLE FLUX DIVERGENCE DUE TO PARTICLE DYNAMICS: IS THERE A SPECTRAL SIGNATURE?. S.C. PRYOR, Indiana University, IN; L.L. Soerensen, S.E. Larsen, Risoe National Laboratory, Denmark

In earlier work we have demonstrated the potential for particle dynamics to cause flux divergence and hence modify particle dry deposition fluxes. In this work we explore whether particle number flux divergence might have a signature in the co-spectra of vertical velocity and concentration that could be used to identify in experimental data when particle dynamics (e.g. coagulation) is significantly altering the particle size spectrum, number concentrations and hence the observed flux. To address this hypothesis we use data collected over a Beech forest in Denmark. Particle size distributions measured using an SMPS will be used to calculate coagulation rates. The co-spectra will be computed using 10 Hz data from a CPC and sonic anemometer and compared to theorized co-spectra to examine whether there is a relationship between the magnitude of the 'missing energy' in the co-spectra and the computed coagulation rates.

1PH10

COMBINED RECEPTOR MODEL FOR AMBIENT AND PERSONAL EXPOSURE SAMPLES. WEIXIANG ZHAO, Philip K. Hopke, Department of Chemical Engineering, and Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY; Gary Norris, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC

In order to study the relationship between PM2.5 exposure and emission sources, particle samples were collected in the four different environments (indoor, outdoor, personal, and community) from June 2000 to May 2001. A 24-h sample was collected on 7 days in each of 4 seasons for thirty-seven individuals living in homes in Raleigh and Chapel Hill, NC. Samples were analyzed by energy dispersive X-ray fluorescence to determine elemental concentrations and thermal optical analysis to determine organic and elemental carbon. In addition, air exchange rate was measured in each home. The goal of this study is to identify the emission sources in the four environments and estimate their contributions. The personal samples include contributions from both indoor and outdoor sources, and sources associated with activities such as time spent in vehicles. Based on prior studies, two types of sources (external and internal) are defined. The outdoor and community samples are attributed only to the external sources while the personal and indoor samples are attributed to external sources and internal sources. An expanded receptor model was developed to extract external and internal sources that are shared by the four sample types and estimate their individual contributions to each sample. This combined receptor model is design to analyze a high-dimensional matrix that includes subject (37 individuals), source (or species), date, and sample type. The results obtained from this model will be evaluated to determine the relationship between sources measured at a community or central ambient site and personal exposure.

Disclaimer - Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

1PH11

ATTRIBUTION OF SULFATE AEROSOLS IN THE CLASS I AREAS OF THE WESTERN UNITED STATES USING TRAJECTORY REGRESSION ANALYSIS.

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Atmospheric aerosols can significantly reduce visibility and result in regional haze. The Clean Air Act amendments established a national visibility goal to remedy exiting impairment and prevent future impairment in Federal Class I areas (national parks and wilderness areas designated by congress), most of which are in the western U.S. To aid the creation of Federal and State implementation plans for the protection of visibility in Class I areas, the Interagency Monitoring of Protected Visual Environments (IMPROVE) monitoring program was established to collect filter samples every three days for aerosol mass concentrations and chemical speciation. In order to identify the major source regions of the atmospheric aerosols in the Class I areas of the western United States, back trajectories are calculated for each Western Regional Air Partnership (WRAP) Class I area every three hours at three starting heights (10, 500, 1500m) for the years 2000-2002 using the NOAA HYSPLIT v4.6 model. For each IMPROVE aerosol sampling day, the amount of time that air spends over each of a group of specific source regions on their way to the receptor location (i.e. the IMPROVE monitoring site) is estimated based on the back trajectories. Under the concept that the amount of time air spends over a region determines that region's contribution to the sulfate concentration measured at the receptor site, multiple-linear regression between the IMPROVE measured sulfate concentration and the residence time in the pre-defined potential source regions is done for each Class I area, and the contribution of each source region to the sulfate concentration at the receptor site is estimated. The methodology and the uncertainties associated with the trajectory regression analysis are discussed. The regression results for several selected sites are presented.

1PH12

SIMULATION OF THE ACIDITY AND GROWTH OF MULTICOMPONENT NUCLEATED PARTICLES IN THE EASTERN UNITED STATES.

JAEGUN JUNG, Peter J. Adams, Spyros N. Pandis, Carnegie Mellon University, Pittsburgh, PA

Nanoparticles can potentially perturb the climate system by growing to cloud condensation nuclei sizes through condensation and coagulation and also may be harmful to human health. Accurate simulation of the nucleation, growth, and removal of multicomponent nanoparticles usually demands enormous computational resources. Most three-dimensional chemical transport models use heavily parameterized descriptions of these processes. A major challenge associated with the simulation of nucleation events is the uncertainty regarding the controlling nucleation mechanism under typical atmospheric conditions. Gaydos et al. (2005) simulated nucleation events in the Pittsburgh area using ternary (H2O-H2SO4-NH3) nucleation theory and were successful in predicting on which day nucleation events occurred during both summer and winter, as well as the beginning and end of the events. One drawback of the Gaydos et al. (2005) model is that it accounts for only sulfate in the aerosol mass distribution. To predict the composition of the nanoparticles we have developed a computationally efficient new approach based on the Two-Moment Aerosol Sectional (TOMAS) microphysics module (Adams and Seinfeld, 2002). The model now simulates both the inorganic and organic components of the nanoparticles describing both the number and the mass distribution of the particulate matter from approximately 1 nm to 10 micrometers. The model has allowed us to explain why nanoparticles were observed to be acidic during the ternary nucleation involving ammonia (Zhang's et al., 2004). The simulation suggests that nanoparticles produced by ternary nucleation can be acidic due to depletion of ammonia vapor during the growth of the particles out of the nucleation sizes. The low CPU time requirements of the model using TOMAS make it suitable for incorporation in three-dimensional chemical transport models. The nucleation/coagulation/growth model has been added to the PMCAMx model and is used for the investigation of nucleation events in the Eastern U.S.

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1PH13

MEASUREMENTS OF URBAN AEROSOL IN A LIGHT INDUSTRIAL AREA – PHYSICAL PROPERTIES, INCLUDING PARTICLE SIZE, NUMBER, AND DIAMETER CONCENTRATIONS.

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The physical properties of urban aerosol particles in a light industrial area in the city of Aachen (Germany) have been investigated. Urban aerosol is typically dominated by ultrafine particles with diameters below 100 nm, which often originate from local sources such as traffic and industry. The sampling site was located within a commercial area, about 250 m away from a freeway and just opposite of the depot of the local public transport company that is used by a fleet of diesel-powered busses. In this study several aerosol measurement techniques were employed.

Scanning mobility particle sizers (SMPS) have been used for many years to characterize aerosol in the atmosphere. The single-box SMPS used in this study is of a novel design that was specifically improved for continuous monitoring. Both differential mobility analyzer (DMA) and CPC are integrated in the same cabinet and operated using a scanning algorithm. The SMPS scanned from 10 to 500 nm in 3 min to achieve size distributions with 54 channels resolution.

Further, two continuous flow CPCs measured the number concentration. The instruments were similar in their continuous operation, but used different working fluids to enlarge the particles for optical detection. The 3022A CPC used n-butanol as its condensing fluid, while the 3785 belonged to a novel series of water-based CPCs (WCPC). Both CPCs were selected based on comparable specifications, particularly their suitability to measure high concentrations.

An electrical aerosol detector (EAD) was included as earlier studies have shown that this device should be a useful indicator of health effects of atmospheric particles. The EAD provides fast response measurements of the aerosol's diameter concentration. This aerosol parameter can be thought of as CPC number concentration times average mean diameter, or simply the d1 weighting. The EAD was used to measure particles from 10 to 1,000 nm with 1 sec time resolution.

Results are discussed under three aspects: 1) The consistency of the total number concentration measured by the CPCs with special attention to a possible material dependency for vehicle emissions depending on the use of water or butanol as working fluid. 2) The CPC number count compared to the total number calculated for the SMPS measurements by integration over all size channels. Finally, 3) the average mean diameter determined from combined EAD and CPC concentration results compared to the one obtained from SMPS statistics calculations.

1PH14

COMPARISONS BETWEEN SAMALAYUCAN AND SAHARAN DUST MICROPHYSICS PROPERTIES.

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Satellite observations of aerosols in the lower troposphere are complicated by several factors, including interferences from clouds, land surface characteristics, and uncertainties in the optical properties of the aerosols themselves. Mineral dust has been postulated to have a significant impact on radiative balance, atmospheric chemistry, and transport of pollutants. A general assumption for most retrieval methods is that all mineral dust, regardless of source, has common enough properties that a single retrieval method can efficiently be used to extract basic microphysical properties (number density, size distributions and optical thickness).

We have undertaken a study to evaluate this assumption by comparing the optical properties of two distinct dust sources (Samalayucan and Saharan), using inverse reconstruction methods. The inverse reconstruction methods are ill-posed and require constrained, regularized solutions (Twomey). We will determine sensitivities of the inversion methods to specific aerosol properties using a combination of in-situ, and laboratory data for dust storms observed in El Paso, Texas; La Parguera, Puerto Rico, and off the west coast of Africa, the latter gathered during the last NCAS expedition.

1PH15

NITRO-PAHS IN THE COUNTRYSIDE OF ROME, ITALY. SYNTHESIS OF POSITIONAL ISOMERS FOR THEIR SPECIATION IN AMBIENT AIR..

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The nitrated derivatives of polynuclear aromatic hydrocarbons (nitro-PAHs) are environmental pollutants recognized to cause adverse effects on human health even at very low concentration levels. Indeed, several nitro-PAHs are known to be mutagenic, while some of them are potential human carcinogens. By means of genotoxicity measurements (i.e., Ames tests) it has been proven that the main portion of direct-acting mutagenicity exploited by diesel particulates is associated with nitro-PAHs, while nitro-PAHs and nitro-PAH-lactones contribute to long-term toxicity of airborne particles. Some nitro-PAHs have been included in the International Agency for Research on Cancer lists of carcinogens (2B and 3 groups).

The aim of this study was to identify and quantify an extended set of nitro-PAHs present in atmospheric particulate matter of the countryside of Rome, including little-industry and dwelling zones. The determination of thirty-eight mononitro-PAHs, comprised of numerous isomers, was performed by capillary gas chromatography coupled with mass spectrometric detection (CGC/MSD) operated in negative ion chemical ionization mode (NICI).
Since several of them are not put up for sale by fine chemical distributors either as native standards or in solution, the nitration of the respective parent PAHs (both protonated and perdeuterated congeners) followed by separation and extensive purification was necessary to achieve our aim. For example, when phenanthrene was dissolved in acetic anhydride solution and reacted with HNO3, five nitro-phenanthrenes were produced, although the position of the nitro group in the molecule of four of them couldn't be assigned.

The reacted mixtures were separated by reversed-phase high-performance liquid chromatography (RP-HPLC), through repeated injections, so single isomers were isolated at ~0.5 mg of extent with a purity exceeding 85%. This operation was performed by eluting MeOH/H2O gradients through a 250 x 4 mm Wakosil-II- C18-RS column. Each isomer was first confirmed as nitro-compound by running mass spectrometric analysis operated in EI mode (scan), then the position of the functional group was identified by 1H-nuclear magnetic resonance (NMR) spectrum. By applying our investigation to the air of Rome, we found that the total content of nitro-PAHs in PM10 was increased for over 60% with respect to that usually monitored, which refer over all to few species associated to diesel exhaust and nitropyrene/nitrofluoranthene isomers. In this way, a better overview of air pollution caused by nitro-PAHs could be acquired. The separation and characterization synthesised nitro-PAHs are important for a future study of relative toxicity of singles compounds.

1PH16

AEROSOL OPTICAL PROPERTIES IN THE ARCTIC REGION.

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The aerosol studies during the four Arctic Experiment (AREX) campaigns were carried out onboard the r/v Oceania research ship between 1996 and 2004. During each campaign the r/v Oceania cruised for seven weeks (June-August) in the area of the Arctic between 0 and 14°E and 69 and 79°N. In 2002 the measurements were also carried out, for 3 weeks, from the station in Ny-Alesund on Spitsbergen. The aerosol studies were conducted using an ensemble of instruments, including the FLS -12 lidar, laser particle counter CSASP-100-HV-SP, sunphotometers and ozonometer (Microtops II). The laser particle counter was placed on a mast of the vessel and moved vertically, which facilitated the determination of the vertical structure of aerosol concentrations and their size distribution at altitudes of up to 20 m a. s. l. Simultaneously lidar FLS-12 provided the vertical profiles of aerosol concentrations at altitudes of up to 600 m a. s. l. Those were further used for the calculation of aerosol optical thickness.

Such a measurement set up facilitated the obtaining of data with good accuracy, since the laser counter data were used for the calibration of the lidar data. The full meteorological coverage (wind speed, direction, relative humidity, air temperature, etc.) was provided by the ship meteo station, which collected data every 10 seconds. Additionally air mass backtrajectories were obtained for each selected day analyzed from the British Atmospheric Data Center.
The preliminary results show that local emissions are not always most important factors, which influence the composition of marine aerosol in the near water atmospheric layer, even for the coarse mode aerosols, also known as the sea salt mode. The air mass history must be taken into consideration.
The aerosol optical thickness obtained from the measurements varied from 0.02 up to 0.5 depending on air mass history. The high values of aerosol optical thickness indicate the impact of aerosol particles of continental origin or, in some cases, perhaps presence of thin cirrus clouds, invisible to the measurement performer. However, in majority of cases, the air mass trajectories for such days show that the particles were carried from over the land. The ozone contents varied from very low values of 180 DB up to 520 DB, indicating a very high variability over the period of 60 days of measurements.

1PH17

DEVELOPMENT AND LABORATORY EVALUATION OF A COUNTER-CURRENT PARALLEL PLATE MEMBRANE DENUDER FOR THE NON-SPECIFIC REMOVAL OF GASES FROM AN AEROSOL STREAM. PABLO A. RUIZ, Joy E. Lawrence, Stephen F. Ferguson, Jack M. Wolfson, and Petros Koutrakis. Department of Environmental Health, Harvard School of Public Health, Boston MA 02215

Toxicological evaluation of coal combustion particulate emissions requires the removal of combustion gases such as carbon monoxide (CO) and nitric oxide (NO). This is a great challenge since conventional denuders cannot be used to trap these gases due to the lack of adequate denuder coatings. To overcome this problem, we developed a counter-current parallel plate membrane denuder. According to this technique gaseous pollutants diffuse from the air sample channel into a purge air channel by crossing a micro-porous membrane.

The ability of the denuder to remove gases was evaluated by measuring trace gas penetration as a function of sample and purge flows, denuder height and length, and gas species used. Using CO as a test gas and a purge flow rate (QP) to sample flow rate (QS) ratio of 1, the measured gas penetration ranged from 0.093 to 0.285 for QS values ranging between 3 and 10 LPM, respectively. Moreover, it was found that penetration decreased with each of the following: increasing QP to QS ratios, increasing denuder length and increasing gas diffusivity. Additionally, mass balance tests showed that there were no losses of inert gases due to wall reactions. Finally, particle losses were marginally significant only for particles smaller than 50nm (10 – 25% losses).

1PH18

LIQUID-TO-SOLID PHASE TRANSITIONS OF AMBIENT AEROSOLS. SATOSHI TAKAHAMA, Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA; Vlasis Karidis, Alexandra Tsimpidi, University of Patras, Greece

The phase-state of the particle (i.e., whether they are solid or liquid) affects gas and aerosol partitioning of semi-volatile species, lifetimes, aerosol optical properties and rates of heterogeneous reactions in the atmosphere. Thermodynamic models are able to predict the deliquescence relative humidity of multicomponent aerosols fairly well, but our capabilities for predicting liquid-to-solid transitions are limited. To this end, Martin et al. (2003) developed a parameterization for homogeneous crystallization of sulfate-nitrate-ammonium aerosols at 293 K. Ambient aerosols, however, are often a mixture of both inorganic and organic compounds, which may deviate from phase-transition behavior characterized by this parameterization. Thus, we evaluate this model against observations of aerosol water content made at the Pittsburgh Air Quality Study (PAQS) from July 2001 to July 2002; furthermore, we prepare an alternative parameterization from PAQS field measurements and incorporate our findings into ISORROPIA. This modified ISORROPIA module is used within a 3D chemical transport model, PM-CAMx, to simulate concentrations of aerosols, which are then evaluated against simulations with the original ISORROPIA algorithm and ambient measurements from PAQS. Finally, recent work in examining phase-transitions in increasingly complex aerosol mixtures of laboratory-generated inorganic compounds and secondary organic aerosols in the CMU smog chamber is discussed in the context of these parameterizations.

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1PH19

AEROSOL MASS DENSITY AND NUMBER DENSITY DISTRIBUTIONS DURING AEROSE-2004. LIZETTE ROLDAN, Vernon R. Morris, Howard University, Washington, DC

The NOAA Center in Atmospheric Sciences (NCAS) Trans-Atlantic Saharan Dust AERosol and Ocean Science Expedition (AEROSE) 2004 was a 27 day mission aboard the NOAA Ship Ronald H. Brown (RHB). The AEROSE mission took place during February 29th thru March 26th, departing from Barbados to the Canary Islands and ending in Puerto Rico. The cruise tracks for AEROSE 2004 coincided with one of the largest dust storms on record for this season. One of the goals of the mission was to provide a set of critical measurements to characterize the impacts and microphysical evolution of Saharan dust aerosol during Trans-Atlantic transport. A quartz crystal microbalance cascade impactor (QCM) was used to retrieve in-situ mass density distributions and a laser particle counter (LPC) was used to retrieve in-situ number density distribution.

We will present data showing the evolution of size-resolved aerosol mass and aerosol number density during one of the major dust storms encountered during the mission. Preliminary analysis shows that the aerosol mass density peaked in the range between 0.6 – 3.0 micron while in the dust storm. The aerosol number density peaked in the 0.5 – 1.0 micron size range during the dust storm. The aerosol mass deposition flux rate was estimated to range between 16 – 27 mg/m^2/day.

1PH20

AEROSOL NUTRIENT CONCENTRATIONS AND DRY DEPOSITION FLUXES IN THE GULF OF AQABA. Ying Chen, Joe Street, Adina Paytan, Stanford University

Nutrient concentrations (dissolved N, P and Fe) in aerosols and their dry deposition fluxes have been investigated at the northwest coast of the Gulf of Aqaba in Eilat, Israel during 2003 -2004. The main inorganic nitrogen (DIN) compounds in the water soluble fraction of aerosol particles are nitrate (63%) and ammonium (35%), with mean concentrations of 41.1 and 22.5 nmol m-3, respectively. Water-soluble Phosphate ranges between 0.13 and 0.95 nmol m-3 with a mean value of 0.45 nmol m-3. The DIN and phosphate account for approximately 90% of total dissolved nitrogen (TDN) and 60% of total dissolved phosphorus (TDP). The mean concentration of the water soluble aerosol Fe (DFe) is 0.46 nmol m-3. Soluble P concentrations show a seasonal pattern with higher levels in the fall and winter months (Sept. to Jan.) than in the spring and summer months (Mar. to Jun.). This seasonal pattern in conjunction with the low levels of NH4+ suggest that transport from the surrounding deserts is a major contributor to aerosols over the Gulf. Deposition fluxes of DIN, PO43- and DFe calculated from the measured soluble nutrient concentrations and deposition velocities are 42, 0.78 and 0.4 micromol m-2 d-1, respectively. DIN / PO43- ratio in the soluble fraction of the dry deposition (50: 1) is about a factor of 3 higher than Redfield ratio (N/P = 16: 1), suggesting that atmospheric input of nutrients increases the likelihood for P limitation in the Gulf. The atmospheric DIN flux can support over 10% of surface primary production during the summer months. Atmospheric input of DFe is in large excess compared to that required for the phytoplankton growth driven by the DIN deposition.

1PH21

LANTHANUM AND LANTHANIDES IN ATMOSPHERIC FINE PARTICLES AND THEIR APPORTIONMENT TO REFINERY AND PETROCHEMICAL OPERATIONS IN HOUSTON, TX.

PRANAV KULKARNI, Shankar Chellam, University of Houston, Houston, TX; Matthew P. Fraser, Rice University, Houston, TX

A study was conducted in Houston, TX with the following objectives: (1) provide comprehensive data on the elemental composition of several currently employed zeolite catalysts, (2) quantify rare earth elements (REEs) present in trace (ng/m^3) and ultra-trace (pg/m^3) amounts in atmospheric fine particulate matter, and (3) determine the relative contribution of loss of catalyst from fluidized-bed catalyst cracking (FCC) operations to PM2.5 in the Houston area.

Houston is an excellent site to conduct this research because the Port of Houston is the second largest in the United States in terms of total tonnage. Additionally, the region around the Port of Houston and the Houston Ship Channel is home to an extensive industrial complex that contains 49% of the petrochemical manufacturing capacity in the United States. Paradoxically, direct quantification of the PM2.5 emissions from Houston's petrochemical complex, has not yet been performed to date.

PM2.5 samples were collected from an ambient air quality monitoring site (HRM3) located in the proximity of a large number of oil refineries and petrochemical industries. Further, the elemental compositions of six different FCC zeolite catalysts employed in a wide range of refining operations in the Houston area were established.

The elemental composition of ambient PM2.5, zeolite catalysts, and local soil was measured after microwave assisted acid digestion using inductively coupled plasma – mass spectrometry. Source identification and apportionment was performed by principal component factor analysis (PCFA) in combination with multiple linear regression.

An important contribution of this work is that we (1) report several additional REEs, (2) analyze the composition of recently formulated catalysts, and (3) include a spent catalyst. These data are important to future chemical mass balance modeling calculations.

REE relative abundance sequence, ratios of La to light REEs (Ce, Pr, Nd, and Sm), and enrichment factor analysis indicated that petrochemical cat cracking operations were predominantly responsible for REE enrichment in ambient fine particles. PCFA yielded five physically meaningful PM2.5 sources viz. cat cracking operations, crustal material, coal burning, oil combustion, and sea spray. Crustal material was the chief contributor (62.5%) to the total mass of atmospheric fine particles (less carbon and sulfur). Factor analysis confirmed that emissions from cat cracking operations primarily contributed to REE enrichment in PM2.5 even though they comprised only 2.0% of the apportioned mass. Results from this study demonstrate the need to characterize catalysts employed in the vicinity of the sampling stations to accurately determine local sources of atmospheric REEs.

1PH22

THE COMPOSITION OF SECONDARY ORGANIC PARTICULATE MATTER FROM THE PHOTO-OXIDATION OF META-XYLENE.

JULIE BENNETT, Michael Mozurkewich, Don Hastie, Centre for Atmospheric Chemistry, York University, Toronto, Canada; Janya Humble, Diane Michelangeli, York University, Toronto, Canada

The particle phase products from the oxidation of atmospherically important hydrocarbons are not well known. We are studying the oxidation of specific hydrocarbons in a photochemical flow reactor where we can collect the particulate phase products on filters for subsequent product identification. The reaction being studied is the HO initiated oxidation of meta-xylene. The HO radicals are generated by the photolysis of isopropyl nitrite in the presence of NO and the residence time in the reactor is approximately 2 minutes. Products in the particles that are collected on a quartz fibre filter can be identified by two mass spectrometric techniques. In the first, the sample is extracted in solvent and analysed by a conventional GC-MS. In the second the sample is evaporated into the APCI source of a Sciex TAGA 6000E triple quadrupole mass spectrometer. In addition, predictions of the species in the particle phase are made using a chemical kinetics model based of the Master Chemical Mechanism.
The GC-MS identifies a number of products, through library spectra. Few of these products can be confirmed by the MS/MS capability of the TAGA 6000. Similarly none of the major products predicted by the model have been identified. The TAGA 6000 has independently identified a number of products. There are clearly shortcomings in our knowledge of the products of meta-xylene oxidation and their vapour pressures. The identification work is ongoing.

1PH23

MICRON SIZE PARTICLE TRANSPORT IN THE EARTH BOUNDARY SUBLAYER. DAVID ALBURTY, Chatten Cowherd, Ph.D, , James Balarashti, MSChE, Jason Downing, Gregory Muleski, Ph.D., Midwest Research Institute, Kansas City, MO

An investigation and delineation of earth boundary sublayer particle transport, which we first observed during wind tunnel tests in the Mojave Desert in California, will be presented. This effect seems to be confirmed by ultraviolet aerosol particle sizing (UV-APS) data taken at a range of heights from 10 to 200 cm above ground level in both urban and rural environments in Missouri. Results from both studies are compared.

1PH24

CHARACTERIZATION OF FUGITIVE DUST FROM ALMOND HARVEST OPERATIONS WITH REAL-TIME MONITORS. KRYSTYNA TRZEPLA-NABAGLO, Paul Wakabayashi, Robert Flocchini, Crocker Nuclear Laboratory, University of California, Davis, CA

Agricultural related sources, including almond harvest, significantly contribute to the PM10 emissions operations in the San Joaquin Valley Air Basin. The current PM10 emission inventory shows almond harvesting to be one of the largest PM10 agricultural sources. Therefore, in order to provide accurate information for PM10 emission inventory, the accurate estimates of PM10 mass concentrations at the receptor sites need to be made.

Different PM10 measuring techniques were employed during these studies, including traditional filter based samplers in an upwind-downwind array, real-time monitors at downwind location and application of the Industrial Source Complex Short-Term Version 3 (ISCST3) modeling techniques.

The on field measurements were performed during almond harvest operations using traditional filter based sampling including total suspended particulate (TSP) and PM10 techniques in upwind-downwind array. In addition, two optical instruments, DataRam manufactured by Mie, Inc and NGN3 by Optec Inc were set up to collect data at the location of the sampler, and lidar instrument was positioned about 500m East or West from the source to provide downwind two-dimensional (2D) scans at the sampler location. This paper will emphasize on analysis of the measurements obtained with real-time monitors and lidar instrument during the almond harvest campaign in summer of 2004.

Despite difficulties to accurately estimate particle concentrations from the light scattering and absorption properties, the effort was made to relate those and further, to correlate with corresponding measurements obtained from the 2D lidar scans at the receptor site. The assumption of the linear relationship between TSP samples collected downwind at 4 heights and the lidar backscatter signal provided detailed picture of the fluxes, and together with modeling techniques, detailed information about vertical and horizontal dispersion of the generated plumes. Particulate size distribution (PSD) analysis performed on TSP filters using Coulter counter yielded on average 25-30% of PM10, with mass mean diameter (MMD)= 17.6µm and geometric standard deviation (GSD)= 2.1, and below 5% of PM2.5 in TSP. Developed modeling techniques allowed for better understanding of fugitive dust dynamics and the capability to predict particulate mass concentrations and consequently validate measured fluxes. The PM10 emission factors derived from on field measurements (optical, lidar, TSP, PM10) ranged from 154 to 1450 kg/km2 and compared well with those validated with model ranging 186 to 1209 kg/km2, depending on the operation.

1PH25

CHARACTERIZATION OF FINE AEROSOLS IN THE SOUTH COAST AIR BASIN.

AMY E. GILDEMEISTER, Philip K. Hopke, Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY

Urban particulate matter is implicated in causing chronic health conditions such as asthma. Periods of high particulate concentration have also been linked to premature mortality from chronic cardiopulmonary ailments. Southern California is well known for having severe air quality problems due to a unique combination of geographical features and a high population density. Source receptor modeling is an important tool that can be used to determine sources of fine particulate matter in urban areas. A multivariate statistical analysis is conducted, based on an assumption that trace elements and other species are emitted from sources in characteristic ratios and that despite dilution and atmospheric mixing with other sources, the atmospheric species that are characteristic of a particular source will covary. The PM 10 Technical Enhancement Program (PTEP) was initiated to comprehensively characterize the fine particulate matter in the South Coast Air Basin. Samples were collected on quartz fiber filters for analysis of organic carbon and elemental carbon. Quartz filters were extracted and nitrate, sulfate, ammonium, chloride, and sodium were analyzed by IC. Samples were also collected on Teflon filters for analysis of mass and 36 trace elements. Mass was determined gravimetrically and elemental analysis was done using XRF. To augment the particulate measurements, gaseous nitric acid and ammonia were also measured. Positive matrix factorization (PMF) addresses shortcomings of other multivariate models that have been used in the past 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 elemental contribution and permits realistic individual data point weights. Using this multivariate technique, contributions made by local industrial sources and long range sources can be distinguished.

1PH26

CHARACTERIZATION OF URBAN AEROSOL IN WILMINGTON, DELAWARE USING A REAL-TIME SINGLE PARTICLE MASS SPECTROMETER.

MELISSA S REINARD, Matthew A. Dreyfus, Michael P. Tolocka, Murray V. Johnston University of Delaware, Newark, DE;

The third-generation real-time single-particle mass spectrometer (RSMS-3) was deployed to the Martin Luther King (MLK) Air Monitoring Station in April 2005 in Wilmington, DE, as part of the Enhanced Delaware Air Toxics Assessment Study (EDATAS). The site is located within 10 km of many PM10 and PM2.5 emitters including power plants, highways, waste treatment and recycling centers, various industrial plants, and hospitals. Four one-month sampling intensives are planned for the year. Fine and ultrafine particles with sizes between 45 nm and 770 nm are analyzed. In contrast to previous studies, RSMS-3 is being operated in a continuous fashion. The instrument begins its cycle through five orifices each hour. Sampling times are fixed; an unlimited number of particle hits are allowed to be collected. The resulting positive and negative ion spectra for each particle are classified using an artificial neural network algorithm, adaptive resonance theory ART 2-a. Ambient number concentrations are determined for each particle class and are correlated with particle size, wind direction and time of day/year. Preliminary results show the MLK site has higher metal concentrations when compared to other sites studied with RSMS-3. Source sampling will be performed to determine the origin of these metal-containing particles. Comparisons will be made with other continuous and mobile measurements at the site.

1PH27

CHEMICAL CHARACTERIZTION OF WATER SOLUBLE AEROSOLS AT AIRBORNE AND GROUND BASED SITES USING A PARTICLE-INTO-LIQUID SAMPLER (PILS)..

DESIREE TOOM-SAUNTY, Katherine L. Hayden, W. Richard Leaitch, Anne Marie Macdonald, Dave Halpin, Amy Leithead, Shao-Meng Li, Kurt G. Anlauf, Sangeeta Sharma, J. Walter Strapp, Meteorological Service of Canada, Toronto, ON

A PILS sampler was used on board the Canadian NRC Convair 580 aircraft as part of the ICARTT field program during 21 July – 18 August, 2004. The main study focused on chemical transport and transformation in cloud (CTC), conducted out of Cleveland, Ohio, as well as two flights looking at long range transport into the Maritimes (TIMS), based out of Bangor, Maine. Additional instrumentation included particle chemistry measured by an Aerodyne aerosol mass spectrometer (AMS), gas phase measurements, and physical characterization of aerosols and cloud.

The PILS sampler used trace concentrator columns coupled to anion and cation chromatographs equipped with eluent generation. Major inorganic species (SO4=, NO3-, Cl-, NO2-, Na+, NH4+, K+, Mg++ and Ca++) were integrated continuously over 10 minute periods, as was used for this study. Alternatively, the PILS can be programmed for 15 or 30 minute integration to include a suite of organic acids, without changing columns, eluents, tubing or flow rates. This paper will explain the methodology behind the sampler, include measurements for select ICARTT flights, and compare results with the AMS and other instruments. Examples from ground based studies will be used to help validate the results.

1PH28

ROLE OF IONS IN ATMOSPHERIC PARTICLE FORMATION: SECOND-GENERATION ION-MEDIATED NUCLEATION MODEL.

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New particle formation has been observed in various locations in the lower troposphere. However, the mechanisms of new particle formation remain illusive. In recent years there is an increasing interest in the nucleation of H2SO4-H2O on ions. Ions generated by cosmic rays and radioactive materials are ubiquitous in the atmosphere and nucleation on ions is known to be thermodynamically favored over the homogeneous nucleation. Yu and Turco [1997, 2000, 2001] developed a novel approach to study the nucleation on ions. The new approach is based on a kinetic model that solves the complex interactions among ions, neutral and charged clusters of various sizes, vapor molecules, and pre-existing particles. The evolution of the size distributions of both charged and neutral clusters in the presence of ionization, neutralization, and scavenging leads to a net flux of clusters crossing critical size (i.e., nucleation). This mechanism was referred as ion-mediated nucleation (IMN). In our earlier version of the IMN model, the evaporation of small clusters is considered through a simple adjustment to the condensation accommodation coefficients due to the lack of thermodynamical data of small clusters. This rough approximation is likely to lead to large uncertainty in the predicted nucleation rate in the atmosphere.

Recently, we have developed a scheme to calculate the evaporation of H2SO4 molecules from neutral clusters [Yu, 2005a]. The scheme is based on liquid droplet approximation using most recent thermodynamic data and our model of kinetic H2SO4-H2O nucleation gives a nice agreement with experimental results. We have also made progress in understanding of the thermodynamics of small charged clusters by deriving a modified Kelvin-Thomson (MKT) equation which takes into account the dipole-charge interactions [Yu, 2005b]. The thermodynamic data for small ion clusters derived from MKT equations are in much better agreement with experimental results than those derived from the classical Kelvin-Thomson equation. A scheme to calculate the evaporation coefficients of H2SO4 molecules from charged clusters based on MKT equation has been derived. Here we present a second generation model of IMN which treats the evaporation of neutral/charged clusters explicitly using the schemes recently developed and show that IMN can lead to significant new particle formation in the atmosphere.

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1PH29

COMPARISON OF SIZE-RESOLVED AEROSOL CONCENTRATIONS FROM MULTIPLE U.S. CITIES.

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Fine (< 2.5 µm) aerosol particles, emitted during combustion and generated from atmospheric chemical reactions, are important to both human health and climate. Despite their important role, knowledge of their sources and atmospheric concentrations is limited. A recent $27 million Environmental Protection Agency study (the Particulate Matter Supersites Program) in several U.S. cities gathered the most complete record to date about fine aerosol number concentrations and size distributions in urban locations. To date, they have only been analyzed individually. We have gathered and begun a comparative analysis of data from several of these sites, including St. Louis, Atlanta, Pittsburgh, and New York (Queens College). The comparison includes site characterization, data QA/QC, and summary statistics. Summary statistics will include average size distribution(s); mean, median, standard deviation, and percentiles of number concentration; diurnal size-resolved concentrations; seasonal patterns in size-resolved 24-hr concentrations; correlations of size distributions with wind direction; diurnal patterns in CO, NO, NOx, O3, temperature, RH; and correlation analysis of particle counts, particle mass, CO, and NO. This work will form an important record of the EPA sampling program and discover new insights about ultrafine particles and their impact on human health and the environment.

1PH30

OXYGENATED ORGANIC COMPOUNDS PRESENT IN MOTOR VEHICLE PARTICULATE EMISSIONS.

CHRIS JAKOBER, Sarah Riddle, Judith Charles, Department of Toxicology, UC Davis, Davis CA; Michael Robert, Michael Kleeman, Department of Civil and Environmental Engineering, UC Davis, Davis CA.

Particle-phase oxygenated organic compounds emitted from combustion sources are suspected to cause negative human health effects, contribute to the formation of tropospheric ozone and secondary organic aerosol, impact cloud formation processes and alter precipitation. These compounds are difficult to measure due to their polar and semi-volatile nature. Using analytical methodologies previously established in our laboratory we measured the compounds containing carbonyl and carboxylic functional groups using derivatization with O-(2,3,4,5,6)-pentafluorobenzylhydroxylamine (PFBHA) and 2,3,4,5,6-pentafluorobenzyl bromide (PFBBr) in concert with gas chromatography-ion trap mass spectrometry (GC-ITMS) and high performance liquid chromatography-ion trap mass spectrometry (LC-ITMS). These chemical analysis methods were applied to phase-separated emissions samples collected using a denuder-filter sampler from both light-duty gasoline (LDV) and heavy-duty diesel vehicles (HDV) operated on chassis dynamometers. Over forty carbonyl and twenty carboxylic compounds have been identified and quantified. The particle-phase carbonyls measured include aliphatic and aromatic aldehydes, ketones, dicarbonyls and unsaturated species. Organic acids identified include alkanoic, alkenoic and aromatic species. Chemical speciation differences were observed between the LDV and HDV emissions, including the first measurements of benzoquinone emission factors. The largest fuel consumption based emission factors of both carbonyl and carboxylic species were associated with the HDV operated under idle and creep conditions. Total carbonyl species emissions for the motor vehicles examined to date ranged from 12-1650 µg km-1 traveled and 110-9650 µg L-1 fuel burned. Total carboxylic species emissions ranged from 6-1600 µg km-1 and 54-29000 µg L-1. The total oxygenated organic species measured comprise 1 -12% of the particulate and 3-26% of the organic carbon emissions. These measurements improve our understanding of the chemical speciation of motor vehicle emissions allowing further mass closure while providing additional toxicologically relevant compounds. This additional chemical speciation will enhance the understanding of environmental and human health risks posed by various motor vehicle emission sources.

1PH31

DEVELOPMENT OF THE AIRCRAFT-AEROSOL TIME-OF-FLIGHT MASS SPECTROMETER (A-ATOFMS). GARY POON, John Holecek, Ryan Moffet, Hiroshi Furutani, Rene Sanchez, Sergio Guazzotti, Yongxuan Su, Thomas Rebotier, Kerri Denkenberger, Joseph Mayer, Kim Prather, University of California, San Diego, San Diego, CA; Marc Gonin, Katrin Fuhrer, TOF Werk AG, Thun, Switzerland

Aerosol time-of-flight mass spectrometry (ATOFMS) simultaneously measures both the aerodynamic size and chemical information on a particle-by-particle basis using laser desorption ionization dual polarity time-of-flight mass spectrometry. The development of an aircraft-based instrument not only extends the applications of the ATOFMS to the free troposphere but also represents a significant improvement in mass resolution, sensitivity, repetition rate, and data processing. To this end, the aircraft instrument builds on 12 years of experience gained with the transportable ATOFMS and incorporates features necessary for aircraft data acquisition including a) an aerodynamics lens system to increase detection efficiency at lower inlet pressures experienced at higher altitudes, b) miniaturization of the aerodynamic sizing and mass spectrometer regions with significantly reduced dimensions, mass, and pumping requirements, and c) a data acquisition system capable of handling the increased rate and quantity of data generated. Because ATOFMS is an on-line technique, it offers the high temporal resolution and sensitivity necessary to study real-time mixing and aging processes of anthropogenic pollution in the troposphere above urban areas on short timescales and long range transport of these particles on longer timescales. Major design highlights and preliminary field results from urban areas will be presented.

1PH32

THE CASSIAR TUNNEL 2001 STUDY: EMISSIONS CHARACTERIZATION FROM VEHICULAR TRAFFIC IN VANCOUVER, BRITISH COLUMBIA, CANADA.. JEAN-PIERRE CHARLAND, Gianni Caravaggio, Penny MacDonald, Tony McPhee, Natural Resources Canada, CANMET Energy Technology Centre-Ottawa, Ontario, Canada; Chung Chiu, Gary Poole, Lisa A. Graham, Environment Canada, Environmental Technology Centre , Ottawa, Ontario, Canada

In 1999, PM2.5 emissions were collected from light duty gasoline motor vehicles during chassis dynamometer tests conducted at the BC AirCare Research Facility in Burnaby. The PM emission data were incorporated in a PM emission profile database used for apportionment of the various transportation sources in ambient PM in major Canadian cities. In 2001, this database was tested in a second study where PM2.5 samples were collected for seven days at the Cassiar Tunnel in Vancouver, BC. 3- and 9-hour integrated samples were collected on teflon coated borosilicate glass filters for organic speciation. 3-hour samples were collected on pre-fired quartz fibre filters for OC-EC determination. It was determined based on license plate identification that the traffic during the study was composed of at least 85% light duty gasoline vehicles.

Samples of fresh lubricating oil for light and heavy duty applications, and diesel fuels were also collected for organic speciation. The following classes of compounds were analyzed by GC/MS: n-alkanes, hopanes, steranes, alkyl-cyclohexanes, PAHs, NO2-PAHs and S-PAHs. Analysis of the n-alkanes in the PM solvent extracts and the lubricating oils was performed also by extraction with a molecular sieve to remove the unresolved complex mixture comprised of other saturates interfering with the chromatography.

Comparison of normalized emission profiles from the PM2.5 samples, the lubricating oils and the fuels in the database, indicates that these suites of compounds, which appear in the PM2.5 samples, arise primarily from the lubricating oil and not the fuel. Compounds readily differentiating lubricating oils from diesel fuel do not appear in the PM2.5 samples. This suggests that these suites of compounds cannot distinguish between light duty gasoline and heavy-duty diesel sources. Comparisons of the dynamometer emission profiles to those collected at the tunnel will also be presented to assess the variability of the profiles from the same sources collected under different conditions.

Significant differences in emission rates were obtained between the 3- and 9-hour integrated samples. So normalizing to OC emission rates obtained over the 3-hour interval generated profiles with very different magnitudes but no difference in relative amounts of individual organic species. Similar differences may be expected depending on the sampling interval used for OC determination and the method by which the sampling artifacts are corrected. These results are clearly raising issues about the uncertainty estimates on emission profiles and attempts to correct them for sampling artifacts.

1PH33

FLOWRATES, CUTPOINTS, AND CONCENTRATIONS IN THE IMPROVE NETWORK. NICOLE HYSLOP, Warren White, Chuck McDade, University of California, Davis, CA

The Interagency Monitoring for Protected Visual Environments (IMPROVE) program utilizes PM2.5 samplers with passive flow control. The flowrate is passively controlled using critical orifices located downstream of the sample filter. Critical orifices are insensitive to downstream pressure changes but sensitive to upstream pressure changes. As the filter loading increases, the pressure drop across the filter increases, lowering the pressure upstream of the critical orifice, and thereby reducing the flowrate. The decrease in flowrate varies significantly among samples depending on the sample deposit area, the PM2.5 concentration, and the particle size distribution. These changes in flowrate result in changes in the particle-size cutpoint of the cyclone. Depending on the particle size distribution, the amount of particulate matter collected can change as a result of the shift in cyclone cutpoint.

The uncertainty of IMPROVE sample concentrations is increased by varying flowrates during sample collection, and this uncertainty must be considered in analyses of the IMPROVE data. The 24-hr average sample flowrates for each filter (nylon, quartz, and Teflon) are included in the IMPROVE database. In addition, new validation flags have recently been implemented to convey flowrate problems more succinctly and consistently. Three different validation flags are used to indicate flowrate problems in the IMPROVE dataset. Approximately 1% of filters/year are invalidated (concentrations replaced with missing values indicators) as a result of severe decreases in flowrate. Approximately 1 -4% of filters/year are flagged as clogging, which is defined as having the cutpoint rise above 4 um. A significant number of samples (4-10% of filters/year) is flagged as having a 24-hr average flowrate 7% below or above the nominal flowrate, which corresponds to a cutpoint above 3 or below 2 um, respectively.

Samples with severe flowrate problems are flagged as described above but even minor deviations from the nominal flowrate can affect the data quality. At the Mesa Verde site in Colorado, two collocated Teflon sample modules were operated for several months with filter cassettes having differing flow resistances. The flowrate in one of the collocated modules regularly decreased more during each 24-hr sampler period than the flowrate in the other module. These differences in flowrate resulted in differences in cutpoint and ultimately differences in the concentrations measured by the two modules. This paper documents the resulting differences in reported concentrations.

1PH34

ANALYSIS OF REACTIVE MERCURY IN ATMOSPHERIC AEROSOL USING PYROLYTIC THERMAL DESORPTION AND COLD VAPOR ATOMIC FLUORESENCE SPECTROSCOPY (PTD-CVAFS). Andrew P. Rutter and James J. Schauer, Environmental Chemsitry and Technology Program, University of Wisconsin-Madison, Madison, WI

Offline filter based methods and semi-continuous online methods presently exist that allow monitoring of atmospheric mercury. The offline filter based methods consist of processing the filters using the EPA 1631e method for mercury in water. The quartz fiber filters are digested with an acidic solution of BrCl overnight in an oven to extract the mercury which is then reduced using SnCl2 and evolved onto a gold trap for CVAFS analysis. The semi-continuous online method offered by Tekran consists of a denuder, particle pyrolyzer and gold amalgamation CVAFS to collect and analyze reactive gaseous mercury (RGM), reactive particulate mercury (RPM) and Elemental Gaseous Mercury (EGM) respectively. The reactive mercury monitoring performance of the Tekran is yet to be fully validated with colocated reactive mercury measurements in the field.

The Pyrolytic Thermal Desorption –Cold Vapor Atomic Fluoresence Spectroscopy (PTD-CVAFS) technique is an alternative to both of these methods as it is cheaper than the Tekran and gives better turn around time for filter based samples than the EPA 1631e method. The University of Wisconsin PTD heats a punch of the sample filter in a furnace at 500ºC in an argon carrier gas. The desorbed analytes are passed through a purification stage which consists of a quartz wool pyrolysis section heated to 900ºC followed by scrubbing traps of sodalime, to remove water and other acidic gases, and tenax to remove unpyrolyzed organics. Finally the desorbed mercury is amalgamated to a gold trap and subsequently desorbed into a Tekran 2500 CVAFS.

The aim of this work is two fold: i) to develop and validate a pyrolytic thermal desorption (PTD) method in the laboratory that can be used to determine reactive mercury contents of both atmospheric and laboratory aerosol, and; ii) to validate atmospheric data from the Tekran atmospheric mercury analyzer.

1PH35

DETERMINATION OF TRACE METALS IN FINE (PM2.5) PARTICULATE MATTER BY ICP-MS IN A LOW POLLUTED AREA IN MEXICO. Mario Murillo-Tovar, MIREYA MOYA, Centro de Ciencias de la Atmósfera-UNAM, Mexico; Claudia Ponce de Leon, Instituto de Geografía- UNAM, Mexico.

Chemical characterization of aerosols is important because allow us to better understand processes related to its formation, transport and removal. In this work we report the determination of trace metals in PM2.5 (PM with aerodynamic diameter less than 2.5 microns). Aerosols were sampled at the Altzomoni site (19° 07' N, 98° 39' W), 11 kilometers in straight line from the Popocatepetl volcano (active from 1993) using a Mini-vol sampler and Quartz fiber substrates. The period of study was from March 31st to April 17, 2005. The determination of the following trace metals V, Mn, Co, Pd, Pb and Cd was successfully achieved using the ICP-MS technique. Our findings indicate that by adapting USEPA Methods IO-3.5 and IO-3.1 with proposed modifications on preparation and extraction of filter material very low concentrations (ng per cubic meter) of trace metals can be determined. Significant lower concentrations of the aforementioned metals were observed for a couple of days (13 and 14 of April) of the period of study when a significant increment in RH and precipitation events was recorded at the Altzomoni site.

1PH36

SEASONAL VARIATION OF PM2.5 IONIC CONCENTRATIONS AND WATER CONTENT IN SEOUL. JUNG YOUN KIM, Yong Pyo Kim, Ewha Womans Univerisity, Seoul, Korea

Water content in fine particles(PM2.5) is an important factor for PM2.5 mass concentration and, thus, various aspects of air quality problems. To characterize seasonal and diurnal variation of PM2.5 water content, (1) inorganic ionic concentrations in PM2.5 and related gaseous species concentration were measured and (2) a gas/particle equilibrium model is applied to the measurement results to estimate water content in PM2.5. Measurements were carried for about 10 days in Nov. 2004, Jan. 2005, Mar. 2005, and will be carried out in Jul. 2005. In each day, two 12-h samples are obtained. A denuder-filterpack system is used to collect PM2.5 for inorganic ion analysis and to sample gaseous species(HNO3, HCl, and NH3).
SCAPE2(Simulating Composition of Atmospheric Particles at Equilibrium2) is used to estimate partitioning of species between gas and particle phase and water content.
It was found that PM2.5 water content and, thus, PM2.5 mass concentration in Seoul are most sensitive to ambient relative humidity.

1PH37

ESTIMATION OF THE EFFECT OF INTERACTION OF ORGANIC AND INORGANIC SPECIES ON AEROSOL WATER CONTENT DURING PITTSBURGH AIR QUALITY STUDY. Nitin Goel, ANDREY KHLYSTOV, Duke University, Durham, NC; Charles O. Stanier University of Iowa, Iowa City, IA; Satoshi Takohama, Spyros Pandis, Carnegie Mellon University, Pittsburgh, PA

Understanding of the aerosol hygroscopic properties is of critical importance for studies of the aerosol effect on climate. 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. The effect of organic aerosol constituents on the hygroscopic properties of ambient particles is also highly uncertain.

The water content of ambient aerosol was 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). The observations of aerosol water content during July 2001 were compared with the thermodynamic equilibrium models GFEMN, AIM and AIOM. The first two models neglect the contribution of organic compounds to water absorption and under-predicted water content by about 35%, which may be an indication of the magnitude of the contribution of the organic compounds to the water absorption. The contribution of the organics to water absorption is estimated using the AIOM thermodynamic model. The AIOM models the inorganic ion - water, organic - water and ion-organic interactions. The aim of the study is to assess how important are the interactions of neutral solute (organics) with ionic species for water absorption by atmospheric aerosol.

1PH38

IN-SITU MEASUREMENTS OF AEROSOL OPTICAL AND PHYSICAL PROPERTIES. A.W. Strawa, A.G. Hallar, NASA Ames Research Center, Moffett Field, CA, USA A.P. Arnott, Desert Research Inst., Reno, NV, USA R. Elleman, D. Covert, U. of Washington, Seattle, WA, USA J. Ogren, NOAA/CMDL, Boulder, CO, USA B. Schmid, J. Redemann, Bay Area Environmental Research Inst., Sonoma, CA, USA A. Bucholtz, Naval Research Lab., Monterey, CA, USA H.H. Jonsson, Naval Postgraduate School, Monterey, CA, USA C. Corrigan, Scripps Inst. of Oceanography, La Jolla, CA, USA

Better characterization of spatial and temporal aerosol characteristics is essential to better understand, model, and predict their effects on global and regional climate. Carbonaceous species (BC and OC) are responsible for most of the absorption associated with aerosol particles. The amount of radiant energy an aerosol absorbs has profound effects on climate and air quality. It is ironic that aerosol absorption coefficient is one of the most difficult aerosol properties to measure.

Cadenza is a relatively new instrument that uses cavity ring-down (CRD) to measure the aerosol extinction coefficient for 675 nm and 1550 nm light, and simultaneously measures the scattering coefficient at 675 nm using a reciprical nephelometer concept. Both measurements are made in the same optical and flow cell at exactly the same conditions with a temporal resolution of about 1 sec. Absorption coefficient is obtained from the difference of measured extinction and scattering within the instrument and single scattering albedo from their ratio. Cadenza has participated the Atmospheric Radiation Measurement (ARM) Program’s Aerosol Intensive Operating Period (AIOP) in May, 2003, Extended MODIS wavelength Validation Experiment (EVE) in April, 2004, the Caldecott Tunnel study in June, 2004, and the Atmospheric Brown Cloud Post Monsoon Experiment (APMEX) in Oct., 2004, and most recently in the DOE the MArine Stratus Radiation Aerosol and Drizzle (MASRAD) study.

This presentation will compare aerosol physical and optical properties (extinction, scattering, and absorption coefficients, single scattering albedo, fRH, wavelength dependence) measured during several of these diverse missions focusing on the vertical distribution of aerosols. Comparisons are made with other instrument that measure similar aerosol properties. One area of focus will be comparisons of absorption coefficient made by Cadenza, the Particle Soot Absorption Photometer (PSAP), and a photoacoustic instrument (DRI).

1PH39

SOURCE APPORTIONMENT OF THE AMBIENT AEROSOL IN ZÜRICH, SWITZERLAND.

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Samples collected to measure the elemental concentrations in airborne particulate matter at Zürich Juchhof, Switzerland from November 25, 2003 to January 31, 2004 have been used for this study. This site is located in an industrial area and is in immediate vicinity of a major railway line. A three stage rotating DRUM impactor (RDI) was deployed to collect ambient aerosol in three size ranges, 0.1-1 µm,1-2.5 µm and 2.5-10 µm with a time resolution of one hour by particle impaction on a thin Mylar substrate tape. The collected RDI impaction tapes were analyzed by synchrotron X-ray fluorescence spectroscopy (SR-XRF). During the RDI campaign, an optical particle counter (OPC Grimm 1.108) was operational at the same site. Hourly PM10 mass concentrations were estimated from the OPC data, by converting the optical number distribution to an aerodynamic mass distribution with subsequent integration. PM10 mass concentrations thus obtained were used for scaling in source apportionment. The multilinear engine-2 (ME-2) was applied to the elemental data for source apportionment in a new three-way model that assumes that the source profile is size dependent. The results of source apportionment, with emphasis on resolution of railway traffic sources will be discussed. The usefulness of the conditional probability function (CPF) using surface wind data and resolved source contributions in identification of local sources will be elucidated.

1PH40

GAS-PARTICLE PARTITIONING OF PAHS AT URBAN AND BACKGROUND AREAS IN KOREA.

JI YI LEE, Yong Pyo Kim, Ewha Womans University, Seoul, Korea, Chang Hee Kang, Cheju National University, Jeju, Korea, Young Sung Ghim, Korea Institute of Science and Technology, Seoul, Korea

Gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) were measured at Seoul, a representative urban site, and Gosan, a background site, in Korea in 2002 and 2003 to characterize gas-particle partitioning of PAHs. Particulate PAH samples collected on quartz fiber filters and gaseous PAHs samples collected in PUF plugs were extracted by ultrasonication and supercritical fluid extraction method, respectively, and analyzed by a GC/MSD/SIM.

The gas-phase concentrations of total ambient PAHs (the sum of 17 compounds) at Seoul (9.35 - 118.22 ng m-3) were about two orders higher than those at Gosan (0.26 - 7.27 ng m-3). However, the particulate-phase PAHs concentrations at Seoul (2.08 - 83.90 ng m-3) were only one order higher than those at Gosan (0.03 - 14.81 ng m-3) indicating lower influence of local emission sources at Gosan.

Partitioning coefficients of PAHs between gas and particulate phases both at Seoul and Gosan were well-correlated with subcoolded liquid vapor pressures (P0L). Seasonal variation of the slope values between partitioning coefficient (Kp) and log P0L was observed at Gosan but not at Seoul. The slope values at Seoul were higher than the equilibrium value of -1 and comparable to those at other urban sites in USA. These higher slope values may reflect the influence of local emission sources at Seoul. At Gosan, the slope value between partitioning coefficient (Kp) and log P0L in winter was –0.52 ± 0.09, closed to -1 while that in summer was –0.25 ± 0.08 suggesting possibility of the larger influence of long-range transport during winter at Gosan.

1PH41

COMPARISON OF PARTICULATE PAHS LEVELS AT GOSAN AND MT. HALLA SITES, JEJU ISLAND, KOREA.

JI YI LEE, Yong Pyo Kim, Ewha Womans University, Seoul, Korea, Chang Hee Kang, Cheju National University, Jeju, Korea, Naoki Kaneyasu, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous organic pollutants some of which are reported to be mutagenic and carcinogenic materials. About 90-95wt% of particulate PAHs are associated with fine particles and airborne particulate PAHs in this size range can transport long distances. Northeast Asia, in particular China, is the world's largest coal consumption region. Thus, it has been speculated that emissions of PAHs and their ambient concentrations would be large and their impacts such as high toxicity and bioaccumulation potentials into human body would be also high over the region.

The sites of this study, Gosan and Mt. Halla are located at Jeju Island and Gosan site is about 35 km west from the Mt. Halla site. Gosan is the least developed area in the Island. The Mt. Halla site is located at a remote mountain area with the elevation of 1100 m. Jeju Island is located at about 100 km south of the Korean Peninsula, about 500 km west of China (Jiangsu province), and about 200 km east of the Japanese Islands (Kyushu) and is regarded as intersection of pollutants' flow in this region.

In this study, (1) temporal trend of atmospheric particulate PAHs levels at Gosan and Mt. Halla sites are observed, (2) main factors that cause difference of the levels and compositions of particulate PAHs between Gosan and Mt. Halla sites are discussed.

1PH42

CLASSIFICATION OF SIZE-RESOLVED SOOT PARTICLES BY POROSITY.

ESTHER COZ, Francisco J. Gómez-Moreno, Manuel Pujadas, Begoña Artíñano, CIEMAT, Environmental Department, Madrid, Spain

The importance of the study of soot aggregates has been increasing during the last years due to the amount of medical research studies that relate this kind of atmospheric particles to several and severe consequences in public health. Their morphology can be also related with other important physical characteristics and environmental effects, i.e. light absorption, being the main absorbing fraction of aerosol [1].

The basic structure of soot particles is a group of primary carbonaceous spherical nanoparticles forming aggregates. These aggregates can be classified into two main groups according with their morphology: fractal-like structure (open soot cluster) and sponge-like structure (closed soot cluster) [1]. These special morphological properties make them having remarkable different behaviours compared with the rest of the ambient particles.

The purpose of this study is to obtain a classification of soot aggregates based on their porosity and other morphological factors to establish a possible relation among them and with the geometric/aerodynamic size ratio (Rga). This will be a step forward towards a better understanding of their different behaviour in air.

Urban samples have been taken with a cascade impactor to previously classify the particles by the aerodynamic sizes, thus making possible a comparison with their geometrical size. The morphological analysis has been carried out by image processing of SEM pictures from the particles, which have been automatically classified by their different morphological properties in four groups: single spheres, compact particles, open soot clusters, and closed soot clusters.

Results have shown up that the Rga is much higher for the closed soot clusters than for the other groups and can reach values of 10. These close structures are usually bigger and have larger number of primary particles of smaller size than the open soot clusters. In the case of that group, their Rga can be directly related with their high porosity and to the measured roughness. As expected, the Rga of the spherical particles always have a value equal or nearly below 1.

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1PH43

AVIATION- RELATED METEOROLOGICAL CHANGES OF FOG IN SOUTHERN NIGERIA. ONIFADE yemi sikiru Wesley College Of science, Ibadan, Oyo State, Nigeria

This work was carried out by making use of Fog measured Data for 5 years 4 months (64) months (1995-2000). The monthly mean valus of Fog days at the three different stations were determined. A Fast Fourier Transform Program was used to obtain their Fourier analysed Data. The monthly frequency and Variational trend of Fog were determined for the three stations. Graphical representations and comparison were made. These show a significant time shifts in their time variations which is an important conclusion for flight plans and forecast of turbulent and other phenomenon.

1PH44

SECONDARY ORGANIC AEROSOL FORMATION IN THE EASTERN US: EFFECT OF TEMPERATURE, NOX, AND UV RADIATION. TIMOTHY LANE, Albert Presto, Kara Huff-Hartz, Ravikant Pathak, Neil M. Donahue, Spyros N. Pandis, Carnegie Mellon University, Pittsburgh, PA; Charles Stainer, University of Iowa, Iowa City, IA

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, potentially posing health hazards and contributing to global climate change. The most important source of SOA appears to be ozonolysis of terpenes, both monoterpenes and sesquiterpenes. The SOA yields of terpenes depend on temperature, the VOC/NOx ratio, and the sunlight intensity. Under typical VOC/NOx conditions, aerosol yields may be a factor of 2 and 4 lower than the yields in NOx-free conditions. Also, current aerosol yields estimated using dark chamber experiments appear to overestimate the yields when compared to the real atmosphere. Photolysis could substantially alter the yields of the various condensable products, however the magnitude of the effect is not yet known.

The goal of this research is to update the current SOA model in PMCAMx+, a three-dimensional chemical transport model, taking advantage of these laboratory results from recent experiments in the CMU smog chamber. The original version of PMCAMx+ uses a one product model for the oxidation of the terpene species. The SOA model has been updated using four product models with temperature, NOx, and UV dependent aerosol yields. PMCAMx+ is used to predict the secondary organic aerosol concentrations for the Eastern United States during July 2001. The results of the updated SOA module are compared to available observations and predictions of the original PMCAMx+.

1PH45

AN ASYNCHRONOUS TIME-STEPPING (ATS) INTEGRATOR FOR SOLVING STIFF ATMOSPHERIC PROBLEMS.

K. Max Zhang, Anthong S. Wexler, University of California, Davis, CA

Mixed time integration methods, also known as multiple time-step method (MTS), have been proposed and implemented successfully to reduce the stiffness of problems in molecular dynamics and solid mechanics, where different time scales are used to integrate different motions or meshes. We apply the similar concept and develop an Asynchronous Time-Stepping (ATS) integrator for atmospheric applications, i.e., gas chemistry and aerosol dynamics. The key components in ATS will be discussed, including 1) global and local time management, 2) dynamic time-scale ordering and 3) integration and iteration methods. The comparisons between ATS and Gear's method in aerosol dynamics simulation are presented. ATS has been implemented in CMAQ-UCD, a sectional, dynamic aerosol model built on USEPA's CMAQ platform.

1PH46

ELEMENTAL ANALYSIS OF AIR PARTICULATE MATTER AND APPLICATION TO SOURCE FINGERPRINTING.

B.A. Begum and S. K. Biswas, Atomic Energy Centre, Dhaka, Bangladesh; PHILIP K. HOPKE, Clarkson University, Potsdam, NY

Ion Beam Analysis (IBA) technique, namely, Proton Induced X-ray Emission (PIXE) in conjunction with Proton Induced Gamma Emission (PIGE) technique has been used to measure about 20 different elements present in coarse (PM10-2.2) and fine (PM2.2) particles in atmospheric air samples. PIXE provided data for selective elements from Al to U while PIGE provided information on elements lighter than Al such as F and Na. These elements cover the most commonly occurring compounds in coarse and fine atmospheric particles at concentration levels above approximately 1 ng/m3 of air sampled. Detection limits for the ion beam techniques on polycarbonate filter papers were typically between 0.02 and 0.2 µ;g/cm2 for a few minutes of accelerator running time. The multi-elemental capability of PIXE in conjunction with PIGE enables the use of elemental measurements to define fingerprints for various coarse and fine particle sources. Principal Component Analysis method was used to find out the fingerprint of different sources, which are responsible for polluting the atmospheric air. These fingerprints include anthropogenic sources such as motor vehicles, biomass burning/brick kiln, as well as natural sources such as sea spray and soil dust.

1PH47

DATA QUALITY OF PAH AND NITRO-PAH DETERMINATIONS IN ATMOSPHERIC AEROSOL.

Patrizia Di Filippo, CARMELA RICCARDI, Donatella Pomata, Federica Incoronato, Sergio Spicaglia, Italian National Institute of Occupational Safety and Prevention, Rome, I

Polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs belong to the group of organic micropollutants of large interest for their adverse health effects. In polluted atmosphere hydrocarbons occur in the vapour phase or are absorbed to particulate matter, depending upon their vapour pressure and the ambient conditions.

They are responsible for part of the high direct-acting mutagenic activity of unknown origin observed for the airborne particulate material.

Organic fraction analyses on particulate material are not usually reported with qualifications of their uncertainty, although the sources of uncertainty affecting measurements of pollutants include sample collection, handling and stocking, and analytical procedure.

The aim of this paper is focused on the optimization of the analytical procedure and in particular on the extraction and clean-up phases.

After optimization on filters spiked of standard mixtures, the procedure was tested on the certified material NIST SRM1649a and on the same certified material absorbed on filters.

PAHs and nitro-PAHs were extracted by using a pressurized-fluid extractor (ASE 200, Dionex)

The recovery percentage is influenced by extraction efficiency, that was tested by extracting blank filters spiked with standard mixtures and programming a different cycles number.

Four repetitions of the static cycles were sufficient to achieve reliable recovery.

A further limitation in extraction efficiency is if organic compounds are absorbed on particulate material, so the extraction tends to be diffusion-limited. Bringing fresh solvent to the surface of the particles enhances extraction efficiency by providing a favorable concentration gradient.

So the four static cycles were tested on a certified atmospheric particulate material collected in an urban area.

As what concern clean-up optimization both spiked filter and certified material extracts were put through purification by neutral alumina column, utilizing as elution solvent a mixture of n-exane/dichloromethane or isooctane/ dichloromethane. Isooctane/dichloromethane mixture showed to give better results.

When this optimized procedure is transferred on the certified material adsorbed on filters, the amount of particulate material proved to be a limiting step, since amount of about 1 mg yielded a good accuracy, but 0.5 mg caused a high uncertainty.

1PH48

DERIVATION OF A GENERAL EQUATION FOR THE CALCULATION OF SECONDARY ORGANIC AEROSOLS (SOA) UNDER THE CONDITIONS THAT BOTH PRIMARY ABSORBING ORGANIC AEROSOL AND THE PRE-EXISTING PARTITIONING SPECIES ARE NOT ZERO.

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The current literature on secondary organic aerosols (SOA) modeling is quite complicated and sometimes confusing due to differences in notation and nomenclature. For example, Odum et al. (1996, 1997), Strader et al. (1999) and Schell et al. (2001) showed slightly different formulations for SOA modeling based on the same absorptive partitioning model of Pankow (1994a, b), sometimes causing confusion. This work reviews the mathematical and physical procedures for SOA modeling to clarify the relationships among these different formulations in the literature. This study also first derives a general equation under the conditions that both primary absorbing organic aerosols and the pre-existing partitioning species (PEPS) (including gas and aerosol phase) are not zero on the basis of the same absorptive partitioning model. Discussions on the cautions that must be exercised when these formulations are used in 3-D air quality models are presented as well.

1PH49

INVESTIGATION OF ELEMENTAL SPECIES IN A REFERENCE MATERIAL FOR PM 2.5 URBAN PARTICULATE MATTER. RABIA OFLAZ SPATZ, Rolf Zeisler, Analytical Chemistry Division, National lnstitute of Standards and Technology, Gaithersburg, MD

For the past 20 years, the only certified reference material (CRM) consisting of industri-alized urban air particulate matter (PM) has been Standard Reference Material®? (SRM) 1648 issued by the National Institute of Standards and Technology (NIST) in 1982. Be-cause epidemiological evidence suggests that human morbidity and mortality are associated with exposure to particulate matter of size 2.5?m or less (PM2.5; fine fraction), NIST and the US Environmental Protection Agency are developing reference materials for urban particulate matter specifically of this size. From this cooperation, an interim PM2.5 reference material has been available for various studies since 2001. In 2002 NIT issued a new reference material, SRM 2783, Air Particulate on Filter Paper. Air-jet milled urban dust is used to prepare the SRM. Appropriate amount of air particulate and pure water were used for suspension. Since using ultra pure water may cause potential loss of soluble compounds, the current study is focused on investigations of the influence of different suspension material in order to find new way to deposit air particulate material on filter. Organic solvents (toluen and ethanol) were investigated. SRM 1648 Urban Particulate Matter was used as control. 1 mg/ml suspensions of samples and control materials were prepared with toluen and ethanol in sterile, acid washed Teflon tubes. After sonification each suspension were brought to equilibrium and centrifuged and transferred into pre-cleaned polyethylene bags for instrumental activation analysis. They were frozen immediately and later freeze-dried. Instrumental neutron activation analysis was employed to determine the fraction of each element leached into organic solvents. Results of the measurements will be presented, and the implications for producing future SRMs will be discussed.

1PH50

UPTAKE OF POLAR VAPOUR MOLECULES BY CLUSTERS IONS: THE EFFECT OF THE AVERAGE DIPOLE ORIENTATION. ALEXEY NADYKTO, Fangqun Yu, Atmospheric Sciences Research Center, State University of New York at Albany, Albany, NY

Uptake of condensable vapour, together with the Gibbs free energy changes, governs the growth rate of charged clusters/particles. Atmospheric aerosol precursors and a big fraction of common gas pollutants are of high dipole moment, and, thus, an accurate theoretical description of the ion cluster growth requires accounting for the dipole-charge interaction [1]. Nadykto and Yu [1] designed a simple uptake model accounting for the electrostatic interaction between neutral polar condensing vapour molecules/molecular clusters and core cluster ion/ charged ultrafine particle and they found significant enhancement in the uptake rates due to the dipole –charge interaction. More recently, Tammet and Kulmala [2] performed a comparison of the predictions of [1] (NY) with those of the Effective Polarizability (EP) model [3] and they found a considerable difference. The purpose of this paper is to examine different capture/uptake models and determine key parameters affecting the uptake efficiency. We investigate the uptake of water, sulfuric acid and ammonia molecules by cluster ions/charged ultrafine particles using NY model, effective polarizability model (EP) and five other 2D capture/uptake models such as Barker-Ridge (BR) model, ADO, AADO, ADO` and AADO`. At ambient temperature of 300 K the enhancement factor for the uptake of water, sulfuric acid and ammonia molecules by 0.5 nm singly charged molecular cluster is in the range of 2.3–12, 2.5–20 and 1.75–9.8 respectively. In addition to the uncertainties in absolute values of the enhancement factor, there is a considerable difference in its temperature dependence. BR, ADO’, AADO’ and NY, which are derived using different capture/uptake conditions and similar dipole orientation models, are in quite a good agreement in most cases, while ADO and ADO’ and AADO and AADO’ models obtained using identical capture/uptake conditions and different orientation models deviate dramatically. Present analysis [4] shows that uncertainties in the enhancement factor are largely arise from the difference in how the relative dipole orientation of the polar molecule in an ion field is expressed. This means that the average dipole orientation in the ion field is an important parameter controlling gas-to-charged particle/cluster conversion and needs to be investigated further.

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1PH51

DETERMINATION OF OLIGOMERIC FRACTION OF SECONDARY ORGANIC AEROSOLS BY TGA. AMANDA NORTHCROSS, Myoseon Jang, University of North Carolina

It has been shown that secondary organic aerosols from the oxidation of biogenic terpenes contain oligomers. It is essential to atmospheric modeling to be able to determine the fraction of oligomers present in SOA. Thermal gravimetric analysis (TGA) is used to determine the fraction of high molecular weight products in SOA created during the ozonolysis of various monoterpenes in the presence and absence of acidic and neutral seed aerosols. These experiments were performed in a 2m3 indoor teflon chamber.

1PH52

EVOLUTIONS OF PARTICLE SIZE DISTRIBUTIONS DURING SECONDARY AEROSOL FORMATION. YEE-LIN WU, Chi-Wen Chang, Department of Environmental Engineering, National Cheng-Kung University, Tainan, Taiwan

The particle size distributions in the ambient atmosphere were measured by SMPS for particle sizes from several nanometers to 900 nm. The sampling duration for each run was about 6 minutes and the measurements were conducted in southern Taiwan. The measured particle size distributions were decomposed into two or three log-normal size distributions. In general, more than 90% were accounted by two log-normal distributions and the two major modes were at mode diameters of 20 to 40 nm and 90 to 110 nm. For the smaller mode diameter, the mode diameter was at about the same and the number concentrations increased at the morning rush hours. At noon, both the mode diameter and number concentration for the smaller mode diameter increased with time, while those for the greater mode diameter were at about the same. Therefore, both nucleation and condensation were important for the evolution of particle size for the smaller mode.

1PH53

PMF VS. CMB: SOURCE APPORTIONMENT OF PM2.5 AT 4 SEARCH SITES. Wei Liu, Sangil Lee, Yuhang Wang, Armistead Russell, Georgia Institute of Technology, Atlanta, GA; Eric S. Edgerton, Atmospheric Research and Analysis, Inc., Durham, NC.

ABSTRACT: Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB), receptor models, have been used for source apportionment of particulate matter (PM). PMF and CMB have some similarities and differences. Here, both source apportionment methods are applied to four SEARCH data sets that include two sites for each urban (Atlanta, GA and Birmingham, AL) and rural area (Yorkville, GA and Centreville, AL). The data includes inorganic chemical speciation (inorganic ionic species and trace metal elements) and elemental and organic carbon fine particle (PM2.5) concentrations covering 3 year measurements from January 2000 to December 2002. The source apportionment results are analyzed with respect to the two methods used. Secondary sulfate and nitrate factors are in good agreement in terms of source contribution results. Motor vehicle source profiles had large differences between CMB and PMF since the PMF-derived source profiles differ from those specified in CMB. From the average source contribution point of view, the source contributions of each factor of both models are quite similar. Both models need post analysis such as wind profiles, back trajectory, time series analysis to elucidate the results. PMF can resolve some unexpected factor such as long range transport dust, while CMB only resolved dust are mixed with local dust.

1PH54

SYNTHESIS OF SUPERSITE PROGRAM FINDINGS: UNCERTAINTIES IN EMISSION INVENTORIES. ANN WITTIG, CUNY City College of New York, New York, NY; Heather Simon, David Allen, University of Texas at Austin, Austin, TX

Recent scientific field studies of fine particulate matter (fine PM), conducted as part of the Particulate Matter Supersites Program and related field measurement programs, are producing information of broad relevance that can help inform public policy decisions. This paper presents a synthesis of recent scientific findings concerning fine PM emission inventories.

This work explores the uncertainties in the methods used to develop spatially and temporally resolved emission inventories which are suitable for photochemical modeling. Emissions of primary PM from point sources, geological sources, biogenic sources, fires, cooking sources, and various categories of mobile sources, and emissions of secondary PM precursors from anthropogenic and biogenic sources, are both considered. At various locations across the United States, the source strengths given in these “bottom up” inventories are compared to estimates of source strengths obtained using receptor modeling. The concentrations of fine PM predicted by photochemical models which used the emission inventory source strengths as inputs are also compared to observed concentrations of fine PM. Based on the analyses, sources inadequately represented in the inventory or in need of better characterization are identified.

1PH55

FTIR REFLECTANCE SPECTROSCOPY OF SIZE-SEGREGATED AEROSOL DEPOSITS.

JUDITH HOPEY, Kirk Fuller, Venkataramanan Krishnaswamy, David Bowdle, The University of Alabama at Huntsville, Huntsville, AL

A method that is based on Fourier transform infrared (FTIR) reflectance spectroscopy is being developed for determining functional group loading in size-segregated ambient aerosol deposits. Atmospheric particulate matter (PM) was sampled with a rotating-stage Micro-Orifice Uniform Deposit Impactor (MOUDI, MSP Corporation) equipped with standard aluminum foil substrates. Each PM sample was analyzed on the foil without extraction, using an FTIR spectrometer (ThermoElectron Nexus 870) and a Seagull reflectance accessory (Harrick Scientific). The rotating stage MOUDI minimizes variations in deposit thickness (such as those encountered in single-nozzle conical impactors), which would otherwise interfere with quantitative spectroscopic analysis. The MOUDI also has an advantage over low-pressure impactors, which are susceptible to losses from volatile aerosol species. Reflectance spectroscopy with foil substrates overcomes some difficulties associated with transmission spectroscopy, including spectral saturation and thin film interference (e.g., from Teflon substrates). Foil substrates are also much easier and cheaper to work with than those made from ZnSe.

For calibration, solutions of pure ammonium sulfate of varying concentrations were prepared in the laboratory and aerosolized in a medical nebulizer. The resulting PM was collected by the MOUDI, analyzed gravimetrically with a microbalance, and then analyzed optically in the FTIR. To assist in the analysis, aerosols of ammonium nitrate, mineral dust, and vehicle exhaust were generated to develop a library of spectra that are representative of individual ambient aerosol species. Spectra of silicone grease (a lubricant for the rotating MOUDI stages) and other possible sample contaminants were also acquired. Initial quantitative analysis was limited to sulfate mass estimation, using the calibration for a relatively isolated sulfate absorption feature in the 570-640 cm-1 region. This method was used to infer sulfate loadings from ambient atmospheric PM samples collected at an urban site in Huntsville, AL, from May through September of 2004. This method has the potential to be expanded for use with other species without physical segregation of functional groups

1PH56

SOURCE APPORTIONMENT OF PM2.5 AT HERCULES-GLADE, MISSOURI, 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 at Hercules-Glade, Missouri, from March 2001 through February 2004 were analyzed using the multivariate receptor model Positive Matrix Factorization (PMF). 328 samples and 23 species were utilized, including the organic carbon (OC) and elemental carbon (EC) analytical temperature fractions from the thermal optical reflectance (TOR) method. Eight factors were identified, with a good comparison between predicted and measured mass (slope = 0.98, r2 = 0.99) and good orthogonality among factors. Bootstrapping over 300 runs determined the uncertainties of each species in the factor profiles. A coal combustion factor was the largest contributor to mass (34% of the average mass on all days and 49% on the worst visibility days), accounting for most of the ammonium sulfate, and was predominantly from coal-fired power plant emissions of SO2 in the Ohio and Mississippi River valleys. Urban southeastern carbonaceous aerosol was responsible for another 20% of the average overall mass, and 18% of mass on the worst visibility days. A background/aged aerosol factor was also identified, accounting for 10% of the overall mass, and 9% of mass on the worst visibility days. Oil combustion and Mississippi River industrial operations factors were minor contributors to the mass (8% and 5%, respectively). Nitrate contributed 11% of the average mass over all days as well as on the worst visibility days, due to nitrate episodes in the winter. Soil and local burning emissions were generally event-driven, and were 5% and 7%, respectively, of the overall mass and 4% and 6%, respectively, of the mass on the worst visibility days, though a handful of burning episodes and one soil episode were important contributors on some poor visibility days. Conditional Probability Function (CPF) analysis applied to air mass trajectories and paired with emission inventory and daily fire location data helped better identify the factors and their source regions.

1PH57

NUMERICAL SIMULATION OF TRANSPORT AND DISPERSION OF VEHICULAR PARTICULATE EMISSIONS NEAR A MAJOR INTERNATIONAL BRIDGE COMPARED WITH EXPERIMENTAL RESULTS.

CHAOSHENG LIU, Goodarz Ahmadi, Kambiz Nazridoust, Andrea R. Ferro, Timothy R. McAuley, Philip K. Hopke, Peter A. Jaques, Clarkson University, Potsdam, NY

PM pollutants due to emissions from a major international bridge (Peace Bridge) between U.S. and Canada are studied. A computational model was developed for evaluating the transport and dispersion of vehicular emissions from the Peace Bridge Plaza Complex (PBC). An unstructured computational grid of Peace Bridge and its vicinity was generated and the mean airflow is simulated by the standard k-epsilon model of FLUENT code. A Discrete Random Walk (DRW) model was used to simulate the instantaneous turbulence fluctuating velocity. A Lagrangian particle-tracking model was used for simulating the transport and dispersion of particulate emissions from the motor vehicle exhausts on the bridge and in the Peace Bridge Plaza area. The particle transport model accounts for the drag and Brownian forces acting on the particle, as well as the gravitational sedimentation effects. For particulate emissions in the size range of 16 to 166 nm, the corresponding simulated particle concentrations are compared with the particulate matter (PM) field measurements and good agreement was observed.

1PH58

DETECTION OF LOW MOLECULAR WEIGHT ORGANIC ACIDS BY ATMOSPHERIC PRESSURE ELECTROSPRAY IONIZATION AND ATMOSPHERIC PRESSURE PHOTOIONIZATION MASS SPECTROMETRY.

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Fine particles in urban atmospheres are composed of highly complex mixtures of organic compounds spanning large ranges of molecular weight and compound group classifications. Use of molecular based instrument detection methods based on mass spectrometry now enables routine detection of molecular tracers to apportion fine particulate mass at urban and rural sites. However, nearly 50% of the organic carbon mass collected as fine particles cannot be analyzed using current molecular level mass spectrometric analytical methods (e.g., gas chromatography/mass spectrometry, GC/MS) due to poor transfer within the gas chromatographic system. The presence of one or more polar functional groups, high molecular weight (> 450 amu), and/or thermal instability are principal factors preventing successful analysis by GC/MS.

Liquid chromatography/mass spectrometry (LCMS) has been introduced by several groups as a new molecular level tool for measuring atmospheric polar organic compounds. In this study, we use an Agilent LCMS ion trap configured with atmospheric pressure Electrospray Ionization (ESI) and Atmospheric Pressure Photoionization (APPI) sources. It is operated under negative mode ionization conditions to target analysis of the acidic organic compounds soluble in water/methanol (1:1 by volume). A suite of diacids and aromatic acids were studied using both ESI and APPI sources. Both acid groups are found commonly in fine particles from urban, suburban, and rural U.S. airsheds. Results are presented for diacids and aromatic acids with LCMS and are compared to reproducibility and limits of detection for the same compounds as methyl ester derivatives determined by GCMS analysis.

1PH59

SOURCE APPORTIONMENT OF SEATTLE PM2.5 USING STN ORGANIC CARBON PEAKS.

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A multivariate receptor model was applied to PM2.5 speciation data collected at Beacon Hill in Seattle by both the EPA's Speciation Trends Network (STN) and the IMPROVE sampling network. In addition to standard OC and EC carbon fractions reported by the STN, we also utilized the four OC carbon peaks whose sum represents OC. Here we compare the PMF receptor modeling results from the three different data sets: STN data with EC and OC (326 samples from 2/15/00 to 3/29/03); STN data with EC and with OC Peaks 1-4 (255 samples from 5/12/00 to 12/31/02); and IMPROVE data (297 samples from 1/1/00 to 2/27/04). For all three data sets, the best fitting model utilized 11 factors and identified four major source features: vegetative burning, secondary sulfate, secondary nitrate, and diesel exhaust. These four sources had similar source contribution estimates across all three data sets, with the exception of diesel exhaust. For this latter source feature, the STN data with the four OC peaks yielded the highest contribution estimates (1.4 micrograms/m3 versus 0.9 micrograms/m3 for the other two data sets). Other features common to all three analyses were (in general order of importance): residual oil combustion (Ni, V); aged sea salt (Na, SO4, NO3); gasoline exhaust (OC, Zn); airborne soil (Si, Fe, Ca); and fresh sea salt (Na, Cl). In addition, all three analyses resolved an additional feature with relatively minor mass contribution that is enriched in Fe, Mn, EC, Ni, and Zn that displays significantly higher weekday versus weekend levels, consistent with fresh diesel exhaust.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy

2A1

INTEGRATION OF SATELLITE-DERIVED AEROSOL DATA INTO AIR QUALITY APPLICATIONS.

FRED DIMMICK, Chief, Process Modeling Research Branch, Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, US EPA, Research Triangle Park, NC

Historically, the only source of aerosol air quality data available on an ongoing and systematic basis at national levels was generated by ambient air monitoring networks put in place for the US EPA's Air Quality Programs. While these networks are being redesigned and updated to address current and anticipated air quality issues, they are still generating routine data.

Over the past several years, the remote sensing of aerosols from space has improved dramatically. The emergence and application of these measurements adds a new dimension to air quality by enabling consistent observations of pollutants over large spatial domains. Current instruments aboard NASA and European Space Agency satellites can provide derived measurements of aerosols and trace gases relating directly to most of the EPA's criteria pollutants: particulate matter (PM10 and PM2.5), ozone, NO2, SO2, and CO.

This talk will highlight some current air quality and public health prototype applications of satellite derived aerosol data sets by EPA in air quality and public health, and discuss potential obstacles for use and acceptance of satellite data sets within the air quality community.

2A2

3-D INTEGRATED AIR QUALITY MONITORING APPLICATION OF SATELLITE SENSOR DATA FOR REGIONAL AND URBAN SCALE AIR QUALITY. JILL ENGEL-COX, Battelle Memorial Institute, Arlington, VA; Raymond Hoff, Raymond Rogers, Joint Center for Earth Systems Technology and the Physics Department, University of Maryland, Baltimore County, Baltimore, MD; Alan Rush, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Washington, DC; Fred Dimmick, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC; James Szykman, U.S. Environmental Protection Agency, Office of Research and Development, c/o NASA Langley Research Center, Hampton, VA.

Air quality has traditionally been monitored at the surface through in situ ground-based monitors, which also are used to determine compliance with regulatory standards. Recent interest on short- and long-distance transport of air pollutants has highlighted the need for new monitoring techniques to understand fine particulate matter (PM) as it moves in multiple spatial and temporal dimensions. In recent years, the capabilities of Earth observing satellites and the technological tools to share and use these images have advanced significantly and the U.S. Environmental Protection Agency (EPA) has been sponsoring research into the use of satellite remote sensing as a way to improve PM monitoring. This presentation summarizes the results of three years of collaborative research on the integrated use of EPA's ground-based monitoring network data, the National Aeronautics and Space Administration's (NASA) Moderate Resolution Imaging Spectroradiometer (MODIS) satellite sensor data, and the University of Maryland, Baltimore County's (UMBC) lidar system. Qualitative case studies using MODIS data were used to document and visualize transport of fine PM and to evaluate the benefits and limitations of satellite remote sensing. Statistical and quantitative analysis of two years of NASA MODIS aerosol optical depth and EPA in situ PM concentration data were conducted to document the relationship between these datasets. A pilot project using a ground-based lidar that measures aerosol scattering provided the vertical dimension and helped evaluate aerosol events as part of a proposed 3-dimensional integrated air quality monitoring system. Internet weblog technology was used to track, sort, and facilitate communication of the use of these multiple data. Recommendations and recent progress to advance the use of satellite and in situ air quality data in an integrated fashion will be discussed.

2A3

AN "A-TRAIN" STRATEGY FOR QUANTIFYING DIRECT CLIMATE FORCING BY AEROSOLS. THEODORE ANDERSON, Robert Charlson, University of Washington, Seattle, WA; Nicolas Bellouin, Olivier Boucher, Jim Haywood, UK Met Office, Essex, England; Mian Chin, Yoram Kaufman, Lorraine Remer, Omar Torres, NASA/Goddard Space Flight Center, Greenbelt, MD; Sundar Christopher, University of Alabama, Huntsville, AL; Stefan Kinne, Max Planck Institute of Meteorology, Hamburg, Germany; John Ogren, NOAA/Climate Monitoring and Diagnostics Lab, Boulder, CO; Toshihiko Takemura, Kyushu University, Kyushu, Japan; Didier Tanré, University of Lille, Lille, France; Charles Trepte, Bruce Wielicki, David Winker, NASA/Langley, Langley, VA; Hongbin Yu, Georgia Institute of Technology, Atlanta, GA

We present a practical strategy for achieving an observationally based quantification of direct climate forcing by anthropogenic aerosols. The strategy involves a four-step program for shifting the current assumption-laden estimates to an increasingly empirical basis using satellite observations coordinated with suborbital remote and in situ measurements and with chemical transport models. Conceptually, the problem is framed as a need for complete global mapping of three parameters: clear-sky aerosol optical depth, radiative efficiency per unit optical depth, and fine-mode fraction of optical depth (where the latter is used to estimate anthropogenic fraction). All three can be retrieved from satellites, but correlative, suborbital measurements are required for partitioning fine-mode optical depth between natural and anthropogenic components, for validating the retrieval of fine-mode fraction, and for quantifying the aerosol properties that control radiative efficiency. The satellite focus is on the \A-Train\, a constellation of six spacecraft that will fly in formation from about 2005-2008. Key satellite instruments for this report are the MODIS and CERES radiometers on Aqua, the OMI radiometer on Aura, the POLDER polarimeter on PARASOL, and the CALIOP lidar on CALIPSO. By designing a strategy around the need for integration of diverse data types, we develop guidelines for both satellite data interpretation and correlative suborbital activities that represent, in many respects, departures from current practice. This strategy is offered as an initial framework - subject to improvement over time - for scientists around the world to participate in the A-Train opportunity.

2A4

GLOBAL RETRIEVAL OF AEROSOL PROPERTIES OVER DESERT AND SEMI-DESERT REGIONS FROM MODIS. N. CHRISTINA HSU, S.-C. Tsay, Michael D. King, and J. R. Herman, NASA/Goddard Space Flight Center, Greenbelt, MD

Mineral aerosols (dust) play an important role in both climate forcing and oceanic productivity throughout the entire year. Due to the relatively short lifetime (a few hours to about a week), the distributions of these airborne dust particles vary extensively in both space and time. Consequently, satellite observations are needed over both source and sink regions for continuous temporal and spatial sampling of dust properties. However, despite their importance, the high spatial resolution satellite measurements of dust near its source have been lacking.

In this paper, we will demonstrate the capability of a new satellite algorithm to retrieve aerosol optical thickness and single scattering albedo over bright-reflecting surfaces such as urban areas and deserts. Such retrievals have been difficult to perform using previously available algorithms that use wavelengths from the mid-visible to the near IR because they have trouble separating the aerosol signal from the contribution due to the bright surface reflectance. The new algorithm, called Deep Blue, utilizes blue-wavelength measurements from instruments such as SeaWiFS and MODIS to infer the properties of aerosols, since the surface reflectance over land in the blue part of the spectrum is much lower than for longer wavelength channels. In addition to aerosol optical thickness information, we could also distinguish dust from fine mode pollution aerosols over land, which helps isolate the effect of human activity on radiation budget.

We have validated the satellite retrieved aerosol optical thickness with data from AERONET sunphotometers over desert and semi-desert regions. The comparisons show reasonable agreements between these two. These new satellite products will allow scientists to determine quantitatively the aerosol properties near sources using high spatial resolution measurements from SeaWiFS and MODIS-like instruments.

2A5

AIR QUALITY ASSESSMENT USING COMBINED SATELLITE AND GROUND MEASUREMENTS. SUNDAR CHRISTOPHER, Jun Wang, Pawan Gupta, Department of Atmospheric Sciences, University of Alabama in Huntsville, Huntsville, AL

Advances in satellite measurements and retrievals now enable monitoring of particulate matter (PM) on global scales. However ground measurements are needed to constrain, validate and improve satellite retrievals of geophysical quantities such as aerosol optical thickness. In this paper we provide an overview of how satellite measurements from NASA's Terra and Aqua satellites can be used for evaluating PM over the continental United States. We combine this information with measurements from the Aerosol Robotic Network (AERONET), Interagency Monitoring of Protected Visual Environments (IMPROVE), and other PM observation stations. We will also discuss case studies of PM forecasting using a mesoscale model with assimilation of satellite-derived aerosol products.

2A6

A LONG SAHARAN DUST EVENT OVER THE WESTERN MEDITERRANEAN: LIDAR, SUN PHOTOMETER AND DREAM MODEL SIMULATIONS.

Carlos Pérez, Slobodan Nickovic, Michaël Sicard, Carlos Toledano, Victoria E. Cachorro, JOSE M. BALDASANO

Due to its proximity to North Africa, the Western Mediterranean area is strongly affected by the presence of Saharan dust. In the last years, a number of studies have focused on understanding the different phases of the dust process (mobilisation, transport, deposition and climate interactions) over the Mediterranean and Europe based on satellite imaging (eg. Moulin et al 1997), in-situ measurements of depositions, concentrations and optical depths (eg. Loye-Pilot and Martin, 1996; Rodriguez et al., 2001), lidar observations (eg. Gobbi et al., 2000; Ansmann et al., 2003) and modelling (eg. Nickovic et al., 2001).

In this context, detailed analysis of a long episode over the Western Mediterranean (11- 30 June 2002) is performed. Synoptic charts and satellite imagery are used to explain the weather conditions and air flow patterns which induced the export of dust-rich air masses towards south-western Europe and qualitatively evaluate the horizontal spread of the dust plume delivered by the operational Dust Regional Atmospheric Modelling (DREAM) (http://www.icod.org) (Nickovic et al., 2001). Intensive backscatter lidar observations performed over the Barcelona region (Western Mediterranean Basin) and data from two AERONET sun-photometers at El Arenosillo (SW Iberian Peninsula) and Avignon (SE France) are used as well to characterize the optical properties of the Saharan dust plume and validate two different model configurations of the particle size distribution.

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2B1

ATMOSPHERIC FIELD STUDY OF ION-INDUCED NUCLEATION.

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Ion-induced nucleation (IIN) occurs when vapor condenses on small ions, leading to the eventual formation of stable particles. This paper addresses atmospheric measurements carried out at NCAR’s Marshal site located 5 miles southeast of Boulder, Colorado. Our sampling system measures the mobility distribution of positively and negatively charged “small’ and “intermediate” ions from 0.4 to 6.3nm, and SMPS measurements from 3–250 nm. The Inclined Grid Mobility Analyzer (IGMA), which was developed by Tammet (2002), measures the ion distributions. The SMPS and IGMA data overlap in the 3 to 6 nm size range, enabling measurements of the charge fraction (f) for those particles. Theory shows that the value of f and derivative of f with respect to size (df/dDP) provide insights into whether nucleation was ion-induced or neutral. We observed that charged fractions, f, for both positively and negatively charged particles in the overlapping size range significantly exceeded expected steady state values early in the day and approached steady state as time progressed. On some days the positive and negative charged fractions were about equal, while on other days negative particles were significantly more abundant than positive particles. We found that on some days the concentration of charged particles increased as particles grew, suggesting that charged particles were being formed by the attachment of small ions to neutrals. This could only occur if significant concentrations of electrically neutral particles, presumably formed by neutral nucleation, were present. On other days the concentrations of charged particles became depleted as particles grew, suggesting that loss of charged particles to preexisting particles or neutralization by oppositely charged ions were dominant. By examining these rates we were able to estimate the relative rates of neutral nucleation and positive and negative ion-induced nucleation. Our analysis suggests that in most cases neutral nucleation dominated particle formation, but that negative and to a lesser extent positive ion induced nucleation likely sometimes played a role.

2B2

ROLE OF IONS IN ATMOSPHERIC PARTICLE FORMATION: MODELING AND COMPARISON WITH MEASUREMENTS.

FANGQUN YU, State University of New York at Albany, Albany, NY

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. New particle formation has been observed in various locations in the lower troposphere. However, the mechanisms of new particle formation remain illusive. In recent years there is an increasing interest in the nucleation of H2SO4-H2O on ions ubiquitous in the atmosphere. We developed a kinetic ion-mediated nucleation (IMN) model that solves the complex interactions among ions, neutral and charged clusters of various sizes, vapor molecules, and pre-existing particles. The evolution of the size distributions of both charged and neutral clusters in the presence of ionization, neutralization, and scavenging leads to a net flux of clusters crossing critical size (i.e., nucleation). Recently we have significantly improved the IMN model with the newly developed schemes which enable the model to treat the evaporation of neutral/charged clusters explicitly. The schemes to calculate the evaporation coefficients of H2SO4 molecules have been verified again the experimental data.

Here we present the evolutions of ion cluster size distributions simulated with the new IMN model and compare them with measurement results from QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer) field campaign. The mobility distributions of both positive and negative air ions were observed during QUEST II along with precursor H2SO4 concentration, T, RH, ionization rates, and particle size distributions. The QUEST II provides a unique set of data to test the nucleation models. The size distributions and properties of air ions predicted by our new IMN model are in very good agreement with those observed. The details of the comparisons will be presented. Simulations based on our new IMN model suggest that ion-mediated nucleation of H2SO4-H2O is an important mechanism of new particle formation in the lower troposphere. The dependence of IMN rates on sulfuric acid vapor concentration, ionization rate, temperature, relative humidity, and pre-existing particle surface area will be discussed.

2B3

CHLORINE CHEMISTRY IN URBAN ATMOSPHERES: AEROSOL FORMATION ASSOCIATED WITH ANTHROPOGENIC CHLORINE EMISSIONS IN SOUTHEAST TEXAS.

SUNGHYE CHANG, David T. Allen, University of Texas at Austin, TX

Recent evidence has demonstrated that chlorine radical chemistry can enhance tropospheric hydrocarbon oxidation in southeast Texas and has the potential to enhance ozone formation in urban atmospheres. Total anthropogenic chlorine releases in southeast Texas have been estimated to be 10,000 kg/day, and HCl is the major product of the reactions of these chlorine emissions. The HCl formed from chlorine reactions can lead to fine particulate matter formation. In order to assess this potential aerosol formation pathway quantitatively, an August-September, 2000 photochemical episode in southeast Texas was simulated using the Comprehensive Air Quality Model, with extensions (CAMx). During this episode, ambient measurements of a unique marker of atmospheric chlorine chemistry, 1-chloro -3-methyl-3butene-2-one (CMBO) were made and model performance was assessed by comparing modeled and observed CMBO mixing ratios. The model predicted ambient CMBO mixing ratios within the uncertainty limits of the emissions inventory, so the model was used to assess the impacts of chlorine chemistry on aerosol formation. The spatial distributions and magnitude of predicted chloride concentrations were compared to chloride concentrations observed during a fine particulate matter measurement program in southeast Texas (the Houston Supersite). Model predicted maximum HCl concentration was in the range of 2 ppb- 5ppb, which contributes up to 12 µg/m3 of particulate matter if all HCl partitions into particulate matter. The simulations were also used to explain anomalously high chloride concentrations in El Paso, Texas.

2B4

MATHEMATICAL MODELING OF THE FINE PARTICLE MASS AND PHASE PARTITIONING OF SEMI-VOLATILE ORGANICS IN DILUTED EXHAUST FROM COMBUSTION SYSTEMS. MANISH K. SHRIVASTAVA, Eric M. Lipsky, Allen L. Robinson, Carnegie Mellon University, Pittsburgh, PA; Charles O. Stanier, University of Iowa, Iowa City, IA

Many combustion and other high temperature sources emit compounds that are semi-volatile or volatile at exhaust temperatures but undergo gas-to-particle conversion as the combustion products mix with ambient air. A challenge is that mixing with ambient air both cools and dilutes the exhaust. Cooling the exhaust reduces the vapor pressures of semi-volatile species which causes gas-to-particle conversion and increased fine particle mass emissions. However, dilution decreases the concentration of semi-volatile species, driving these species from the particle to the gas phase and lowering fine particle emission rates. These competing effects complicate interpretation of measurement of fine particle mass emission rates from sources that emit semi-volatile compounds.

In this talk we use an absorptive partitioning model to describe changes of phase partitioning and fine particle mass in diluted exhaust from a diesel engine and a wood stove. The model treats the organic matter in the exhaust as a two component mixture. The vapor pressure and mass fraction of each component are determined by fitting the model to measurements made using multiple dilution samplers operated at different dilution ratios. These measurements show large changes in fine particle mass with increasing, isothermal dilution; for example, increasing the dilution of wood smoke from a dilution ratio of 20:1 to 120:1 decreases the dilution-corrected fine particle mass emission rates by more than a factor of 2 (Lipsky et al., 2005). Excellent fits to the experimental data are obtained when assuming one of the two components is non-volatile and solving for the mass fraction and vapor pressure of the second species (two free parameters). For example, changes of phase partitioning of exhaust from the diesel engine operating at low load are accurately described by a mixture that consists of 0.63 (mass fraction) of a compound with a saturation concentration of 1270 ug/m^3 (comparable to a C-19 alkane) with the balance organic matter being non-volatile. Increasing the number of free parameters does not improve the quality of the fits. The implications of these results on interpreting fine particle emission rates are discussed.

Lipsky, E.M., and A.L. Robinson, Effects of dilution on fine particle mass and partitioning of semi-volatile organics in diesel exhaust and wood smoke, Environmental Science & Technology, under review, 2005.

2B5

MOLECULAR DYNAMICS STUDY OF WATER UPTAKE BY NACL NANOPARTICLES. RANJIT BAHADUR, Lynn M. Russell, Scripps Institue of Oceanography, San Diego, CA

Water uptake by particles in the nanometer size range (10-100 nm) is critical in determining their role in forming haze and clouds, as well as sites for heterogeneous chemical reactions. Earlier studies and measurements to determine the relative humidity at which water uptake is initiated (deliquescence), and the amount of water accreted, have focused on larger (>100 nm) particles. Recent models developed for the nanosize regime show a strong dependence of the deliquescence point on particle size.

Here we apply Molecular Dynamics (MD) to the 10-100 nm size range, using a NaCl nanoparticle interacting with water in the vapor phase as a deliquescence model. Typical simulations are carried out using time steps of 0.5 fs for a total of 300,000 steps. The system shows agglomeration of water on the particle surface, with very limited surface mixing. Varying run parameters allows us to establish the effect of run time, temperature, and water/NaCl ratio. Increasing these parameters results in the formation of a more complete liquid-like water layer on the particle surface. The use of polarizable water models, as opposed to fixed charge models such as SPC and TIP4P also results in better coverage.

To gain a better understanding of the water/NaCl surface interaction, we model a computationally smaller system consisting of equal sized slabs of solid NaCl and liquid water. Solvation is not observed in systems where the NaCl is modeled as a supercell consisting of crystal unit cells. The system structure, as defined by Radial Distribution Functions (RDFs) remains unchanged at the end of 100 ns simulations. The introduction of voids in the bulk of the salt, as well as steps on the surface of the NaCl slab results in a qualitative change of system RDFs, as well as mixing of the salt and water layers around 50 ns. The RDFs obtained in this fashion match the RDFs determined by simulating concentrated NaCl solutions. The void fraction (which combines both bulk and surface defects) required to trigger solvation varies between 20-25% and decreases with temperature. A complete study of solvation should now be possible by sequentially combining the two processes, i.e. the condensation of water onto the NaCl surface and solvation at the surface triggered by defects present in the solid NaCl phase.

2B6

GAS-PARTICLE PARTITIONING COEFFICIENTS OF REACTIVE MERCURY IN ATMOSPHERIC AEROSOL.

Andrew P. Rutter and James Schauer, Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI

Although more than 90 percent of the atmospheric mercury typically exists as non-reactive elemental mercury, non-reactive elemental mercury is a minor contributor to the mercury that deposits to the Earth's surfaces. Reactive mercury, which is comprised of oxidized mercury compounds that are predominately present in the Hg (II) oxidation state, is the largest source of wet and dry deposition of mercury. Reactive mercury compounds are semi-volatile at atmospheric conditions and simultaneously exist in both the gas and particle phases of atmospheric aerosol. Due to the fact that the physical processes controlling the deposition of water soluble gaseous reactive mercury (RGM) are different from the processes controlling the deposition of particulate mercury that is present in aerosols, proper representation of the factors that control the gas-particle partitioning is necessary for accurate mercury deposition models. Although there has been considerable efforts directed at understanding the factors controlling mercury partitioning to coal fly ash at coal combustion stack temperatures, very little information exists concerning the factors controlling the partitioning of reactive mercury to atmospheric aerosols.

Gas to particle partitioning coefficients of reactive mercury in a variety of atmospherically relevant inorganic and organic aerosols have been measured in the laboratory and will be presented. Measurements of the coefficients were made with a purpose built aerosol flow tube reactor in which aerosol particles could be generated that contained reactive mercury and were of well defined bulk chemical compositions, sizes and relative humidities. Collection of the aerosol before and after passage through the flow tube reactor allowed the reactor to be mass balanced with respect to both reactive and elemental mercury. The collection of reactive mercury was achieved by filter based methods, whilst elemental mercury was collected using gold trap amalgamation. Analysis of the reactive mercury collected on the filters was achieved by two methods. The first was the standard EPA 1631e method for measuring mercury in water, and the second was the UW version of the pyrolytic thermal desorption method that allows direct measurement of the reactive mercury load on the filter. Elemental mercury measurements were made using two stage gold amalgamation. In all cases mercury detection was performed using CVAFS.

2C1

SINGLE-PARTICLE LASER-INDUCED FLUORESCENCE AND BREAKDOWN SPECTROSCOPY FOR HIGH-DISCRIMINATION BIOAEROSOL SENSING.

JOHN HYBL and Shane Tysk, Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA

Methods for accurately characterizing ambient biological aerosols are required for detecting biological warfare agents. Currently, fluorescence-based bioaerosol sensors provide reasonable rejection of inorganic background clutter, but fluorescent combustion products and natural biological aerosols may cause interference. Biological organisms contain a wide variety of inorganic elements such as Ca, Mg, Mn, Fe, P, Na, K, and Si, suggesting that elemental analysis of aerosol particles has potential for enhancing the performance of current fluorescence-based sensors. Laser-induced breakdown spectroscopy (LIBS) is an attractive means to incorporate elemental analysis into a fieldable bioaerosol sensor.

As part of the Rapid Chemical/Biological Agent Aerosol Detection (CB-RAAD) program, which is a collaborative effort among the Naval Research Lab, ECBC/RDECOM, and MIT Lincoln Lab, a transportable UV-fluorescence-LIBS aerosol sensor has been developed. The sensor utilizes a 266-nm pulsed microchip laser to stimulate fluorescence from single aerosol particles. The fluorescence signal is used to cue a 50-mJ Q-switched Nd:YAG laser to fire at individual particles. The LIBS spectrum of each particle is recorded using a spectrometer equipped with an intensified CCD camera. This instrument has been used to evaluate the utility of LIBS for bioaerosol detection by comparing the LIBS signatures of laboratory simulants to those of naturally occurring fluorescent aerosol particles. Performance improvements expected from the addition of LIBS to a fluorescence-based sensor are estimated by comparing discrimination with and without the LIBS information.

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2C2

PREVENTING THE SPREAD OF AIRBORNE RESPIRATORY INFECTIOUS DISEASE. WESLEY DEHAAN, Jeff Kastra, Karim Kokash, Matthew Brande, Robert Clarke, and Wiwik Watanabe, Pulmatrix Inc., Cambridge, MA; Megan Murray, Harvard School of Public Health, Boston, MA

Exhaled bioaerosol particles contribute significantly to the spread of airborne respiratory infectious disease (ARID). Unfortunately, infection control measures are still lacking. The explosive spread of measles in the pre-vaccination era and the recent SARS outbreak are clear examples of the potential threat of airborne transmission.

Exhaled bioaerosols (EB) are known to be produced during coughing and sneezing; the role of the most common exhalation maneuvers like tidal mouth breathing, nose breathing and talking is less understood. Our evaluation of these maneuvers in a healthy human population (n = 6) found that tidal mouth breathing was the largest contributor to EB production.

To examine the population variability in EB production from tidal mouth breathing, EB production has been assessed in over 100 patients to date. After flushing the lungs with particle free air, the number and size distribution of particles produced in the range of 0.3-25 micrometers were measured with an optical particle counter while the flow rate was measured using a low resistance pneumotachometer. Significant interperson variability has been observed with total count values ranging over 4 orders of magnitude. In a sample of 114 subjects, it was found that 30% of the subjects produced 97% of the total particles measured. Variation of exhaled bioaerosol production for various ages, sexes and health conditions were also observed.

In the event of natural pandemic or bioterrorist attacks, identification of the highest EB producers would augment clinical outcomes in prevention of ARID. The diagnostic used in the evaluation of patients in this study would assist in identifying the highest exhaled bioaerosol producers. Development of a countermeasure to suppress exhaled bioaerosol production would provide a first-line defense beyond quarantine.

Pulmatrix is developing a pathogen-independent anti-infectivity aerosol (AIA) that will safely limit the production of exhaled bioaerosols. An initial pilot clinical study involving 11 human subjects (Edwards, et al. (2004) PNAS, 50, 1783-1788) showed that aerosol treatment with respirable isotonic saline as an AIA can suppressed bioaerosol exhalation up to 72.9 + 8.0% of untreated baseline for six hours. A second study in cattle indicated AIA suppression is dose dependent. With 1mL administration, similar suppression was seen as that in the human study while at 0.3 and 2mL administrations, bioaerosol suppression was not evident. The combination of exhaled bioaerosol assessment and intervention in exhaled bioaerosol production by an anti-infectivity aerosol provides a novel approach to the concept of limiting airborne respiratory infectious disease transmission.

2C3

MALDI OF INDIVIDUAL BIOMOLECULE-CONTAINING AIRBORNE PARTICLES WITH AN ION TRAP MASS SPECTROMETER. WILLIAM A. HARRIS, Peter T.A. Reilly, William B. Whitten, Oak Ridge National Lab, Oak Ridge, TN

We have demonstrated ion trap-based MALDI of individual biomolecule-containing particles in near real time by on-line coating of the particles with matrix. Biomolecule-containing particles were laboratory generated and passed through a heated region containing a solution of matrix in equilibrium with the gas phase. Passage into a cooler region created a supersaturation resulting in rapid deposition of the matrix vapor onto the biomolecule-containing particles whereupon they were sampled into the inlet of our spectrometer. The coated particles were collimated with an aerodynamic lens and individually sized by light scattering-based time-of-flight. When the sized particle reached the center of the ion trap, it was irradiated with a focused 266-nm or 355 nm laser and the resulting ions were mass analyzed.

Mass spectra of leucine enkephalin, bradykinin, substance P, polylysine, melittin, and insulin chain b-containing particles were demonstrated with attomole sensitivity. For example, a MALDI mass spectrum from a 730 nm particle containing substance P resulted from only 43 amol of analyte. Isotopic structure was displayed in the mass spectra for peptides. As little as 30 amol were observed for higher mass analytes, such as insulin chain b. Even higher sensitivity was obtained for particles containing multiple analytes. For bioaerosol coating experiments, the typical matrix-to-analyte ratio could range from 10:1 to 100:1. To obtain higher matrix-to-analyte ratios, the matrix and analyte were premixed in solution. With premixing, zeptomole sensitivity was observed for bradykinin. Structural information of the peptides contained in an individual particle was obtained by tandem mass spectrometry. Collision-induced dissociation of peptides typically yielded b- and y-type fragments. Analysis of the results yields insights into the aerosol laser ablation ionization process that suggests an optically limited mechanism for ion production that has interesting ramifications on the utility of aerosol-based MALDI as an analytical technique. This technique promises to yield an extremely sensitive method for continuous on-line MALDI MS/MS analysis of biomolecules.

2C4

SINGLE PARTICLE FLUORESCENCE & MASS SPECTROMETRY FOR THE DETECTION OF BIOLOGICAL AEROSOLS. Keith Coffee, Vincent Riot, Bruce Woods, Paul Steele, Eric Gard, Lawrence Livermore National Laboratory, Livermore, Ca.

Biological Aerosol Mass Spectrometry (BAMS) is an emerging technique for the detection of biological aerosols, which is being developed at Lawrence Livermore National Laboratory. The current system uses several orthogonal analytical methods to improve system selectivity, sensitivity and speed in order to maximize its utility as a biological aerosol detection system with extremely low probability of false alarm and high probability of detection. Our approach is to pre-select particles of interest by size and fluorescence prior to mass spectral analysis. The ability to distinguish biological aerosols from background and to discriminate bacterial spores, vegetative cells, viruses and toxins from one another will be shown. Data from particle standards of known chemical composition will be discussed. Analysis of ambient particles will also be presented.

2C5

AERODYNAMIC SIZE DIFFERENCES IN SPORES OF BACILLUS ANTHRACIS AND OTHER BACILLUS SPECIES.. EDWARD W. STUEBING, Jose-Luis Sagripanti, US Army Edgewood Chemical Biological Center, Abredeen Proving Ground, MD

Spores of pathogenic strains of Bacillus anthracis (Ba) are a very important threat to be defended against in Homeland Security measures. In particular, aerosol sampling systems for biodetection must be designed to sample Ba spores effectively and be properly tested to assure this. However, single Ba spores are among the smallest pathogenic aerosol particles amenable to use as a weapon and therefore present a difficult challenge to inertial types of aerosol concentrators and collectors such as virtual impactors, impactors, and cyclones. The size of Ba spores is commonly taken to be 1 micrometer. Geometrical size distributions have recently been determined in detail for spores of several strains of Bacillus anthracis and a number of other Bacillus species, along with the wet and dry densities of several of them. This data is used here to calculate effective aerodynamic diameters for these spores. Various spores used or suggested for use a simulants for Bacillus anthracis are included in this study to assess whether their use in quantitatively testing the performance of aerosol samplers for Biodetection systems accurately represents their expected performance against Ba spores. We investigate the hypothesis that Bacillus globigii spores and Bacillus subtilis spores, commonly used to simulate Ba spores in testing, have significantly smaller effective aerodynamic diameters than pathogenic strains of Ba. In this case, while good collection performance against these simulants assures even better performance against Ba (i.e., they establish a lower bound to sampling system performance with high confidence), the simulants also place more stringent than necessary demands on samplers with consequences for R&D cost, system operating cost especially power consumption, and may lead to rejecting equipment that would be satisfactory in sampling Ba.

2C6

DISTINGUISHING SEVEN SPECIES OF BACILLUS SPORES USING BIOAEROSOL MASS SPECTROMETRY.

DAVID P. FERGENSON, Maurice E. Pitesky, Matthias Frank, Joanne M. Horn and Eric E. Gard, Lawrence Livermore National Laboratory

The single particle mass spectrometric technique BioAerosol Mass Spectrometry (BAMS) was used to analyze seven different species of Bacillus spores grown in duplicate under identical growth conditions. Several thousand dual polarity mass spectra were acquired from each growth of B. cereus, B. thurginiensis, B. megaterium, B. coagulans, B. atrophaeus, B. sphaericus and B. simplex. In addition, a third growth of three of the species was prepared and submitted for analysis blind-coded. Rules trees were induced from one growth and applied to the other of each species to ensure that the rules were general and did not result from subtleties or impurities of the growths. The number of spectra of a given species required to accurately classify that species varied, depending on the species. The first four species listed above were difficult to differentiate from one another while each of the subsequent three was easily distinguished from any of the other six based with an accuracy of approximately 85% based on a single spore spectrum. The blind coded unknowns were all identified correctly. The rules which differentiated the species tended to be based on relatively minor spectral differences. Most of the major peaks were common to all species. This suggests that spectra in the environment can be identified as resulting from Bacillus spores using the major peaks and separated by species using the minor peaks. All of the spectra had mass ranges in the low hundreds of Daltons, far below the protein peaks ordinarily used to distinguish microorganisms in off-line mass spectrometric methods. Generating and measuring higher mass ions, including ions of these proteins, should improve the results of this technique for species identification.

2D1

SECONDARY ORGANIC AEROSOL FORMATION FROM MIXTURES OF HYDROCARBONS IRRADIATED IN THE PRESENCE OF NOX.

JOHN H. OFFENBERG, Tadeusz E. Kleindienst, Edward O. Edney, Michael Lewandowski, National Exposure Research Laboratory, U.S. Environmental Protection Agency, RTP, NC 27711; Mohammed Jaoui, Alion Science and Technology, RTP, NC 27709.

Secondary organic aerosol is formed through the condensation of non- and semi-volatile oxidation products of biogenic and anthropogenic hydrocarbons. In many areas in the Eastern United States during summertime, SOA makes up a significant component of the organic fraction of PM2.5. To date, chamber measurements of SOA have largely been based on irradiations of single hydrocarbons in the presence of NOx. In this study the influence of hydrocarbon mixtures on the overall SOA yield is investigated. Chamber experiments were conducted using mixtures of α-pinene, isoprene and propylene in the presence of NOx. The chamber experiments were conducted in the dynamic mode with a single extent of reaction for each run. This approach permitted collection of SOA samples for gravimetric mass, organic carbon, and detailed chemical composition analyses. The approach also allowed a direct comparison of these parameters through the change of a single variable while leaving all other conditions identical in back-to-back experiments. Results of the experiments showed the addition of a non-SOA forming hydrocarbon may increase the SOA yield of the SOA forming hydrocarbon by apparently increasing the reactivity of the mixture. For example, the addition of isoprene or propylene to an irradiated α-pinene / NOx / air mixture resulted in the formation of about one-third more SOA. The implications of these studies on SOA formation under ambient conditions will be discussed.

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2D2

SECONDARY ORGANIC AEROSOL FORMATION FROM BIOGENIC PRECURSORS: ISOPRENE AND ALPHA-PINENE.

JOSEF DOMMEN, Jonathan Duplissy, Kathrin Gaeggeler, Axel Metzger, M. Rami Alfarra, Astrid Gascho, Andre S.H. Prevot, Ernest Weingartner, Urs Baltensperger, Paul Scherrer Institute, Villigen, Switzerland; Markus Kalberer, Mirjam Sax, Christian Emmenegger, Alain Reinhardt, Renato Zenobi, Swiss Federal Institute of Technology, Zurich, Switzerland

Recently it has been recognized that high molecular weight compounds, oligomers of VOC photooxidation products, are major constituents in secondary organic aerosols (SOA). However, the chemical nature, the concentrations and the formation mechanisms of these compounds are largely unknown. These oligomeric compounds may constitute the main fraction of the large unidentified mass of organic aerosols. Oxidation products of isoprene were found in ambient aerosol samples implying a potential large source to SOA formation [Claeys et al. 2004].

We investigated the formation and properties of SOA and their oligomeric fraction generated from α-pinene and isoprene as biogenic SOA-precursors in smog chamber photolysis experiments at the PSI smog chamber. The aerosol yield from isoprene is larger than previously reported [Pandis et al. 1991] and particle growth is observed over the whole duration of the experiment (12h). Laser desorption/ionization mass spectrometry was used to determine the masses of these oligomers. Regular mass pattern with distinct differences of 14 or 16 mass units were observed for oligomers formed from the biogenic precursors above. These oligomers were found to have molecular weights of up to about 600 Da, which is similar to oligomers formed from aromatic precursors [Kalberer at al. 2004].

Evidence for oligomer formation from both precursors was also obtained from an increasing thermal stability of the aerosol with increasing aging time. An Aerodyne aerosol mass spectrometer revealed that both m/z 43 and 44 are the most dominant fragments in the SOA. This indicates that the particles produced from the photooxidation of both precursors are highly oxidized in nature.

Particles were also sampled with a wet effluent diffusion denuder / aerosol collector system and were analyzed online using ion chromatography coupled to a mass spectrometer for the determination of organic acids in the gas as well as the particle phase. More results on the aerosol characteristics were obtained from FTIR, proton-transfer mass spectrometry and evaporative light scattering detection (ELSD) coupled to size exclusion chromatography.

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2D3

EFFECT OF NH3 ON SECONDARY ORGANIC AEROSOL FORMATION FROM A- AND ß-PINENE OZONOLYSIS IN THE PRESENCE AND ABSENCE OF WATER VAPOR.

KWANGSAM NA, Chen Song, David R. Cocker III, University of California, Riverside, CA

Secondary aerosol formation is known to be a significant contributor to PM2.5 levels in the atmosphere. Classic cases of secondary aerosol formation include the acid-base chemistry of ammonia and nitric acid and/or sulfuric acid. To date, environmental chamber studies have not investigated the potential formation of SOA derived from acid-base reaction between acidic organic compounds (such as carboxylic acids) and alkaline ammonia. Products resulting from such reactions may have significantly lower vapor pressure than the corresponding carboxylic acids. Lower vapor pressures, in turn, will drive the gas-to-particle conversion toward increasing aerosol yield.

In this study, the effect of ammonia on SOA formation in both dry and humid conditions was investigated through a series of experiments with different concentrations of α-pinene and ß-pinene. CO was used as an OH radical scavenger. α-Pinene and ß-pinene were selected as surrogates for endo- and exocyclic monoterpenes respectively, in order to examine the effect of the structure on organic acid formation. α-Pinene possesses a carbon double bond located inside the C6-ring structure, while ß-pinene has a double bond located outside the ring structure. The location of the double bond will affect the oxidation mechanism leading to particle formation, forming oxidation products with a ring-retaining (ß-pinene) or a ring-opening (α-pinene) structure.

It was found that the added NH3 clearly enhanced SOA formation in both α-pinene and ß-pinene ozone reactions, regardless of the presence of water vapor. However, this enhancing effect of NH3 on SOA formation was more pronounced for the dry condition compared with for the humid condition. In the presence of water vapor and NH3, the SOA yield obtained from α-pinene ozonolysis was lower than that by ß-pinene ozonolysis. SOA formed in the dry condition for α-pinene without NH3 was nearly identical to that observed in the humid condition with NH3. A potential mechanism for ozonolysis of both monoterpenes in the presence of water and ammonia was developed.

2D4

IDENTIFICATION AND CHARACTERIZATION OF SEMIVOLATILE ORGANIC CARBON USING PROTON TRANSFER REACTION - MASS SPECTROMETRY (PTR-MS). ALBERT A. PRESTO, Kara E. Huff Hartz, Neil M. Donahue, Carnegie Mellon University, Pittsburgh, PA

We present an analysis of volatile and semivolatile species produced during monoterpene oxidation using proton transfer reaction - mass spectrometry (PTR-MS). Partitioning theory dictates that atmospheric organic species with finite saturation vapor pressures must exist in both the gas and aerosol phases. Such species are typically defined as semivolatile, and a number of semivolatile species, particularly monoterpene oxidation products, have been identified using filter-based methods. However, the relative abundances of these semivolatile products in the gas and aerosol phases has not been investigated previously. The high time resolution of the PTR-MS allows us to investigate changes in organic concentrations on the order of a few minutes; this time resolution starkly contrasts filter-based measurements, which may take hours to collect.

Secondary organic aerosol (SOA) is generated in an environmental chamber by the ozonolysis of a monoterpene precursor (typically α-pinene or limonene) in the presence of an OH radical scavenger. The resulting particle-laden air is either sampled directly or is passed through a dilution sampler. The particle mass and number distributions are measured with an SMPS, and gas-phase organic concentrations are monitored using PTR-MS. Dilution of the chamber air produces a decrease in aerosol mass as well as an increase in the gas-phase concentration of semivolatile organic species. Species identified with PTR-MS are consistent with results from filter-based measurements, and include limononaldehyde, 7-hydroxy-limononaldehyde, and 7-hydroxy-keto-limononaldehyde from limonene ozonolysis.

2D5

IMPACT OF PROPENE ON SECONDARY ORGANIC AEROSOL FORMATION FROM M-XYLENE. CHEN SONG, Bethany Warren, Kwangsam Na, David R. Cocker III, University of California, Riverside, CA

Aromatic hydrocarbons are an important class of volatile organic compounds (VOC) in the atmosphere. It was reported that aromatic hydrocarbons contribute 19% to VOCs in the atmosphere of Los Angles urban area and 30% to VOC in the urban atmosphere of Boston. Smog chamber experiments have shown significant secondary organic aerosol (SOA) formation from the photooxidation of alkyl-substituted aromatic hydrocarbons (Odum et al., 1996; Odum et al., 1997) in the presence of NOx. Since SOA contribute 30% to 70% to the fine particle load present in the atmosphere in regions heavily impacted by photochemical smog (Na et al., 2004; Turpin et al., 1991) it is expected that ambient aromatic hydrocarbons are important contributors to urban particulate matter that is related to increased mortality and morbidity.

The main atmospheric degradation of aromatic hydrocarbons is through reaction with hydroxyl radical (OH) (Atkinson, 2000), leading to formation of a variety of oxidation products from ring-retaining and ring-opening pathways. Due to the critical role of OH in atmospheric photooxidation of aromatic hydrocarbons, previous researchers (Odum et al., 1996; Odum et al., 1997; Jang et al., 2001; Forstner et al., 1997) added propene (C3H6) as an additional VOC to their smog chamber experiments to raise OH levels (at least to ambient levels) and assumed that the addition of propene did not significantly influence the total amount of SOA formed. However, propene can also react with OH at a reaction rate constant that is at the same magnitude of most major aromatic hydrocarbons. Additionally, the OH yield of reaction between propene and O3 is only 0.32 (Rickard et al., 1999). Therefore, the existence of propene in the aromatic hydrocarbon photooxidation experiment should suppress OH concentrations instead of increasing OH levels.

We conducted a series of m-xylene/NOx photooxidation experiments in the presence of propene in the new UCR EPA atmospheric chamber facility that is specially designed for low hydrocarbon and NOx experiments. These experimental data are compared with previous work (Song et al., 2005) of m-xylene/NOx photooxidation performed in the same chamber facility without propene. The result shows that for similar initial conditions, experiments with propene have lower reaction rates of m-xylene than those without propene indicating that propene suppressed the OH present in the system. Furthermore, for a fixed reacted m-xylene concentration, experiments with propene generated obviously less SOA yield than experiments without propene. This result provides key insights into the chemistry leading to SOA formation from aromatic hydrocarbons, enabling us to more accurately predict SOA formation from m-xylene photooxidation in the presence of NOx and propene. A predictive model based on the SAPRC-99 chemical mechanism will be presented to explain these findings.

2D6

LABORATORY STUDIES OF SECONDARY ORGANIC AEROSOL FORMATION FROM REACTIONS OF LINEAR ALKANES WITH OH/NOX.

Yong Bin Lim, PAUL J. ZIEMANN, Air Pollution Research Center, University of California, Riverside, CA

Secondary organic aerosol (SOA) is an important component of atmospheric fine particles (diameter < 2.5 micrometer), and can potentially have important effects on global climate, visibility, and human health. This material is formed in the atmosphere through gas-to-particle conversion processes that include gas-phase (and possibly heterogeneous) oxidation of volatile organic compounds emitted by biogenic and anthropogenic sources, followed by nucleation and/or condensation of low-volatility products. Here we report results of studies of SOA formation from reactions of alkanes with OH radicals in the presence of NOx. Alkanes comprise the largest class of anthropogenic VOC emissions, and also provide an ideal system for exploring the basic chemical reaction mechanisms involved in SOA formation (i.e., hydrogen abstraction, isomerization, and decomposition) that apply to many hydrocarbon oxidation reactions. These studies are the first detailed investigation of the chemistry of SOA formation from alkane-OH/NOx reactions, and yield important and interesting new insights into the reaction mechanisms.

Our studies of SOA formation have focused on the homologous series of C6-C16 linear alkanes. SOA was formed in an ~7000 L Teflon film environmental chamber containing an alkane and OH radicals created by photolysis of methyl nitrite in the presence of NO. Aerosol products were analyzed using a thermal desorption particle beam mass spectrometer (TDPBMS) to determine the chemical composition and volatility, and a scanning mobility particle sizer (SMPS) and a gas chromatograph with flame ionization detection were used to measure aerosol yields. TDPBMS mass spectra showed that the products consisted of compounds containing various combinations of carbonyl, hydroxyl, and nitrate groups. More specifically, SOA formation can involve both first- and second-generation reaction products. The major first generation aerosol products are bifunctional 1,4-hydroxynitrates. First generation monofunctional carbonyls, alcohols, and nitrates, and bifunctional 1,4 hydroxycarbonyls are too volatile to form aerosol in all the systems studied. However, the 1,4-hydroxycarbonyls isomerize to a cyclic hemiacetal, which then dehydrates to a dihydrofuran that reacts rapidly with OH/NOx to form more highly functionalized products with very low vapor pressures. Our results show that this is a key pathway to SOA formation, which was previously unknown. Second generation aerosol products include linear and cyclic carbonylnitrates, dinitrates, hydroxycarbonylnitrates, hydroxydinitrates, and carbonyl dinitrates. The aerosol yields increase with carbon number from negligible values for C6 to greater than 50% for C16. Measurements of aerosol volatility by TDPBMS analysis indicate that the proportion of first generation products in SOA also increases with carbon number.

2E1

RESUSPENSION OF FIBERS FROM FLOORING SURFACES DUE TO HUMAN ACTIVITY.

JACKY ROSATI, U.S. EPA National Homeland Security Research Center, Research Triangle Park, NC; Jonathan Thornburg, Charles Rodes, RTI International, Research Triangle Park, NC; Mark Maddaloni, U. S. EPA Region 2, New York, NY

The World Trade Center (WTC) collapse on 9/11 and the subsequent cleanup released a large particulate loading into the environment. This dust included building materials, such as manmade vitreous and asbestos fibers. A significant quantity of this fiber-laden dust penetrated into buildings in the surrounding area. As these fibers may resuspend from surfaces as a result of human activities such as walking and vacuuming, and as these resuspended fibers may translocate to other indoor locations and surfaces, a study was designed to better assess potential exposures to these fibers due to resuspension.

This research sought to relate carpet concentration (loading) of fibers to the concentration of fibers resuspended in indoor air during normal human activities. To achieve this objective, the work investigated fiber resuspension from carpeted flooring surfaces due to human activities, such as walking and vacuuming. Additionally, relationships were developed (size dependent emission factors) between resuspended fibers and fiber concentration present in the carpeted surface (loading). The effect of variables, such as carpet age, carpet wear, and relative humidity, on resuspension of fibers was considered. Finally, a comparison was performed of current sampling/analysis methods for fibers in carpets including microvac (ASTM Method D5755-03), ultrasonication, and scanning electron microscopy.

Results showed that size dependent fiber emission factors generally fell between 0.01 and 0.10 with RH and carpet age/wear having a significant affect. At low RH (40%), fiber emission factors from new carpet were significantly lower than those from older, worn carpets. At higher RH (90%), emission factors for the new carpet were up to four times greater than for new carpet at the lower RH. Vacuuming of both new and old carpets resulted in lower emission factors than walking on the carpet. Additionally, a comparison of sampling/analysis methods for fibers in carpets showed that the microvac technique best estimated particulate available for resuspension, with SEM analysis accurate only for new carpets, and ultrasonication overestimating available PM.

This study provides data on the basic relationship between fiber loads in carpets and indoor air as well as useful information on the factors that influence that relationship such as carpet sampling methods, air sampling location, loading, carpet age, activity (e.g., walking, vacuuming), and relative humidity. The results of this study will assist in the management of exposure from catastrophic events, such as occurred at the WTC site, in addition to building demolition and asbestos contamination situations.

2E2

PARTICULATE MATTER TRANSLOCATION MECHANISMS AND THEIR DIFFERENCES.

JONATHAN THORNBURG, Charles Rodes, RTI International, RTP, NC; Jacky Rosati, U.S. EPA NHSRC, RTP, NC; Jack Edwards, NCSU, Raleigh NC

Each day adults and children are exposed to particulate matter (PM) from flooring and other surfaces in their homes and offices. The PM available for exposure stems from indoor generation, shoe tracked-in dusts, and ambient particle penetration from outside that deposits on the flooring and other horizontal surfaces. Translocation within the residence can occur via natural or mechanically induced convection of resuspended particles, as well as tracking resulting from human movement. This presentation will discuss these translocation mechanisms and the parameters influencing their relative importance. The goal is to gain a better understanding of translocation mechanisms to reduce the uncertainty in exposure models such as SHEDS.

Resuspension of PM from medium pile carpet by walking or vacuuming is one source. Resuspended PM then may be circulated throughout the residence by the HVAC system or by pressure differentials between rooms. Depending on the carpet characteristics, up to 40% of the PM mass available will be resuspended. Carpet age, ambient relative humidity, and foot pressure will influence the resuspended PM concentration and size distribution. For a given set of conditions, airborne concentration varies linearly with mass loading and yields concentrations up to 200 ug/m3. However, the large resuspended PM mass median diameter, between 4 to 6 um, suggests that PM translocation a significant distance from the source does not occur before PM gravitationally settles to the surface.

Currently, the parameters influencing tracking as a translocation mechanism are being investigated. The mass tracking rate as a function of flooring type, PM loading, shoe characteristics, is being measured in laboratory and field experiments. The tracking and resuspension translocation data will be combined into a model that will identify the importance of each mechanism on PM transport within a residence under different environmental conditions.

2E3

DETACHMENT CHARACTERISTICS OF DIFFERENT MICROPARTICLE CONFIGURATIONS ON SURFACES BY TURBULENT AIR FLOW.

ABDELMAGED H. IBRAHIM and Patrick. F. Dunn University of Notre Dame, Notre Dame, IN, USA

Microparticles have different physical configurations in many natural and industrial situations. This work presents the results of experiments conducted to characterize the detachment of different configurations of microparticles from surfaces exposed to turbulent air during accelerated mean free-stream flow. The work compares the characteristics of detachment of [1] single microspheres deposited in a sparse monolayer, [2] single microspheres deposited in a crowded monolayer, [3] monolayer of agglomerates and [4] multi-layer of agglomerates. Different microparticles materials and sizes are studied. The microparticles are deposited on smooth glass plates under controlled conditions. The plates are scanned with an atomic force microscope and a stylus profilometer to determine their roughness-height distributions at different length scales. Microvideographic observations of the detachment characteristics of each category are reported first, followed by quantitative and qualitative descriptions of the detachment process.

2E4

FULL-SCALE CHAMBER STUDY TO ESTIMATE RESUSPENSION RATES FROM HUMAN ACTIVITY.

Jing Qian, ANDREA FERRO, Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY

Although indoor resuspended particles contribute substantially to human exposure to PM, the resuspension mechanism is not well characterized. To estimate the range of resuspension rates resulting from people walking across different flooring types, fifty individual participants were recruited to perform a prescribed set of activities in a fully characterized, temperature/humidity controlled, stainless steel experimental chamber. The activities included sitting, tapping feet while sitting, and walking across a 1.2-m by 4-m flooring area. The flooring was seeded with test particles and raised and instrumented to measure the vibration frequency and amplitudes caused by the human activities. The airflow characteristics (airflow pattern, mean velocity and turbulence intensity) were measured using flow visualization and an array of hot sphere probes to determine the impact of human activities on the airflows and transport of resuspended particles to the breathing zone. Real-time particle counters were located in an array inside the chamber to determine spatial and temporal distribution of the particle resuspension, and size-resolved deposition and resuspension rates were quantified under various experimental conditions. This study reveals a relationship between floor vibration characterized by human activity and particle detachment for resuspension. The resuspension rate was found to vary with flooring type and relative humidity.

2E5

BIOAEROSOL LEVELS IN OFFICES AND RESIDENCES: A PILOT STUDY OF AIRBORNE PROTEIN, ENDOTOXIN AND (1-3)-BETA-D-GLUCAN.

QING CHEN, Lynn M. Hildemann, Stanford, University, Stanford, CA

Traditionally, bioaerosols in the indoor environment have been studied using culture-based techniques. However, these techniques are of limited use, because they do not include unculturable or nonviable bioaerosols even though these can still be toxic or allergenic. The aim of this study was to test three sensitive, reproducible chemical assay techniques to measure bioaerosol levels (including both viable and nonviable) in office buildings and residential houses in the Bay Area. Environmental parameters were recorded to assess how factors such as type of ventilation (for offices), ventilation rate, and the presence/absence of building occupants influenced bioaerosol levels.

Three chemical measures were chosen to characterize the bioaerosol levels: (i) protein was used as a surrogate measure of “total” bioaerosols, because it exists in all biological materials; (ii) endotoxin was used to assess Gram-negative bacterial aerosol levels, because it is found only in Gram-negative bacterial cells; and (iii) (1→3)-Beta-D-glucan was used to monitor airborne levels of fungi, because it is found primarily in fungal cell walls. Sets of 24-hour filter samples were collected from a total of 39 Bay Area buildings in 2003-2004 – offices in 30 office buildings were sampled, and both the living rooms and unoccupied (guest) bedrooms/workrooms in 9 residential houses were sampled. The office buildings were selected to span a range of ages, sizes, and ventilation types, while the residential houses were selected without any consideration of age or size. Environmental parameters such as relative humidity, temperature and air exchange rate were simultaneously monitored in each sampling location.

Our results show that residential houses are more likely to have elevated bioaerosol levels than offices. The presence of occupants in both the offices and in the living rooms of homes was associated with higher bioaerosol levels than unoccupied rooms. Several residential houses were found to have higher levels of protein (n=5), endotoxin (n=5) and (1→3)-Beta-D-glucan (n=2) indoors than outdoors; this was not observed in the office buildings. These data suggest that some homes may have significant microbial reservoirs indoors. Results from the thirty office buildings suggest that older buildings are more likely to have elevated bioaerosol levels, as are buildings that are naturally ventilated; these results indicate well-maintained HVAC systems can effectively reduce bioaerosol levels indoors.

2E6

EXPERIMENTAL MEASUREMENT OF PARTICLE TRACKING AND RESUSPENSION BY FOOT TRAFFIC. MARK SIPPOLA, Tracy Thatcher, Indoor Environment Department, Lawrence Berkeley National Laboratory, Berkeley, CA

After depositing on floor surfaces, particles can spread throughout a building as a result of foot traffic. Particles can be tracked from one area to another by adhering to shoes and then re-depositing to floors. Footsteps can resuspend deposited particles into the air where they can be further transported. Tracking and resuspension have not been quantified often and the factors that control them are not well understood. Transport by tracking and resuspension may influence inhalation and dermal exposures of building occupants to aerosols and certain particle-phase contaminants.

Bench-scale laboratory experiments are being conducted to measure particle tracking and resuspension rates from foot traffic. A footstep simulator in a small chamber has been constructed to conduct bench-scale experiments. This footstep simulator mimics human footsteps in a repeatable manner over a range of step speeds and weights. The bench-scale experiments involve the following general steps: uniform deposition of particles on a floor sample in a deposition chamber, quantification of the particle mass on the floor sample, and simulation of footsteps on the floor sample in the footstep simulation chamber with measurement of particle tracking and resuspension. Measurement of airborne concentrations in the step simulation chamber during step simulation yields information on resuspension. Tracking is evaluated by direct measurement of the particle mass on shoes and floor surfaces. Particle uptake from the floor to shoe is measured, as is re-deposition from particle-laden shoes to clean floor surfaces. Fluorescent techniques are used to quantify both the airborne concentrations and the deposited mass of the experimental particles.

The experiments are being conducted with fluorescent particles in three size ranges: 1-5 µm, 5-10 µm and 10-20 µm. For each particle size range, tracking and resuspension rates are evaluated for three types of floor surfaces (vinyl tile, short-pile carpet, and long-pile carpet) and two types of shoes (treaded and untreaded). The experiments also explore the influence of step speed and step weight on the tracking and resuspension processes.

3A1

THE GEMS AEROSOL PROJECT: EARLY RESULTS AND EXPECTED PROGRESS. Olivier Boucher, Hadley Centre, Met Office, Exeter, U.K. Jean-Jacques Morcrette, European Centre for Medium-range Weather Forecasts, Reading, U.K. and the GEMS-aerosol project members

In response to a call related to the Global Monitoring for Environment and Security, the Global and regional Earth-system (Atmosphere) Monitoring using Satellite and in-situ data (GEMS) Integrated Project will mobilise considerable European scientific and technical expertise to provide new operational services and capabilities. GEMS-aerosol will develop and implement at ECMWF a comprehensive, validated, and novel operational global data assimilation / forecast system for atmospheric aerosols, which combines all available remotely sensed and in-situ data to achieve global monitoring of atmospheric aerosols from global to regional scales and covering the troposphere and stratosphere. The role of the aerosol sub-project is threefold: I) to provide operational aerosol products to end-users, II) to fulfil the requirements for aerosol products from the other GEMS sub-projects, and III) to improve weather analysis and reanalysis products (and possibly ultimately weather forecasts). In this presentation we will discuss our plans for GEMS-aerosol and early results.

3A2

POSSIBILITIES AND CHALLENGES IN USING SATELLITE DATA FOR PM2.5 FORECASTS. MIAN CHIN, NASA Goddard Space Flight Center, Greenbelt, MD; Hongbin Yu, Allen Chu, University of Maryland at Baltimore County, Baltimore, MD

Satellite remote sensing has brought our observation of the earth's atmosphere into a new era, and remote sensing capability could lead to a quantum leap in our ability of air quality monitoring and prediction. In terms of aerosols, the most common quantity from satellite retrieval is the atmospheric column aerosol optical thickness (AOT), and the most common quantity indicating air quality at the surface is the concentration of PM2.5. We present here the relationship between the column AOT and the surface PM2.5 from a global aerosol model GOCART and from recent satellite AOT measurements by the MODIS and MISR instruments and the surface PM2.5 data from the EPA and IMPROVE networks. We will discuss the possibilities and challenges in using satellite data for PM2.5 forecasts, and if model-satellite assimilation can improve the forecast quality.

3A3

CALIPSO IMPACTS ON ASSESSMENT OF GLOBAL AND REGIONAL SCALE AEROSOL TRANSPORT. RAYMOND HOFF and Lynn Sparling, University of Maryland, Baltimore County, Baltimore MD David M. Winker, NASA Langley Research Center, Hampton, VA

The Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) wil be launched in the summer of 2005. This presentation will present the status of the CALIPSO instrument and early results from the mission. Focus will be placed on the use of CALIPSO to assess the distribution and transport of global and regional scale aerosol sources, both natural and man-made. Initial results from the integration of CALIPSO \curtain plots\ of aerosol backscatter and a WRF transport model will be presented.

3A4

THE APPLICATION OF MISR AOT IN INTERPOLATING SURFACE LEVEL PM2.5 CONCENTRATIONS. YANG LIU and Meredith Franklin, Harvard School of Public Health, Boston, MA

Fine particulate matter (PM2.5) has been shown to be correlated with adverse health effects, and understanding the distribution of its concentrations in the atmosphere is of great importance to both health scientists and policy makers. Air pollution monitoring data is typically sparse over large geographical areas, making it difficult to use typical spatial analyses to interpolate concentrations in a meaningful manner. Remote sensing provides a tool whereby fine particulate concentrations are obtained from satellite's measurements of aerosol optical thickness (AOT). Currently, AOT measurements are routinely taken by satellite remote sensors such as the Multi-angle Imaging SpectroRadiometer (MISR). These measurements have good spatial resolution and almost complete spatial coverage, therefore may vastly increase the amount of concentration data available for analysis.

We present a simple approach to estimating ground-level PM2.5 concentrations by applying local scaling factors from a global atmospheric chemistry model to MISR AOT. The resulting MISR PM2.5 concentrations are compared with measurements from EPA's PM2.5 compliance network for the year 2001. Regression analysis shows that the annual MISR PM2.5 concentration is strongly correlated with EPA PM2.5 concentration ($r = 0.81$), with an estimated slope of 1.00 and an insignificant intercept, when three outliers from Southern California are excluded. The MISR PM2.5 concentrations have a Root Mean Square Error (RMSE) of 2.20 mg/m3, which corresponds to a relative error (RMSE over mean EPA PM2.5 concentration) of approximately 20%. This approach presents a significant improvement in predicting PM2.5 concentrations relative to a previous study where only MISR AOT and a few meteorological parameters are used. The estimated seasonal mean PM2.5 concentrations exhibited substantial uncertainty, particularly in the western United States. With improved MISR cloud screening algorithms and global model dust simulation, as well as a higher model spatial resolution, we expect that this approach will be able to make reliable estimation of seasonal average ground level PM2.5 concentration or at even higher temporal and spatial resolution.

3A5

AEROSOL OPTICAL PROPERTIES AND MICROPHYSICS FROM THE NASA DC-8, J-31 AND R/V RON BROWN COMPARED TO SATELLITE RETRIEVALS BY MISR DURING INTEX-A. CAMERON S. MCNAUGHTON, Antony D. Clarke, Steven G. Howell, University of Hawai`i, Honolulu, HI Ralph Kahn, NASA Jet Propulsion Laboratory, Pasadena, CA Philip B. Russell, NASA Ames Research Center, Moffett Field, CA John M. Livingston, SRI International, Menlo Park, CA Beat Schmid, Jens Redemann, BAERI, Ventura, CA Patricia K. Quinn , Timothy S. Bates, NOAA Pacific Marine Environmental Laboratory, Seattle, WA

We present results from two case studies of concurrent aerosol measurements during NASA's INTEX-A experiment (summer 2004). In-situ measurements of aerosol size distributions and chemistry were made aboard the R/V Ron Brown in the Gulf of Maine on July 22nd and Aug. 7th while vertical profiles of in-situ aerosol size distributions, chemistry and optical properties were measured aboard the NASA DC-8 and J-31. LIDAR systems aboard the R/V Ron Brown and DC-8 remotely sensed tropospheric aerosol structure while the MISR sensor on board NASA's TERRA satellite imaged the region at its highest spatial and spectral resolution using all nine viewing angles.

The July 22nd case features a dry (RH=20%), 1 km deep layer of biomass burning aerosols centered at 4 km. The vertically resolved aerosol area distributions show that the biomass-burning plume aloft has mean dry particle diameters between 0.4 and 0.5 um and exists as an internal mixture with relatively large refractory black carbon (BC) species. The biomass-burning layer is located above continental pollution being advected out over the Gulf of Maine. The pollution plume is largely confined to the boundary layer and aerosol area distributions show mean dry particle diameters between 0.2 and 0.4 um. These particles are also internal mixtures containing a smaller fraction (by volume) of refractory BC but have number concentrations 5 times those in the biomass-burning layer (700 versus 3500 cm-3). Relative humidity near the surface exceeds 90% resulting in higher ambient aerosol extinction for the pollution layer compared to the layer aloft. Column integrated AOD measured in-situ aboard the DC-8 and measured directly by the J-31 agree within 10% and ranged from 0.60 at a wavelength of 450 nm to 0.30 at 700 nm.

The Aug. 7th case features clean conditions in cloud free air after heavy precipitation. Dry particle diameters are 0.11 – 0.25 um within the boundary layer and are present at concentrations of ~1500 cm-3. Boundary layer relative humidity did not exceed 80% and ambient aerosol optical depths were 0.10 at a wavelength of 450 nm and 0.04 at 700 nm. In-situ measurements aboard the DC-8 and direct measurements from the J-31 were within 10%.

We evaluate variability observed in the aerosol fields from each of the independent platforms in an effort to determine whether the terrestrial observatories can provide a comprehensive description of the regional aerosol field. The July 22nd case represents a complex mixture of aerosol types that can be used to test whether the MISR satellite retrieval algorithm has appropriate analogs to the aerosols observed by in-situ measurements. The near background conditions on Aug. 7th can be used to test the limits of detection for the MISR instrument in the community's efforts to calibrate/validate the MISR retrievals.

3A6

SIMULATIONS OF BIOMASS BURNING SMOKE PLUMES AND COMPARISONS TO IN SITU AND REMOTE SENSING OBSERVATIONS FROM SAFARI 2000.

REBECCA I. MATICHUK, Jamison A. Smith, and Owen B. Toon, Laboratory for Atmospheric and Space Physics, Program in Atmospheric and Oceanic Sciences, University of Colorado, Boulder, CO; Peter R. Colarco, NASA Goddard Space Flight Center, Code 916, Greenbelt, MD

We model the evolution of biomass burning aerosols and investigate their optical properties. Our model is an offline three-dimensional aerosol and microphysical transport model driven by assimilated meteorology from the NCEP/NCAR reanalyses and constrained with measurements collected during the Southern African Regional Science Initiative campaign (SAFARI 2000). Detailed simulations were conducted to examine the model's sensitivity to aerosol emissions and microphysical processes. Here we investigate the model sensitivity to the diurnal cycle and injection altitude of aerosol emissions and particle coagulation. Additionally, we test the sensitivity of the model aerosol optical properties to our choice of initial aerosol particle size distribution and refractive indices. Modeled smoke aerosol optical thickness, aerosol extinction, angstrom exponent and single scattering albedo are compared to satellite, aircraft and ground-based observations made over central and southern Africa. The results from this study will be useful in future applications relating to the transport and evolution of biomass burning aerosols by testing source functions and illuminating microphysical processes that must be treated in models.

3A7

EVALUATION OF REGIONAL PM PREDICTIONS WITH SATELLITE AND SURFACE MEASUREMENTS.

YANG ZHANG North Carolina State University, Raleigh, NC Hilary E. Snell Atmospheric & Environmental Research, Inc., Lexington, MA Krish Vijayaraghavan Atmospheric & Environmental Research, Inc., San Ramon, CA Mark Z. Jacobson Stanford University, Stanford, CA

The U.S. EPA Models-3/Community Multiscale Air Quality (CMAQ) modeling system is used to simulate the mass concentrations and optical properties of atmospheric particulate matter (PM) and to estimate the PM mass exported from the urban/regional scale to the global atmosphere. The simulation is conducted for the full year of 2001 with a horizontal resolution of 36 km for a domain that covers the contiguous U.S., southern Canada, and northern Mexico. The aerosol optical depths (AOD) and other aerosol radiative properties are calculated online using a parameterization of the Mie theory implemented in CMAQ and offline using several empirical approaches. The model results are evaluated using the measurements from satellite instruments such as the Moderate Resolution Imaging Spectroradiometer (MODIS) and ground-based monitoring networks such as the Interagency Monitoring of Protected Visual Environments (IMPROVE), the Aerometric Information Retrieval System-Air Quality System (AIRS-AQS), the Clean Air Status and Trends Network (CASTNet), and the Speciation Trends Network (STN). The evaluation is conducted in terms of spatial/temporal distributions of gas and PM species and quantitative statistical metrics that include both traditional measures such as the normalized mean bias (MNB) and new unbiased symmetric measures such as the normalized mean bias factor (NMBF). The process analysis tool in CMAQ is used to gain an in-depth understanding of the controlling processes for the fate of PM and total odd oxygen (Ox) on urban/regional scales.

Our evaluation results for January-March 2001 have shown that CMAQ's PM performance is generally consistent with current PM model performance, with worst performance at STN sites and relatively high biases in nitrate, ammonium, and organic carbon based on NMBF at all sites. CMAQ generally reproduces the magnitudes and spatial variations of the monthly-mean AOD obtained from MODIS. The single scattering albedo (SSA) predicted by CMAQ is within the typical range of satellite measurements. The process analysis has shown that the net export is 0.75 Gigamoles/day for Ox and 1.54 Gigagrams/day for PM2.5 out of the planetary boundary layer (0-2.9 km) during January-March 2001 over the entire modeling domain. Monthly and seasonal-mean results are being analyzed and contrasted. The predicted AODs with the online Mie parameterization will be compared with those from offline empirical approaches. Uncertainties and likely causes of discrepancies between simulation results and observations and between model results with different approaches for AOD calculations will be analyzed and identified.

3B1

CHARACTERIZATION OF THE CARBONACEOUS FRACTION OF PARTICULATE MATTER USING HOT PRESSURIZED WATER FRACTIONATION AND NEAR-EDGE X-RAY ADSORPTION FINE STRUCTURE (NEXAFS) SPECTROSCOPY.

ALENA KUBATOVA, Steven B. Hawthorne, Energy & Environmental Research Center, University of North Dakota, Grand Forks, ND; Artur Braun, Department of Chemical & Materials Engineering, Consortium for Fossil Fuel Science, University of Kentucky, Lexington, KY

Due to the complexity of organic speciation analysis of particulate matter (PM), carbonaceous PM is frequently characterized by organic and elemental carbon (OC,EC). To find a compromise between a too-complex and an oversimplified approach, we have developed a method differentiating extractable OC into three fractions: highly polar (e.g., acids, alcohols), moderately polar (e.g., quinones), and nonpolar (e.g. PAHs), which may be related to bioavailable, primary, and secondary emissions, respectively.

We have previously shown that hot pressurized water (25°–300°C) extracts a wide-polarity range of organics from PM. The advantage of hot pressurized water is its ability to extract polar organics at lower temperatures, and moderately polar and nonpolar organics at higher temperatures. Nonpolar alkanes can be extracted with superheated steam. Methylene chloride is frequently employed for the extraction of PM, but is suitable only for extraction of slightly polar or nonpolar organics. Thus, in an attempt to fractionate a higher proportion of OC, we have compared two solvent systems: (1) pressurized water (25°–150° C) followed by methylene chloride, and (2) pressurized water (25°–250° C) followed by steam (250°C, 5 bar). Three different PM were extracted: diesel exhaust PM (SRM 2975), urban air PM (SRM 1648), and wood smoke PM, containing 7%, 10%, and 58% of OC, respectively.

Based on lower OC/EC ratio in residues (after extraction), the pressurized water followed by steam was more effective than pressurized water followed by methylene chloride for wood smoke and urban air PM. No difference between the two solvent systems was observed for diesel exhaust PM. The overall OC recoveries (determined as total OC) achieved with hot pressurized water (25°–250°C) were 37%, 53%, and 56% for wood smoke, urban air, and diesel exhaust PM, respectively. An additional 1% of OC was extracted by steam from all PM samples. OC of wood smoke and urban air PM was evenly distributed over all three fractions (10–20% in each fraction). For diesel exhaust PM, only 4% of OC was found in the polar fraction, and surprisingly, the majority of OC was found in the moderately polar fraction (35%).

Further characterization of the extracts employing NEXAFS spectroscopy will be presented. For example, for wood smoke PM, high-intensity bands of C=C, C-OH, and COOH (corresponding to high concentrations of aromatic acids and methoxy phenols) were observed in the polar fraction.

Thus, hot pressurized water together with NEXAFS spectroscopy appears to be promising tool in characterizing carbonaceous PM.

3B2

QUANTITATIVE DETERMINATION OF AMBIENT AEROSOLS USING ATTENUATED TOTAL REFLECTANCE FOURIER TRANSFORM INFRARED SPECTROSCOPY AND MULTIVARIATE CHEMOMETRIC TECHNIQUES.

CHARITY COURY, Arizona State University, Tempe, AZ; Ann Dillner, University of California, Davis, CA

Ambient organic carbon particulate samples are typically analyzed after collection on substrates by thermal optical methods (TOM), which give information only on the total elemental carbon and total organic carbon levels present in a sample. Gas Chromatography/Mass Spectrometry (GC/MS) is used to quantify individual organic compounds. This method is a proven method for identifying specific tracer compounds, but only has the ability to identify around 10% of the organic mass in ambient aerosol (Rogge et al., 1993). GC/MS has difficulty detecting very polar compounds and is time consuming and expensive. Infrared (IR) spectroscopy is a more specific spectroscopic technique than TOMs, and gives more detail on the classes of organic compounds that are present within the organic carbon concentration. It also has the ability to identify the entire organic component of the aerosol, regardless of polarity.

An on-site Fourier Transform Infrared (FTIR) spectroscopic sampling method utilizing attenuated total reflectance (ATR) has been developed and used to analyze size segregated organic and inorganic ambient aerosols. By using multivariate calibration techniques, the vast amount of data in one ATR-FTIR spectra of size-segregated aerosol can be deconvoluted and constituent groups can be individually quantified. The FTIR calibration method development will be discussed. Also, the results of the FTIR analysis of size segregated aerosols collected in a remote and urban location will be presented.

Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., and Simoneit, B.R.T. (1993) Quantification of Urban Organic Aerosols at a Molecular Level: Identification, Abundance and Seasonal Variation. Atmospheric Environment, 27A(8), 1309 -1330.

3B3

DETERMINATION OF AMINO ACIDS AND PROTEINS IN AIR PARTICULATE MATTER. Tobias Fehrenbach, REINHARD NIESSNER, Institute of Hydrochemistry, TU Muenchen, Germany; Ulrich Poeschl, Max Planck Institute of Chemistry, Mainz, Germany

The chemical composition of fine air particulate matter (PM2.5) is highly diverse and variable. It influences the chemical and physical properties as well as health effects of atmospheric aerosols. The organic carbon fraction (OC) accounts for up to 30% of PM2.5, but only 10 to 40% of the compounds contributing to the organic carbon pool including macromolecular components like proteins and humic-like substances (HULIS) have been identified so far. These biopolymers are considered to make up 20 to 60% of the water-soluble organic carbon fraction (WSOC) and influence the formation of clouds and precipitation due to their hygroscopic properties.[1][2] Because of their nitrogen content they become an important nitrogen source for ecosystems upon deposition.[2] Appropriate sample preparation steps and analytical methods for the determination of proteins and amino acids were developed and characterized.

After extraction of rural and suburban atmospheric fine particle samples the macromolecular fraction is obtained by size exclusion chromatography (> 5 kDa). The protein content of the macromolecular fraction is determined by a microBCA-assay (Uptima). For determination of protein bound amino acids the macromolecular fraction is exposed to microwave induced acid hydrolysis (5 bar, 150°C, 30 min) with 6 M hydrochloric acid, 10% trifluoroacetic acid and 0,1% phenol as hydrolyzing agents. Non protein type amino acid Norvalin is used as an internal standard to compensate for sample losses. The obtained amino acids are then derivatized with o-pthaldialdehyde and mercaptopropionic acid (OPA/MPA). Sixteen amino acid derivatives including the internal standard are separated by RP-C12-HPLC by a multi-step gradient using 50 mM sodium acetate buffer and acetonitrile/methanol (1:1) as eluants. The detection limits are in the low nanomolar range.
The protein content determined by the microBCA-Assay will be evaluated with the results obtained by amino acid analysis. The amino acid content and its correlation to WSOC and WSN in PM2.5 samples will be presented and discussed.

[1] Zappoli, S., Andracchio, A., Fuzzi, S., Facchini, M.C., Gelencsér, A., Kiss, G., Krivácsy, Z., Mészáros, E., Hansson, H. C., Rosman, K., Zebühr, Y., Atmos. Environ. 1999, 33, 2733 -2743.
[2] Zhang, Q., Anastasio, C., Atmos. Environ. 2003, 37, 2247 -2258.

3B4

AMINES IN FINE PARTICLES: MYTH, TRACE SPECIES, OR MAJOR COMPONENTS?. Mark Erupe and PHILIP J. SILVA, Department of Chemistry and Biochemistry, Utah State University, Logan, UT

Organic nitrogen compounds in the particulate phase have been of interest to aerosol scientists for some time as a possible sink involved in the nitrogen cycle. Most reports on organic nitrogen have focused on the oxidized fraction (organic-nitrates). Sporadic studies of reduced nitrogen in atmospheric particles have also been reported. However, few studies have attempted to identify or quantify the species present. We present here data acquired using an Aerodyne aerosol mass spectrometer aimed at measuring and identifying amines in airborne particles.

Laboratory experiments conducted with the aerosol mass spectrometer show that amines can easily form particles by interacting with acids to form salts. A series of alkylamines have been studied using mass spectrometry to understand the particulate-phase products.

Ambient fine particles were monitored in Logan, Utah during winter inversions. Logan is close to being classified as non-attainment for PM2.5, and can have very high mass loadings during winter due to severe inversions. Ammonium nitrate is the major identified component, however, the presence of alkylamines in fine particles is readily apparent in mass spectra acquired in Logan. Calibration experiments show that amines are a major component of the organic carbon fraction, and not simply a function of high detector efficiency. The majority of particulate-phase reduced-nitrogen species in Logan appear to be tertiary amines, dominated by trimethyl- and triethylamine.

3B5

A METHOD TO ISOLATE CARBONACEOUS AEROSOLS SOLUBLE IN WATER BY ORGANIC FUNCTIONAL GROUP USING SOLID PHASE EXTRACTION AND SIZE-EXCLUSION CHROMATOGRAPHY. AMY P. SULLIVAN, Rodney J. Weber, Georgia Institute of Technology, Atlanta, GA

A two-step method has been developed and tested to isolate chemical fractions of the ambient organic aerosol based on chemical functional groups. The resulting aqueous samples containing isolated fractions can be analyzed by a variety of approaches to test the chemical and physical properties of isolated compounds. In this paper the carbonaceous fraction is quantified by Total Organic Carbon (TOC) analysis.

In the first step, carbonaceous aerosols soluble in water are extracted from integrated filters and separated into hydrophilic and hydrophobic fractions using XAD-8 resin. C-NMR analysis (presented in a companion paper) and laboratory calibrations with atmospherically relevant standards suggest that the hydrophilic fraction is composed of short chain aliphatic carboxylic acids and neutral compounds and saccharides. In contrast, the recovered hydrophobic fraction contains aromatic functional groups. Hydrophobic cyclic compounds and organic nitrates cannot be recovered and isolated by this method. In the second step, following a newly developed method, Size-Exclusion Chromatography (SEC) is used to chromatographically separate by organic functional groups the WSOC hydrophobic and hydrophilic compounds.

Results from an analysis of urban Atlanta summer, urban Atlanta winter, and biomass burning samples collected via integrated Hi-Volume quartz filters and isolated by the XAD-8/SEC method will be presented.

3B6

FUNCTIONAL GROUP ANALYSIS BY NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY: AN OVERVIEW OF THE RESULTS ON WATER-SOLUBLE ORGANIC COMPOUNDS IN AEROSOLS AND CLOUD/FOG DROPLETS.. STEFANO DECESARI, Maria Cristina Facchini, Mihaela Mircea, Fabrizia Cavalli, Lorenza Emblico, Sandro Fuzzi, ISAC-CNR, Bologna, IT; Emilio Tagliavini, Fabio Moretti, Department of Chemistry, University of Bologna, Bologna, IT.

Water-soluble organic compounds (WSOC) have a potential impact on physico-chemical properties of aerosol particles as surface tension, density and solubility, thus influencing aerosol water uptake and cloud droplet formation. To date, the chemical speciation of WSOC at the molecular level has been challenging, because WSOC typically occur in very complex mixtures of thousands of different compounds. Recently, various attempts have been made to characterise the chemical composition of WSOC by means of spectroscopic and chromatographic methods. During the past few years, we have exploited Nuclear Magnetic Resonance (NMR) spectroscopy to provide the functional group budget of the whole WSOC mixture, as well as WSOC chemical classes separated by chromatographic methods. We discuss the advantages and drawbacks of the method, and present the applications of a novel technique employing derivatisation of the carboxylic groups and their subsequent determination as methyl-esters by proton NMR spectroscopy. Functional group compositions have been determined by NMR on aerosol samples collected in continental polluted (Italy, UK) and clean (Finland) areas, as well as at coastal polluted (Korea) and clean (Ireland) sites in the Northern Hemisphere. Further aerosol characterisation studies employing NMR spectroscopy were performed in tropical areas impacted by biomass burning emissions (Brazil, Indonesia). Finally, fog and rain water samples were collected in polluted sites in Italy and Korea and subjected to NMR analysis of dissolved WSOC. An overview of the results is presented, showing that the functional group analysis by NMR provides a fingerprint of different sources and transformation processes of aerosol WSOC in the various environments. Moreover some applications of the functional group budgets derived by proton-NMR are presented: 1) formulation of model compounds which reproduce quantitatively the average chemical and physico-chemical properties of WSOC; 2) comparison of the observed composition with the results of models of secondary organic aerosol formation, allowing for their validation.

3B7

DETERMINATION OF WATER-SOLUBLE ORGANIC AND INORGANIC ATMOSPHERIC AEROSOL COMPONENTS.

Ulrike McKeon, REINHARD NIESSNER, TU Muenchen, Institut of Hydrochemistry Ulrich Pöschl, Max Planck Institute for Chemistry Mainz

Aerosol particles serve as cloud condensation nuclei and play a central role in atmospheric chemistry and physics, climate, and the hydrological cycle. Water-soluble organic and inorganic aerosol components strongly influence the formation of clouds and precipitation, but the knowledge of their molecular structures and atmospheric abundance is very limited. Earlier investigations have shown that macromolecular compounds contribute significantly to the organic carbon fraction in aerosols. Most of these compounds are not yet identified but 20-60 % of the water-soluble organic carbon (WSOC) have been attributed to humic-like substances (HULIS) and biopolymers like proteins. Appropriate methods for the analysis of these macromolecu-lar substances have been developed, characterized and applied to the characterization of water-soluble atmospheric aerosol components.

Atmospheric aerosol samples have been collected on filters and impaction plates on Hohenpeißenberg mountain, located in a rural area in southern Germany. Data sets were collected for the annual cycles of the years 2003 and 2004. The mass concentra-tion of particulate matter was determined gravimetrically. After aqueous extraction and size exclusion chromatography, several parameters of the low molecular (< 5 kDa) and macromolecular (> 5 kDa) fractions of the samples were determined, including WSOC, water soluble nitrogen (WSN), protein content, inorganic ions as well as total and ele-mental carbon (TC/EC). WSOC and WSN were measured with a C/N-analyser (multi nc 2000). Protein was determined with a microBCA-assay (Uptima). The TC and EC contents were analysed thermochemically with a Coulomat 702 DR.

Similar seasonal cycles could be observed for all investigated components. A primary maximum was observed in spring and a secondary maximum in late summer. The total content of WSOC ranged from 0.2 to 2.6 µg/m3 with an average of 1.1 µg/m3. The total WSN was found to be between 0.1 and 4.6 µg/m3, the average being 1.0 µg/m3. The mean WSOC/WSN ratio was 2 for the low molecular and 12 for the macromolecular fraction. The ratio between protein and macromolecular WSN found was 14,5. This agrees well with the nitrogen content of Bovine Serum Albumin that was used as a model protein. Up to 100% of the MWSN found can be explained by the presence of protein but only 50% of the MWSOC. The results will be complemented by Raman-Microspectroscopic analysis carried out on impaction samples as well as data on parti-cle number concentration and size distributions (electric low pressure impactor (ELPI)).

3C1

AN EVALUATION OF SHELTER-IN-PLACE STRATEGIES IN INDUSTRIAL AND RESIDENTIAL BUILDINGS.

JOSEPH FRADELLA III, Jeffrey Siegel, Department of Civil, Architectural, and Environmental Engineering, The University of Texas at Austin, Austin, TX

Shelter-in-place (SIP) strategies are designed to protect building occupants from extraordinary circumstances, such as an accidental release of hazardous airborne materials, fire, or acts of bioterrorism. We evaluated several shelter-in-place strategies for 0.1 - 10 µm particles in four industrial buildings and four residential buildings. The air tightness and air exchange rates of the buildings were found using fan pressurization and tracer gas techniques. Indoor and outdoor measurements of particles from 0.1 to 10 µm were taken to determine the effectiveness of the building envelope at preventing outdoor particle penetration into the indoor space. The SIP strategies of deploying portable HEPA filters, sealing known air leakage sites, and operating HVAC fans were evaluated at these structures by determining the ratio of indoor to outdoor particle concentrations. HEPA filters reduced indoor particles levels in all buildings and showed increasing effectiveness in smaller buildings with lower air exchange rates. After sealing leaks, indoor particle concentrations tended to remain similar to pre-sealing levels. Operating the HVAC fan, a strategy tested only in residential buildings, did not significantly affect the concentration ratio, unless the system included a high-efficiency filter, in which case the concentration ratio decreased significantly. Indoor to outdoor concentration ratios were a strong function of particle diameter and SIP strategy, with the impacts of SIP varying between buildings. The tested SIP strategies were only moderately effective in larger and very leaky buildings. The results of the research were used to design a particle protection protocol (P3) which can be used to design a SIP strategy before an extraordinary event occurs.

3C2

SAMPLING/CONCENTRATION EFFICIENCY OF SOLID, LIQUID, AND BIOPARTICLES IN SAMPLERS/CONCENTRATORS.

JANA KESAVAN, Jerold Bottiger, Robert Doherty, US ARMY, Aberdeen Proving Ground, MD

Air samplers are important in the war against terrorism and on the battlefield to detect the presence of chemical, biological, and nuclear aerosols. Samplers and detection systems must be tested and their performance efficiencies determined so that suitable samplers and detectors can be used in air sampling. In general, samplers are characterized using the standard inert (nonbiological) particles such as solid polystyrene latex (PSL) micro spheres, solid aluminum oxide particles, and liquid fluorescent oleic acid particles. It is a topic for research how the solid, liquid, and bioparticles behave in samplers and whether there are any differences in the sampling/concentration efficiency of the same size solid, liquid, and bio particles. This paper summarizes sampling efficiency results of a sampler using solid and liquid particles and sampling /concentration efficiencies of four types of samplers using inert and bioparticles. The following types of samplers were tested: concentrator-impinger, 1-stage aerosol concentrator, 3-stage aerosol concentrator, 4-stage aerosol concentrator, and personal samplers. The results show that the sampling efficiency is similar for solid, liquid, and bio-particles for particles smaller than 6 microns. However, solid particles larger than about 6 microns tend to bounce after impaction, unlike similar sized liquid particles and give a significantly different efficiency . Currently, data is unavailable for large (> 6 microns) bioparticles, therefore, more research needs to be done to determine and to compare the collection efficiency of large bio-particles to the inert particles.

3C3

INVESTIGATION OF COLLECTION EFFICIENCIES AND INHALATION CONVENTION CONFORMITY OF PORTABLE MICROBIAL SAMPLERS.

MAOSHENG YAO, Gediminas Mainelis, Rutgers, The State University of New Jersey, New Brunswick, NJ

Accurate bioaerosol exposure estimates require advanced microbial samplers, especially those that follow convention for inhalable airborne particles. Currently, the use of portable microbial samplers is increasing. However, little information is available about the performance characteristics of such samplers, including their conformity to inhalable particle convention.

The objective of this study was to investigate the physical collection efficiencies and conformity to inhalation convention of several portable microbial samplers including RCS HighFlow, BioCulture, Microflow, Microbiological Air Sampler (MAS) and SMA MicroPortable. All these samplers collect biological particles on agar media and their built-in sampling flow rates range from 30 to 141.5 L/min. The physical collection efficiencies of portable samplers were determined using Polystyrene Latex particles ranging from 0.5 to 5.22 µm in aerodynamic size. Our investigation revealed that a classical collection efficiency testing approach, which compares particle concentrations upstream and downstream of a sampler, cannot directly be applied to these portable samplers because many of them feature air movers positioned next to the sampling media and act as particle collectors themselves. Therefore, we developed a new testing procedure which allows differentiating the collection efficiency between the collection media (agar) and the air movers, thus allowing estimation of effective collection efficiency, i.e., fraction of incoming particles deposited on collection medium.

Experimental results have shown that all evaluated samplers collect approximately 5% of 0.5µm particles. The effective d50, or cut-off sizes, of the investigated samplers depended on the sampler model and ranged from 1.2µm for the RCS High Flow operating at 100 L/min to 2.8 µm for the MAS sampler operating at 100 L/min; the effective cut-off sizes for other three samplers (SMA Microportable operating at 141.5 L/min, BioCulture operating at 120 L/min and Microflow operating at 120 L/min) were above 5.2 µm. The experimental cut-off sizes of the portable samplers agreed well with their theoretical estimates. Comparison of the samplers' collection characteristics with the sampling convention for total inhalable particles revealed that relative to the inhalation convention most of the investigated portable microbial samplers would under-sample particles between 0.5-5.2 µm, a size range which encompasses most of the single bacterial and fungal particles.

The obtained results indicate that application of the tested portable bioaerosol samplers for biological exposure assessment may result in underestimation of the airborne microorganism concentrations. As the continuation of this study, the biological performances of the portable bioaerosol samplers will be determined.

3C4

DE NOVO IDENTIFICATION OF VIABLE BIOLOGICAL SPECIES IN AMBIENT AIR. ANN M. SNELLINGER, Murray V. Johnston, University of Delaware, Newark, DE

Many studies have shown bioaerosols, particularly viable species, as vectors for disease transmission, making them a particular environmental concern. Consequently, there is a need to detect and identify the viable bioaerosols in the air we breathe. Experimental results will be presented in which microbial species in ambient air are collected, isolated and amplified for identification with proteomics and mass spectrometry.

This proof of concept study incorporates environmental aerosol research with proteomic applications to gain a better understanding of the biological contribution to naturally occurring ambient aerosols. Initial studies are directed towards method development and defining ideal experimental conditions to cover the breadth of bioaerosol diversity. The goal is to characterize the type of microbes present in air, not to assay specific target microbes. Generic culturing protocols are used in order to adapt to the growing conditions of the most microbes.

Particles were collected with an SKC BioCassette filled with Luria-Bertani (LB) agar at ~28.3 L/min for 10 min. Collected samples were incubated at room temperature for 48 hours then isolated via streaking of individual cultures. Pure cultures were incubated at 37C for 18 hours to increase biomass. Several different microbe colonies were observed, isolated and amplified. Microbe cells were lysed via french press and prepared for proteomic studies. SDS PAGE gels stained with Coomassie° dye displayed different protein spot profiles depending on the culture lysate loaded. In-gel tryptic digestion of spots excised from the SDS PAGE gels followed by peptide mass fingerprinting with MALDI-Tof (BRUKER Biflex III) and sequence tag identification with LC-MSMS (Micromass QTof Ultima) was used to identify proteins contained in the microbe lysates. Identifying the proteins for a specific microbe allowed for classification of the corresponding microbe. Preliminary results confirm that microbes can be collected and identified without prior knowledge of the specific microbes present in the sampled air mass.

3C5

PROPERTIES OF PATHOGENIC ANTHRACIS AND OTHER BACILLUS SPORES IN AEROSOL PARTICLES. Monica Carrera, Jana Kesavan, and JOSE-LUIS SAGRIPANTI Edgewood Chemical Biological Center, US Army, Aberdeen Proving Ground, MD

Under quality controlled conditions we prepared spores of fourteen different Bacillus strains, including four pathogenic B. anthracis. We measured the length and diameter distributions of spores by transmission electron microscopy. We calculated the aspect ratio and volume of each spore. Spores of B. subtilis and B. atropheus, two commonly used B. anthracis simulants, were considerably smaller in length, width and volume than most B. anthracis spores, while B. cereus spores were closer to B. anthracis in length and width, and B. thuringiensis was closer to B. anthracis in volume. We developed methodology to reveal the number of microbial spores within aerosol particles. The procedure involves visualization under differential- interference-contrast microscopy enhanced by high-resolution photography and further analysis by computer-assisted imaging. The method was used to analyze spores generated by a small (pressured metered-dose inhaler type) generator. Particles consisting in 1 or 2 spores accounted for 85 % of all generated particles. This percentage rose to 91 % when the same aerosol was collected on an Andersen cascade impactor that collected particles larger than 0.65 µm and was even higher (95 %) when particles larger than 3.3 µm were also eliminated. These results demonstrate that the imaging analysis of aerosol particles collected on glass slides is sensitive to even relatively small changes in aerosol particle composition. The accuracy of the enhanced microscopic method described herein (approximately 3%) seems adequate to determine the spore composition of aerosols of interest in biodefense.

3C6

SAMPLING PERFORMANCE FOR BIOAEROSOLS BY FLOW CYTOMETRY WITH FLUOROCHROME. Chih-Shan Li, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University Pei-Shih Chen, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University

Although culture-based analysis remains the primary method for environmental bioaerosol analysis, for better understanding and quantifying of bioaerosols, both culture and nonculture-based methods should be used and compared. Here, flow cytometry with fluorochrome (FCM/FL) was applied to evaluate the sampling performance of impingement (AGI-30 all-glass impinger) and filtration (track-etched polycarbonate filter) with different types of fluorescent dye staining (cell membrane integrity and metabolism) and then compared with a traditional culture method (culturability). Two bacterial aerosols (Escherichia coli and endospores of Bacillus subtilis) and two fungal aerosols (Candida famata and Penicillium citrinum spores) were studied. The bioaerosol viability during the sampling processes was highly influenced by bioaerosol characteristics (hardy or fragile), as well as by the fluorescent dyes with different physiological mechanisms. For better viability of the sampled bioaerosol, the impinger was superior to the filter. Moreover, it was found that sampling stress from filtration had more influence on the bioaerosol metabolism mechanism than cell membrane integrity. Furthermore, the differences between cell membrane integrity and the metabolism by sampling stress were found related to the bioaerosol species.

3C7

TEST PARTICLES FOR CALIBRATION AND VERIFICATION OF EXPLOSIVES TEST INSTRUMENTATION. ROBERT A. FLETCHER, George A. Klouda, Jennifier Verkouteren and Greg Gillen, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD

Explosives screening is conducted by swipe based and automated Portal based technologies. Swipes are used to remove trace explosives from objects, and the residue is analyzed by ion mobility spectrometry. The Portal systems use air jets to aggressively remove explosives particles and detection is performed by either mass or ion mobility spectrometry. For both systems, there are no standards to test various operating and performance processes. We are exploring methods to make uniform particles containing the appropriate analyte for testing collection efficiencies by swipe based processes and by air jet removal in the Portal. The vibrating orifice aerosol generator (VOAG) and drop-on-demand ink jet printing are being examined to make uniform particles containing trace explosives and surrogate compounds tagged with trace dyes for identification. The precision for making uniform particles using the VOAG has been documented. We are developing a method to quantitatively collect aerosol from the VOAG onto suitable substrates for testing by detection systems. We are also determining the accuracy and precision of making particles using adrop-on-demand ink jet technique. Fluorescence and scanning electron microscopy as well as ion mobility spectrometry and gas chromatograph mass spectrometry are being utilized in the research.

3D1

EVALUATION OF RESPIRATOR FILTERS FOR ASBESTOS FIBERS. YUNG SUNG CHENG, Thomas Holmes, Lovelace Respiratory Research Institute; Bijian Fan, Amgen

Fiber aerosols are known to have different aerodynamic behaviors than spherical particles and usually carry higher electrostatic charges. We have investigated the effects of flow rate and charge status of filter cartridges on the penetration of spherical and fiber aerosols. Four types of test respirator filters were selected: two for passive respirators, one for a powered respirator, and one disposable face mask. Surface charges on respirator filters were determined using a non-contact field electrostatic field meter. Penetration tests were performed for filter cartridges before and after charge neutralization. The surface charge measurements on the respirator filters showed that some filters, including those used in disposable facemasks, are charged to enhance the collection efficiency. Our data also showed that the surface charges decreased in a 38°C and > 90% relatively humidity environment and disappeared after 1 week. Following NIOSH test procedures, dual filter cartridges were tested at 16 and 42.5 L min-1, whereas single cartridge filters were tested at 32 and 85 L min-1. Spherical DOS particles (0.30 µm and sg of 1.27) were generated using a condensation aerosol generator (model 3076, TSI, St. Paul, MN). Three asbestos fibers of different diameters were tested: an ultrafine chrysotile (Calidria); a UICC crocidolite with a mean diameter of 0.08 to 0.1 µm; and a UICC amosite. The diameters of these fibers ranged from 0.02 to 1.4 µm. The fiber aerosols were generated by a small-scale powder disperser (Model 3433, TSI Inc.). Fibers upstream and downstream the test filter were examined under an electron microscope to determine the concentration and fiber dimensions. From these measurement penetration of asbestos fiber were estimated.

Only high-efficiency particulate air filters performed consistently for both spherical test aerosols and the three types of asbestos fibers. The surface charge potential of filter cartridges and flow rate did not appear to affect the performance of these filters. In contrast to the high-efficiency filters, the aerosol penetration performance of low-efficiency filters and face masks deteriorated when the charge potential on the filter was removed. Deposition of spherical particles and fibers in the charged disposable facemask filter was enhanced. For charged-neutralized low-efficiency filter cartridges, asbestos fibers may penetrate more as compared to spherical particles with a mean particle size of 0.3 µm diameter. We also observed the penetration of asbestos fibers as a function of fiber dimensions. (This research was supported by a National Institute for Occupational Safety and Health grant 1R01 OH03900).

3D2

PERFORMANCE OF FIBROUS FILTERS OF N95 RESPIRATORS: WHAT IS THE MOST PENETRATING PARTICLE SIZE?. SERGEY A. GRINSHPUN, Anna Balazy, Mika Toivola, Tiina Reponen, University of Cincinnati, Cincinnati, OH, USA; Albert Podgórski, Warsaw University of Technology, Warsaw, Poland

N95 filtering facepiece respirators are often recommended for the exposed workers and the public since the conventional wisdom is that they are highly (>95%) efficient for protecting human respiratory tract against airborne particles if properly fitted. The most penetrating size is assumed to be about 300 nm. We tested four N95 respirator models at two inhalation flow rates (30 and 85 L/min) challenging them with NaCl particles as well as viruses in the size range of 10 to 600 nm. Each respirator was perfectly face-sealed, and a manikin-based protocol was followed to measure the aerosol concentrations inside and outside the facepiece using the Wide-Range Particle Spectrometer (WPS, model 1000 XP, Configuration A, MSP Corp., USA). The particles were charge-neutralized by a 85Kr source. The experiments revealed that the filter collection efficiency could drop below the 95% threshold when the respirators are used against nanoparticles in the size range of about 30 and 70 nm. The shift of the most penetrating particle size towards nano-sized particles is attributed to the electret filter media that is conventionally utilized in N95 respirators. Following the experimental phase, the modeling of the particle penetration through mechanical and electret filters was performed using the classic theory of depth filtration and utilizing the fiber and facepiece characteristics, which were measured in the investigators' laboratories. The theory confirmed the experimentally observed most penetrating particle sizes. This finding suggests that the N95-type filtering respirators may not provide the expected protection level when used against nanoparticles. It also raises the need in revisiting the protocols established for the evaluation and certification of facepiece respirators.

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3D3

INACTIVATION OF VIRUS AEROSOL PARTICLES IN AN ELECTROSTATIC PRECIPITATOR.

ERIC KETTLESON, Bala Ramaswami, Christopher Hogan, Myong-Hwa Lee, Pratim Biswas, Largus Angenent, Environmental Engineering Science Program, Washington University in St. Louis, St. Louis, MO

Quantitative microbiological and molecular techniques were used to study the capture efficiency and inactivation of aerosolized MS2 bacteriophages (i.e., a single-stranded RNA, bacterial virus) and T3 bacteriophages (i.e., a double-stranded DNA, bacterial virus) with an X-ray enhanced electrostatic precipitator. Soft x-ray irradiation has been shown to enhance ESP capture efficiencies of ultrafine inorganic and organic particles in similar size ranges as virus particles (Hogan et al., 2004; Kulkarni et al., 2002). In this work, both positive and negative ion bombardment were investigated with viral particles by varying the applied voltage from +10 kV to -10 kV. For each charging scenario, samples were collected from the effluent air stream, as well as from the collection electrode. The samples were assayed for viable phages using traditional plaque assays, and for total nucleic acid mass using quantitative reverse transcription-polymerase chain reaction (qRT-PCR) and quantitative polymerase chain reaction (qPCR) assays. Inactivation was estimated as the difference between the mass of nucleic acid attributable to viable phages and the total mass of nucleic acid present.

Results with qRT-PCR and qPCR assays showed that the higher the voltage, the more viral particles were captured from the air. In addition, comparisons of molecular and plaque assays showed that in-flight inactivation (i.e., inactivation without capture) was also superior for the high voltages, especially for the voltages above corona inception. Thus, performing viable plaque assays alone would have overestimated capture efficiencies, because non-viable particles were unaccounted for. The viral particles that were captured on the electrode showed fewer viable phages at ± 10 kV compared to ± 5 kV. These voltages represent conditions above and below corona inception, respectively, indicating the potential for virus inactivation via continual ion bombardment.

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3D4

NEUTRALIZATION OF CHARGES ON ELECTRET FILTER MEDIA FIBERS BY BIPOLAR IONS.

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Electret filter media are widely used in many filtration applications requiring high filtration efficiency and low pressure drop, such as air cleaners and respirators. In addition to the mechanical filtration mechanisms (impaction, interception and diffusion) two other filtration mechanisms, the columbic attraction and dielectrophoresis, are involved in the particle removal using electret media. The charge-related filtration mechanisms enhance the particle collection efficiency without increasing the flow resistance when particle laden flow is forced through the media. In reality the charge-related filtration mechanisms dominate the filtration process especially in the initial phase of the filtration. The charge density on media fibers is thus the key parameter to predict the filtration efficiency of electret filter. Many theoretical models had been proposed to predict the particle filtration efficiency of electret media. However, direct measurement of the fiber charge density on electret filter remains a technical challenge.

Baumgartner et al.(1987) developed a technique to scan the charges on a single fiber, but it requires intensive experimental effort and the charges on the single fiber might be altered as it is withdrawn from the material. Brown (1988, 1993) proposed to use X-ray for fiber charge neutralization and consequently inferred the fiber charge density for the applied X-ray dose. Romay et al. (1998, 1999) reported an alpha-ray irradiation method and calculated the discharge dose of bipolar ions generated by alpha-ray. However, both proposed methods can not completely neutralize the electrical charges on electret media fibers possible due to the interaction between fibers and alpha particles/X-ray.

In this study we propose a new neutralization method to neutralize charges on electret media fibers. The proposed method use bipolar ions to directly neutralize the charge on electret filter media. In the testing, the bipolar ion cloud was generated using the Po210 radioactive material. Ions of alternative polarity were driven out from the bipolar ion cloud by an external AC electrical field and directed to the surface of test filter media, which was located outside the bipolar ion cloud. The concern of the interaction between filter fiber and alpha-particle is, thus, not an issue in this method. A sensitive electrometer was used to monitor the ion current downstream test filter to identify the ion breakthrough point. By choosing a proper voltage and frequency of AC power supply it increases the dose of bipolar ions and frequency. The fiber charge density was then derived from the applied dose of bipolar ions. In this study the comparison was also made between the measured charge density data and those inferred from the experimental penetration curve and theoretical models. Our study further indicates the proposed bipolar ion method can neutralize electret filter media to its completely neutral stage and evidences that the proposed method is more efficient than the alpha-ray irradiation for neutralizing electeret filter media.

3D5

PORTABLE ION GENERATORS AS PARTICLE REMOVAL DEVICES. XIAORUI YU, Nasim Mullen, Ping Zhao, Richard Corsi, Jeffrey Siegel, Department of Civil, Environmental, and Architectural Engineering, The University of Texas at Austin, Austin, TX

A conservative assessment suggests that over 1% of homes in the U.S. use ionizing air cleaners. They work by charging incoming particles with a corona and removing them to oppositely charged electrodes. In the present investigation, five ionizing air cleaners from different manufacturers were evaluated. Size resolved (0.1 - 10 μm) particle removal efficiency and clean air delivery rate (CADR) were measured in a well-mixed stainless steel test chamber for each cleaner. Two different test aerosols were used for the experiments: a combustion aerosol from incense and KCl particles from a large particle generator. The results suggest that the ionizing air cleaners are effective at removing supermicron particles with efficiencies that ranged from 20 – 100%, but that CADRs were relatively low (5 – 60 m3/hr), considerably lower than most HEPA air filters. Applying these CADRs to a model of a typical residence suggests that most portable ion generators will not cause a large decrease in indoor particle concentrations. Furthermore, most ionizers generate ozone as a byproduct of their operation. Ozone emission rates were comparable to those from photocopiers and laser printers (1 - 4 mg/hr). Although the ozone emission rates are not as high as a dedicated ozone generator, they can raise indoor ozone levels enough to cause concern about potential human exposure. These results allow for a more complete analysis of the positive and negative indoor air quality impacts of portable ion generators as air cleaners and suggest caution in using them in indoor environments.

3D6

MERCURY EMISSIONS CONTROL WITHIN ELECTROSTATIC PRECIPITATORS: MASS TRANSFER LIMITATIONS. HEREK CLACK, Illinois Institute of Technology, Chicago, IL

Electrostatic precipitators are installed on the majority of coal-fired boilers in the U.S. Anecdotal and some pilot- and full-scale results indicate varying degrees of mercury capture and/or oxidation occur within an ESP. This is true with and without upstream injection of a powdered sorbent like activated carbon. It has been hypothesized that the oxidation and/or adsorption of mercury within an ESP occurs at the surfaces of the particulate-laden plate electrodes. This analysis uses the Reynolds analogy between heat and mass transfer phenomena to assess the mass transfer limits of such a mechanism. Further, this analysis considers an alternate mechanism by which the particulate matter (fly ash and/or injected powdered sorbent) suspended in the flue gas captures (or oxidizes) gas-phase mercury collaterally within an ESP. Results, when compared against reported full- pilot-scale data, show good agreement, suggesting that the electrostatic drift of the charged aerosol within an ESP is responsible for observed reductions in mercury concentrations across an ESP.

3D7

THE CASE FOR CONTROLS ON AMMONIA AS A COST-EFFECTIVE STRATEGY FOR ACHIEVING PM2.5 COMPLIANCE.

ROBERT W. PINDER, Peter J. Adams, Carnegie Mellon University, Pittsburgh, PA

Ammonia is frequently the limiting reactant in the formation of ammonium nitrate aerosol, which is a significant fraction of PM2.5. However, most PM2.5 control strategies focus on reductions in SO2 and NOx. Large uncertainties in the sources of ammonia emissions and the sensitivity of PM2.5 to ammonia reductions have made regulation difficult. In this work we seek to resolve these uncertainties and estimate the potential of ammonia reductions as a cost-effective control for PM2.5.

A large fraction of ammonia emissions are from agricultural sources. This research has developed a process-based inventory of ammonia emissions from dairy farms consisting of a partially mechanistic model of ammonia volatilization and a statistical model of the distribution of farming practices. This approach is used to derive emissions from other livestock groups and is combined with non-agricultural emissions from the CMU Ammonia Inventory. This inventory is used as input to a PMCAMx, a chemical transport model, for representative time periods in spring, summer, winter, and fall. We find that the seasonally-varied ammonia inventory significantly improves the model prediction of total ammonia concentrations during the winter, when PM2.5 concentrations are especially sensitive to reductions in ammonia.

We calculate the cost-effectiveness of a control strategy by first calculating the effectiveness, the change in PM2.5 due to the change in precursor emissions, and then calculating the cost, the dollars per unit of reduction for each precursor. The effectiveness is estimated by PMCAMx simulations over a range of precursor emission changes (SO2, NOx, and NH3). This defines a three-dimensional space of control strategies, where the effectiveness of that strategy is the percent reduction in PM2.5. The cost of each strategy is calculated, and for each reduction in PM2.5, the strategy with the lowest cost is selected. These steps are repeated with and without controls of ammonia. The “ammonia savings” is difference between the most cost-effective strategies with and without ammonia controls.

We find in the winter in the Eastern United States, the ammonia savings is positive, and is especially large for large reductions in PM2.5, as the costs of deep reductions in NOx and SO2 become prohibitively expensive. Given uncertainty in the effectiveness of the control strategies, additional reductions in ammonia emissions cause an increase in the likelihood of achieving the attainment goals. Ammonia controls can reduce the cost and increase the robustness of PM2.5 control strategies and should be considered in addition to controls on NOx and SO2.

3E1

PARTICLE DEPOSITION IN TURBULENT DUCT FLOWS – COMPARISONS OF DIFFERENT MODEL PREDICTIONS.

LIN TIAN, Goodarz Ahmadi, Parsa Zamankhan, Department of Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY

Nano and micro-particle transport and depositions in various passages and different flow fields have been a research topic for past decades. Recently, there has been substantial renewed attention to the subject due to its numerous industry and biomedical applications. Many theoretical and experimental studies have been carried out, and numerical simulations been performed. Commercial software package are now commonly used to predicate particle transport and deposition processes in addition to flow field simulations. In this study, extensive computer simulations of transport and deposition of nano and micro-scale particles in turbulent duct flow are conducted. The simulation results are compared with the available experimental data and the predications provided by commercial codes. The influences of turbulence model used and turbulence near wall treatment are studied. It is shown that the Reynolds Stress Model (RSM) provides for a more accurate description on nano and micro-particle depositions in turbulent duct flow. Furthermore, accounting for the near wall quadratic variation of turbulence instantaneous fluctuation is crucial for accuracy of the numerical simulation.

3E2

ANALYTICAL MODELING OF PROTECTION SCHEMES FOR EUVL MASKS TO PREVENT NANOPARTICLE CONTAMINATION AT LOW PRESSURE.

CHRISTOF ASBACH, Jung Hyeun Kim, Se-Jin Yook, David Y.H. Pui, 1Particle Technology Laboratory, University of Minnesota, Minneapolis, USA Heinz Fissan, Institute for Energy and Environmental Technology (IUTA) e.V., Duisburg, Germany

Nanoparticle contamination is one of the major challenges for the semiconductor industry. Due to the continuously decreasing structure sizes, the diameters of the particles of interest are steadily decreasing. With the introduction of Extreme Ultraviolet Lithography (EUVL), even particles as small as 30 nm can act as killer particles, when they are deposited on the mask.

To avoid any gravity driven particle sedimentation onto the mask inside the low pressure (50 mtorr) EUVL scanner, the mask's critical surface is usually facing down. Additionally, thermal and/or electrical gradients can be established near the critical surface to enable thermophoresis and/or electrophoresis in order to counteract potential particle motion towards the critical surface. We developed an analytical model to quantify the different protection schemes for contamination control (Asbach et al., 2005). The model allows the calculation of the particle stopping distance as a function of the initial particle velocity, particle diameter, gas pressure and thermophoretic and/or electrophoretic variables. The model can also be used to determine the minimum velocity, a particle needs to reach the critical surface, as a function of the initial distance. These values can be used as standards to judge the risk of particle contamination inside EUVL scanners, depending on the scanner dimensions and the velocities, particles can reach inside the scanner, e.g. due to any moving actions, such as robotic handling. Due to the high Knudsen numbers Kn, i.e. low pressure and small particle sizes, forces that arise from gas particle interactions (Thermophoresis: Waldmann and Schmitt, 1966; Drag Force: Epstein, 1924) are assumed to be in the free molecular regime (Kn >> 1).

The modeling results show that making use only of gravity and drag force can already be very effective in stopping particles before they reach the critical surface. Generally, electrophoresis offers the highest protection potential. However, electrophoresis also introduces the highest uncertainty, because the particle charge distribution must be unipolar. Since particles do not get intentionally charged, the polarity of the particles is highly uncertain. Electrophoresis might therefore not be considered as protection scheme. Thermophoresis can effectively protect the critical surface of a mask from particles that travel at low, e.g. diffusion driven, initial velocities. If particles have a high initial velocities (in the range of several meters per second), thermophoresis cannot significantly shorten the stopping distance.

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3E3

DESIGN AND PRELIMINARY RESULTS OF AN ATMOSPHERIC CHAMBER TO EVALUATE NANOPARTICLE PROTECTION SCHEMES FOR EUVL CARRIER SYSTEMS.

SE-JIN YOOK, Christof Asbach, Jung Kim, David Pui, University of Minnesota, Minneapolis, MN; Heinz Fissan, University of Duisburg-Essen, Duisburg, Germany; Kevin Orvek, Intel Corporation, Hudson, MA; Arun Ramamoorthy, Pei-Yang Yan, Intel Corporation, Santa Clara, CA

An atmospheric chamber was constructed to evaluate thermophoretic and electrophoretic protection schemes for EUVL carrier systems. A wafer or a mask is mounted upside down above a cover plate and inside the chamber. Polystyrene Latex (PSL) test particles can be injected from the top, side or bottom injection ports into the chamber. For the thermophoresis studies, a heating plate is mounted on top of the mask or the wafer to give a temperature gradient relative to the cover plate. For the electrophoresis studies, a voltage is applied to the cover plate while the wafer or the mask is grounded. The wafer/mask and the cover plate are separated by insulating spacers. Preliminary particle deposition tests were performed using charged and uncharged PSL particles. The wafer was scanned using a PMS SAS 3600 XP Surface Analysis System before and after sampling. Particles added to the wafer or the mask will be evaluated for various cover plate distance, with and without the protection schemes. The chamber design and preliminary results of the thermophoretic and electrophoretic experiments will be presented.

3E4

3-DIMENIONAL FLOWFIELD SOLUTION IN AERODYNAMIC LENSES. Omid Abouali, Vahid Yavari, Shiraz University, Shiraz, Iran GOODARZ AHMADI, Clarkson University, NY, USA

In this study the performance of aerodynamic lenses under various operating conditions is analyzed using a computer simulation model. The study is focused on the effect of the nozzle upstream condition on the performance of aerodynamic lenses. In our earlier work [1], the computational domain starts from the exit of the nozzle with a sonic boundary condition. In the present study, the computational domain includes the upstream of the nozzle where the flow and particles enter with at low velocities. 3-Dimentional forms of the compressible Navier-Stokes and energy equations were solved and the gas flow and thermal condition in the impactor were for evaluated. A Lagrangian particle trajectory analysis procedure was used and the deposition rates of different size particles under various operating conditions were studied. For dilute particle concentrations, the assumption of one-way interaction was used and the effect of particles on gas flow field was ignored. The importance of drag and Brownian forces on particle motions in aerodynamic lenses was analyzed. Sensitivity of the simulation results to the use of different expressions for the drag force was also examined. It was shown that the Stokes-Cunningham drag with variable correction coefficient was most suitable for computer simulation studies of nano-particles in supersonic/ hypersonic impactors. The results were compared with the results of reference [1] and the effects of the nozzle upstream flow field on particle trajectory and collection efficiency of aerodynamic lenses were examined. The computer simulation results were shown to compare favorably with the experimental data.

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3E5

NUMERICAL SIMULATION OF PARTICLE MOTION IN A VIRTUAL IMPACTOR. SRIDHAR HARI, Yassin A. Hassan, John S. Haglund, Andrew R. McFarland, Texas A&M University, College Station, TX

Efficient concentration of ambient aerosol particles is critical for rapid detection of airborne pathogens. Virtual impaction is a technique widely employed for the concentration of aerosol particles; however, such virtual impactor/concentrators must be designed and operated to prevent losses of particles by collision with the walls of the device. Flow fields and particle trajectories in virtual impactors are strongly sensitive to the geometry of the impactor nozzles. Computational fluid dynamics was used to characterize the performance of a two-dimensional virtual impactor (2D-VI) where the geometry of the numerical model was based on measurements obtained from a previously studied experimental device. Impactor efficiency and wall loss curves generated from the simulations were compared against the experimental results.

Numerical investigations were also performed to determine the effects of geometrical modifications on wall losses. For example, use of an elliptical inlet section increased the range of particle sizes over which efficient concentration of particles could be achieved. However, use of the elliptical inlet section resulted in an increase in wall losses for particles near the cutpoint size because of a reduction in the aerodynamic focusing effect. A compromise between the two effects was achieved by increasing the radius of curvature in the receiver section. An optimum combination of radius of curvature values in the acceleration and receiver sections was determined for concentration of particles over a broad dynamic size range.

3E6

ESTIMATION OF POLYDISPERSED PARTICLE SCAVENGING COEFFICIENT AS A FUNCTION OF RAIN INTENSITY USING MOMENT METHOD.

SOOYA BAE, Yong Pyo Kim, Ewha Womans Univerisity, Seoul, South Korea, Chang Hoon Jung, Kyungin Women's College, Incheon, South Korea

Removal of particles by precipitation or wet scavenging is one of the most efficient particle sink. However, in most atmospheric chemical transport modes, wet scavenging process rate is assumed to be a simple form such as constant due mainly to computational burden.

In this work, an analytical form of the scavenging coefficient that is computationally efficient and includes important characteristics of wet scavenging process is developed and sensitivity analysis is carried out.

Important factors determining the scavenging coefficient are collision efficiency, terminal velocity of a raindrop, raindrop size distribution, and particle size distribution. The collision efficiency form by Slinn (1983) is used and Kessler's formula for terminal velocity is applied. Both Marshall-Palmer and lognormal raindrop distributions are considered and lognormal particle size distribution is assumed. To obtain an analytical expression for scavenging coefficient, two approaches were adopted; (1) the parameters on raindrop size distributions were expressed as a function of rain intensity, and (2) the moment method was applied to the expression. Sensitivity analysis shows that standard deviation of particle is the most important factor affecting scavenging coefficient.

3E7

MODELING NANOPARTICLE TRANSPORT IN LOW-PRESSURE PLASMAS.

LAVANYA RAVI, Steven L. Girshick, Mechanical Engineering, University of Minneapolis, MN

Nanoparticle transport and deposition on wafers is important in semiconductor processing, including both film deposition and etching processes. Nanoparticle transport depends on various effects, including diffusion, gas flow, thermophoresis, electrostatic forces and ion drag. The goal is to avoid or to control particle deposition on the substrate. A Monte Carlo model has been developed to simulate the transport of nanoparticles in a two-dimensional axisymmetric low-pressure plasma reactor. The particle concentration is assumed to be sufficiently low so that particle-particle interactions can be neglected. For the conditions studied particles lie well within the free molecule regime. Random collisions between nanoparticles and gas molecules are simulated. The time step between the collisions is based on the inverse of the collision frequency of the gas molecules with the nanoparticles. Molecules are assumed to come from a distance of one mean free path away from the nanoparticle, and the momentum transfer during these collisions is computed. The gas molecules are assumed to have a Maxwellian velocity distribution. Simulations have been conducted for neutral silicon nanoparticles in an argon plasma at a pressure of 8 Pa (60 mTorr), with particle diameters ranging from 1 to 50 nm. The effects of particle size, diffusion, gas flow and thermophoresis on the transport and deposition of nanoparticles are explored. Depending on flow rates and on temperature gradients, gas drag and thermophoresis can dominate the transport of larger nanoparticles, whereas the transport of smaller nanoparticles is dominated by diffusion. The simulation results can aid in the optimization of reactor conditions.

4A1

PROGRESS TOWARDS AEROSOL DATA ASSIMILATION FOR NAVY OPERATIONAL VISIBILITY FORECASTING. DOUGLAS L. WESTPHAL, Nancy L. Baker, Ming Liu, Jeffrey S. Reid, Annette L. Walker, Naval Research Laboratory; J. Zhang, UCAR; Piotr Flatau, Scripps Institute of Oceanography

The Navy and DoD are faced with aerosol analysis and forecasting issues unlike those of other U.S. agencies. The peculiarities of Navy needs include: 1) the need for visibility analyses and forecasts, as opposed to the health interests of the AQM community; 2) the need for the vertical distribution of aerosol for the calculation of slant-path visibility, as opposed to the conventional concern with only surface concentrations; 3) the need for accurate forecasts of onset, duration and cessation, as opposed to general forecasts of air quality for the next day; and 4) Navy interest in all parts of the globe, as opposed to only CONUS. Fortunately, all models and methodologies that are developed to satisfy these Navy and DoD needs are directly applicable to the fields of air quality and climate change, and vice versa.

This paper will discuss aerosol analysis and forecasting activities at the Naval Research Laboratory. Emphasis will be placed on the use of operational data for use in aerosol data assimilation and validation of aerosol forecast models. The variability in size, shape, and composition of aerosols must be considered and add degrees of complexity not present in the assimilation of conventional meteorological variables, such as winds and water vapor. This paper will discuss the use of practical data from the operational satellites and data streams. Other issues that arise are 1) daytime-only retrievals; 2) spatial averaging and cloud contamination; 3) size or composition retrieval; and 4) use of surface-based data.

4A2

AN AEROSOL ANALYSIS USING NASA AQUA AND TERRA SATELLITE OBSERVATIONS. WILLIAM COLLINS, National Center for Atmospheric Research, Boulder, CO; David Fillmore, Laboratoire des Sciences du Climat et l'Environnement (LSCE), Saclay, France

We present a global analysis of aerosol distributions and aerosol radiative forcing covering 2001 through 2005. The analysis includes sulfate, sea salt, dust, and black and organic carbonaceous aerosol species. It is based upon the Model for Atmospheric Chemistry and Transport (MATCH) constrained by satellite retrievals of aerosol optical depth. The retrievals are obtained from the NASA Moderate Resolution and Multi-angle Imaging Spectroradiometers (MODIS and MISR). These instruments are deployed on the NASA EOS Aqua and Terra satellites. The assimilation acts like a source or sink of aerosols and is comparable to 10 to 20% of the emissions for individual species. The analysis can be used to estimate the global direct shortwave radiative forcing by aerosols under present-day conditions relative to an aerosol-free atmosphere and to pre-industrial conditions. We compare our estimates of shortwave forcing to other estimates from the IPCC Third Assessment Report and from the Aerosol Model Intercomparison (AEROCOM) project.

4A3

TOWARDS AN A-TRAIN AEROSOL ASSIMILATION SYSTEM: ASSIMILATION OF MODIS AEROSOL OPTICAL THICKNESS RETRIEVALS INTO A GLOBAL AEROSOL TRANSPORT AND RADIATION MODEL.

PETER COLARCO, Arlindo da Silva, Mian Chin, NASA GSFC, Greenbelt, MD, Clark Weaver, GEST-UMBC/NASA GSFC, Greenbelt, MD

To understand the role of atmospheric aerosols in Earth's climate system we ideally require a global, three-dimensional, and temporally continuous system of measurements. The view of aerosols provided by a single polar-orbiting satellite instrument (e.g., MODIS), while providing the greatest spatial coverage of any measurement system available, can offer only a single relevant observation per day of a particular location. Furthermore, the quantitative interpretation of those observations is subject to considerable uncertainty because of we do not know the aerosol optical properties or vertical profiles well enough. Ground-based and in situ measurements can provide missing detail about aerosol vertical and optical properties, but lack the spatial (and sometimes temporal) coverage desired. Chemical transport models treating the aerosol lifecycle complement this picture by providing three-dimensional, global, and continuous aerosol fields, but suffer from poor constraints on their initial conditions (e.g., the aerosol source, sink, and transformation mechanisms). Here we present a global, three-dimensional aerosol transport model and assimilation system. The model assimilates the MODIS aerosol optical thickness product to constrain its aerosol distributions and burdens. We provide an analysis of the model aerosol distributions as constrained by ground-based sun photometer measurements and aerosol products from other satellite measurements.

4A4

SATELLITE-BASED ASSESSMENT OF MARINE LOW CLOUD VARIABILITY ASSOCIATED WITH AEROSOL, ATMOSPHERIC STABILITY, AND THE DIURNAL CYCLES.

TOSHI MATSUI, Hirohiko Masunaga, Roger A. Pielke Sr. and Sonia M. Kreidenweis, Department of Atmospheric Science, Colorado State University, Ft. Collins, CO Wei-Kuo Tao, Mian Chin, and Yoram J. Kaufman, Laboratory for Atmospheres, NASA Goddard Space Flight Center, Greenbelt, MD

This study examines variability in semi-global marine low clouds derived from the Tropical Rainfall Measuring Mission (TRMM) satellite, as linked to the aerosol index (AI) and lower-tropospheric stability (LTS) from the NCEP/NCAR reanalysis. AI is derived from the Moderate Resolution Spectra Radiometer (Terra MODIS) sensor and the Goddard Chemistry Aerosol Radiation and Transportation (GOCART) model, representing column-integrated aerosol concentrations. LTS is derived from the NCEP/NCAR reanalysis, and represents background thermodynamic environments. Global statistics reveal that cloud droplet size tend to be smallest in polluted and strong inversion environments. Statistical quantification shows that AI determines cloud droplet size more so than LTS. Simultaneously, high AI significantly reduces the cloud liquid water path (CLWP), and does not support the hypothesis or assumption of constant or increased CLWP associated with high aerosol concentrations. Global variability in corrected cloud albedo (CCA), or the product of cloud optical depth and cloud fraction, is very well explained by LTS, while both AI and LTS can explain local variability of CCA. Most of the local correlations between AI and cloud properties agree with the results from the global statistics, while weak local aerosol-cloud correlations appear in the regions where simultaneous high (low) AI and low (high) LTS offset affects? each other. The daytime diurnal cycles explain additional variability in cloud properties. CCA has the largest diurnal cycle in the high LTS regions. Cloud droplet size and CLWP show the weak different diurnal cycles between clean and polluted environments. All of the results suggest that marine cloud radiative forcing and the aerosol indirect effect must be investigated with aerosols, thermodynamics, and the diurnal cycle considered together.

4A5

A WEIGHTED, LEAST-SQUARES APPROACH TO DETERMINING THE BEST-ESTIMATE OF CLOUD DROP SIZE FROM A VARIETY OF REMOTE SENSING INSTRUMENTS. GRAHAM FEINGOLD, NOAA, Boulder, CO; Reinhard Furrer NCAR, Boulder, CO; Peter Pilewskie, CU Boulder; Lorraine. A. Remer, NASA/GSFC; Qilong Min, SUNY Albany, Haflidi Jonsson, CIRPAS/NPS, CA

We present a methodology for merging satellite and surface-based remote measurements of cloud drop size from a number of different passive and active sensors, each with their respective sample volumes, temporal resolutions, and sensitivities to various parts of the cloud. The approach is based on a generalized least squares approach, i.e., minimization of a cost function consisting of the weighted squared errors. The method incorporates information on the height dependence of drop size from a radar, and temporal/spatial averages for various spectrometers and radiometers, with their respective vertical weighting functions. Data for this exercise were acquired in May 2003 during an Intensive Operations Period conducted by the Department of Energy's Atmospheric Radiation Measurement Program. A suite of both in-situ and remote sensing instruments were available to measure aerosol and cloud parameters. On May 17 2003 there was a fortuitous, near-simultaneous sampling of a stratus cloud by five different methods. The retrievals of drop size agreed with one another to within ~ 20%, which is approximately the error estimate for most methods. The least squares methodology is applied to this event and a best-estimate drop-size profile is determined. Sensitivity of this retrieval to some of the applied weighting functions is explored. It is suggested that methodologies of this kind should be considered when attempting to reconcile geophysical measurements made by a variety of different instruments.

4A6

OUTSTANDING ISSUES REGARDING ROLE OF ATMOSPHERIC AEROSOLS ON TERRESTRIAL BIOSPHERE AND REGIONAL CLIMATE. DEV NIYOGI, Hsin-I Chang, Purdue University; Fitzgerald Booker, ARS-USDA Raleigh, NC; Roger A. Pielke Sr., Toshihisa Matsui, Colorado State Univerity; Lianhong Gu, Oak Ridge National Lab; Vinod K. Saxena, Randy Wells, N C State University; Yongkang Xue, UCLA.

Atmospheric aerosols have a complex feedback on the earth's climate. Past studies related to studying the impact of aerosols on the earth's climate had focused on cloud-aerosol- radiative interactions. Recent evidence from field studies and model studies indicates that aerosols could also have a significant feedback on the earth's climate by affecting the land surface processes. These changes in the land – atmosphere interactions can further impact the regional climate by redistributing radiative energy, and impacting the regional hydrological and biogeochemical response. Using a combination of satellite, surface data, field experimentation, and numerical model results, we will present a synthesis of the aerosol – land surface interactions in a scale down mode, i.e., impacts seen at continental to global scales, to regional scale, and at the plot scales. The focus is on carbon and water vapor fluxes, and the integrated feedback within the regional environment. We conclude that the aerosol effects and the effects due to "global dimming" are still uncertain, since the complexity caused by the various interactions determines which feedbacks are dominant when assessing the impacts. This complexity, with its nonlinear interactions appears to increase at smaller scales (i.e. the highest uncertainty is at individual field scales, with more certainty at regional to continental scales). Results indicate there is a potential for increased regional productivity when higher aerosol amounts are present through a more vigorous carbon / biogechemical cycle, but the water cycle feedback is more complicated with a reduction in total evaporation, but with increased transpiration. One possible mechanism causing the change in the surface hydrology is the effect aerosols have in increasing the surface albedo, which in turn can modulate the regional climate. The integrated effect of aerosols on the regional productivity and the water cycle depends on these complex land-atmospheric interactions.

4B1

DIRECT MEASUREMENTS OF THE MIXING STATE OF AMBIENT AEROSOLS USING SINGLE PARTICLE MASS SPECTROMETRY.

K. A. PRATHER, X. Qin, M. T. Spencer, J. C. Holecek, L. G. Shields, University of California, San Diego, La Jolla, CA

The combinations of chemical species within an aerosol population (i.e. mixing state) can provide insight into health effects related to air pollution, climate change, PM sources, and heterogeneous chemistry occurring in the atmosphere. In order to address how strongly particles are impacting climate, global models must begin to incorporate a more realistic picture of the mixing state of ambient particles. Single particle mass spectrometers directly measure the mixing state of all chemical species (i.e. organic carbon, elemental carbon, sulfate, nitrate, ammonium, sea salt, dust) within an ambient aerosol population. A summary of the size-resolved single particle mixing state measured using an aerosol time-of-flight mass spectrometer (ATOFMS) in multiple environments (i.e. marine, urban, rural) will be presented. A comparison will be made between the measured ambient mixing state and traditional assumptions regarding the mixing state of ambient particles based on bulk chemistry measurements. The implications of these findings will be discussed as well as how spatial and temporal changes in mixing state can be correlated with other co-located measurements of absorption and scattering. This presentation will conclude with a discussion of how on-line single particle measurements of mixing state are providing new insights into atmospheric aerosol processes such as cloud processing and heterogeneous chemistry.

4B2

SPECIATION OF IRON IN ATMOSPHERIC AEROSOLS AND PERSONAL EXPOSURE SAMPLES.

BRIAN J. MAJESTIC, Martin M. Shafer, and James J. Schauer, Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI

Toxicological studies have shown that inhalation of particles containing trace metals may have a deleterious effect on lung function in occupational settings. Biological effects and toxicity of trace elements are clearly related to the chemical species present, with oxidation state a primary variable and strong predictor of toxicity. We have chosen to study iron, where toxicity is a strong function of metal speciation, and are using a wet chemical method to quantify the amount of Fe(II) and Fe(III) in atmospheric aerosol samples. The method includes the collection of atmospheric aerosols on a Teflon filter, which are then leached in a well defined aqueous solution for subsequent chemical analysis. As we are looking to study the metals from a human health perspective, we are using a physiologically relevant pH and buffering system [pH = 7.4 NaHCO3], as well as a pH = 4.3 sodium acetate buffer; both of which target certain chemical forms of iron. For oxidation state specific chemical analysis of the leachates, we are adapting UV-VIS spectrophotometric methods previously employed in aquatic chemistry. However, in applying these methods to atmospheric samples, we need to improve detection limits while constraining extract volumes to less than 1 mL. For these reasons, we are using a 1 meter path length liquid waveguide spectrophotometric cell (World Precision Instruments), which allows us to quantify Fe(II) at levels below 100 ng / L using less than 1 mL of solution. In our current method, this corresponds to 0.08 ng of the target metal per m3 air. Analysis of the leachates by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) provides information on the oxidation state selectivity of the extraction (Fe (II) / Fe (III) ratios). Sample collection was performed at the inlet and outlet of the Caldecott motor vehicle Tunnel in San Francisco. Soluble Fe(II) and Fe(III) emissions data will be presented.

4B3

UNDERSTANDING SYSTEMATIC MEASUREMENT ERROR IN THERMAL-OPTICAL ANALYSIS FOR PM BLACK CARBON USING RESPONSE SURFACES AND SURFACE CONFIDENCE INTERVALS.

JOSEPH M. CONNY and George A. Klouda, Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD; Gary Norris and David Olson, National Exposure Research Laboratory, U.S. EPA, Research Triangle Park, NC

Thermal-optical analysis, a principal method for measuring elemental carbon (EC) associated with atmospheric soot, relies on changes in the optical behavior of aerosol carbon to indicate when EC “separates” from organic carbon (OC) and carbonate, if present. However, we cannot assume that pyrolyzed OC produced by the instrument (OC char) and EC that is native to the sample separate physically during analysis. More to the point, OC char and native EC do not necessarily oxidize before and after the thermogram split time, respectively. Nevertheless, if we specifically define EC as light-absorbing carbon (i.e., black carbon), it makes no difference where OC char and native EC appear in the thermal-optical transmission (TOT) thermogram if the optical absorptivities of OC char and native EC are equivalent.

Response surface models provide for unique insights into the behavior of thermal-optical instruments. For example, our lab has determined that the EC-to-total carbon ratio in two intensively studied samples decreased in first-order fashion at a rate of 7 % to 9 % per 100 deg. C increase in the highest step temperature in helium (from 500 deg. C to 900 deg. C). In addition, the response surface of the maximum laser attenuation in TOT has been used to avoid systematic measurement error from uncharred OC being detected as native EC (positive bias).

We have recently used response surface methods to study the absorptivities of OC char and native EC, calculated as the apparent specific absorption cross sections. Here, response surfaces are polynomial models of the cross sections based on an orthogonal rotatable central composite experimental design with factors for the temperature of the highest-temperature step in helium and in its duration. Accompanying the calculated response surfaces are surface confidence intervals, which are functions of the factor levels in the experimental design as well as the uncertainty in the measured signals.

The intersection of the response surfaces for the OC char cross section and native EC cross section reveal the thermal conditions (step temperature and duration in He) where the cross sections are equivalent. The intersection between the cross sections is then overlaid on the response surface for the maximum charring in the helium phase. In this way, TOT thermal conditions are selected where the cross sections of OC char and native EC are equivalent and the likelihood of the positive bias from uncharred OC being measured as native EC is minimized.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

4B4

INVESTIGATION OF THE LIGHT TRANSMISSION METHOD FOR MEASURING BLACK CARBON CONCENTRATION.

THOMAS W KIRCHSTETTER, T Novakov, Lawrence Berkeley National Laboratory, Berkeley, CA Jeffery Aguiar, University of the Pacific, Stockton, CA

Black carbon (BC) is a component of global warming, climate change and visibility reduction. Soot, the main component of which is BC, is a carcinogenic air pollutant. Given the numerous important roles of BC in the atmosphere, it is important that scientists and policymakers know well the amount of BC in the atmosphere and in the effluent of combustion systems. This requires an accurate method for measuring BC concentrations.

It is widely recognized, however, that measuring BC concentrations is difficult. Many studies indicate that the most widely used thermal-optical and light-transmission methods are subject to significant uncertainty. This presentation investigates the application of the light transmission method for measuring BC.

Laboratory experiments have been conducted using particles produced from an inverted, diffusion flame. These particles are composed almost entirely of light absorbing BC, which allows for precise quantification of BC mass concentration using the thermal-optical method, and artifact free light attenuation measurements because the particles do not appreciably scatter light. We collected these particles on quartz filters and applied the light transmission method (LTM). Our findings clearly demonstrate that the measured light attenuation (ATN) does not increase linearly with increased BC mass loading of the filter. As a result, the value of the attenuation cross-section (σ) decreases with increased BC loading of the filter. Therefore, the simple relationship $BC = ATN/\sigma$ does not accurately predict BC concentration based on measured ATN if σ is assumed to be constant in value.

Since the LTM method employed in our experiments is essentially the same as that employed in the widely used aethalometer, and σ is assumed to be constant in the aethalometer algorithm, we included the aethalometer in our experiments. Results show that the aethalometer inaccurately measures the BC concentration in the diluted flame effluent, in a manner expected based on our experimental observations. We find that σ is not constant, but varies as a linear function of light transmission. This finding is consistent with the calibration of the particle soot absorption photometer, which measures aerosol absorption coefficient.

In a manner similar to the above mentioned laboratory experiments, we are evaluating the LTM for measuring BC produced from other sources, beginning with diesel vehicles in a roadway tunnel. Results of these experiments will be compared to our laboratory experiments and presented at the conference.

4B5

VERTICAL PROFILES OF SINGLE PARTICLE COMPOSITION.

DANIEL MURPHY NOAA Aeronomy Laboratory

This presentation will review single particle data from the PALMS instrument on the composition of aerosol particles near the surface and in the rest of the troposphere. The vast majority of particles sampled in the free troposphere are internal mixtures of sulfates and organics. This observation may provide an important simplification for models of cloud formation. Biomass burning has a significant influence on the composition of particles even at continental distances from the fires. Single particle analysis also shows that dust particles efficiently take up nitrate and possibly chloride.

4B6

NIST REFERENCE MATERIALS FOR QUALITY ASSURANCE IN CONTEMPORARY AIR PARTICULATE MATTER RESEARCH.

ROLF ZEISLER, Barbara J. Porter, Rabia Oflaz Spatz, Michele M. Schantz, Analytical Chemistry Division, National Institute of Standards and Technology, Gaithersburg, MD; John Ondov, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

The National Institute of Standards and Technology (NIST) provides several certified reference materials, Standard Reference Materials (SRMs), for air particulate matter research: SRM 1648 Urban Particulate Matter and 1649a Urban Dust representing bulk samples of total suspended particulate matter (TSP) certified for inorganic and organic constituents respectively, and SRM 2783 PM Air Particulate on Filter Media certified for elemental content. Only the latter is serving some of today's interests in fine particulate matter, PM2.5; there are no bulk SRM materials currently available characterized for inorganic or organic constituents in this fine fraction.

NIST has explored the feasibility of preparing a reference material of PM2.5 with several collections of PM2.5 material from a site located in Baltimore, MD. The ultra-high volume collector (UHVC) used for this collection utilizes commercially available cyclone separators for particle-size selection and Teflon membrane filters for capturing the particulate matter. A 20 g Baltimore PM2.5 sample has been characterized for its inorganic and organic components and is available as an interim reference material (IRM) for laboratories involved in organic analysis in EPA's PM 2.5 research program. An additional smaller collection has been similarly characterized and made available for inter-laboratory comparison. The IRM has been also used in studies of biological activities, of available inorganic species, and in the validation of novel on-line measurement procedures for marker elements in PM2.5. Initial results from these studies point to the relevance of such reference materials.

Inefficiencies in the collection and preparation of a large sample of PM2.5 from ambient air have led to the exploitation of the Baltimore UVHC system to collect a PM2.5 fraction from re-suspended TSP; a 15 g sample has been produced from about 150 g SRM 1649a material. A future production of a large sample SRM is planned when several kilograms of contemporary TSP become available. The results for particle size distributions, homogeneity, and chemical composition of the various materials will be presented and advanced uses of this critical class of reference materials will be discussed.

4B7

DRIFTS STUDIES OF THE EFFECTS OF OH PROCESSING OF SEA SALT AEROSOLS ON SO2 UPTAKE AND OXIDATION.

William Robertson, HUDA SHAKA', Barbara Finlayson-Pitts, University of California, Irvine, CA

Sulfate particles are known to cause a variety of adverse health effects in addition to playing a major role in global climate change. Current atmospheric models describing gas-phase SO2 and sulfate aerosol concentrations tend to overpredict SO2 and to underpredict sulfate, particularly in marine regions. Recent laboratory studies on the chemical and physical changes in sodium chloride on reaction with gas phase hydroxyl radicals have shown that sodium hydroxide is generated. Experiments are underway to investigate the effect of this previously unaccounted for source of alkalinity in aerosols on the uptake and oxidation of SO2 to sulfate in NaCl/MgCl2 salt mixtures. Diffuse reflectance FTIR is used to monitor the uptake and oxidation of S(IV) species in the salt samples. Preliminary results indicate that, unlike fresh samples, OH processed salt samples rapidly take up and oxidize gas-phase SO2 to produce sulfate. Current results and potential atmospheric implications will be discussed.

4C1

A MINIATURE ELECTRICAL AEROSOL SPECTROMETER.

MANISH RANJAN and Suresh Dhaniyala, Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY

Accurate characterization of particles in micro-environments and large-scale deployment of instruments for ambient and indoor monitoring, require compact, inexpensive instruments that can provide in-situ, real-time measurements. In particular, temporal and spatial variations in ultrafine and nanoparticle populations complicate exposure analysis and assessment of their impact on human health based on time-average measurements at single locations. The popular technique for nanoparticle characterization involves electrical mobility measurements, typically made using a differential mobility analyzer (DMA) (Knutson and Whitby, 1972). While, the DMA provides high-resolution measurement, it is expensive, requires multiple flow measurements, and is large in size. We will present a design of a compact instrument [Miniature Electrical Aerosol Spectrometer (MEAS)] for particle sizing using the principle of electrical mobility. The EAS has rectangular flow geometry and is divided into two major components: an electrostatic precipitator (ESP) section and a classification section. The classification section has a parallel plate precipitator design with high voltage on one plate and grounded potential on the other. The grounded section is split into several thin strips of collection plates which are separated by small insulating sections, where collected charged particles are sized by detection using electrometer circuits. The introduction of charged particles into the classification section is through the ESP section, where several thin parallel plates are used to divide the height of the flow region into smaller channels (~ 2 mm in width). These plates are maintained at user-controlled potentials and are operated such that selected channels between the plates can either trap or pass all the charged particles. Thus, by trapping charged particles through all channels but one, charged particles can be injected into the classification section at a desired distance from the collection plates in the classification section. Thus, the particle injection location can be easily varied and permitting particle sizing over a wide-range in a relatively compact instrument. The use of the ESP section enables operation of the instrument with a single flow measurement. The current development efforts will be highlighted and preliminary comparisons with other particle sizing instruments will be presented.

References:

E. O. Knutson and K. T. Whitby. Aerosol classification by electric mobility: apparatus theory and applications. J. Aerosol Sci., 6:443–451, 1975.

4C2

A NEW AEROSOL MOBILITY SIZE SPECTROMETER: DESIGN, CALIBRATION, AND PERFORMANCE EVALUATION.

PRAMOD KULKARNI, Jian Wang, Brookhaven National Laboratory, Upton, NY

An Aerosol Mobility Size Spectrometer (AMSS) for the fast measurement of entire submicron aerosol size distributions (12nm -1000nm) has been developed. In AMSS, particles are first separated based on their electrical mobility in parallel plate geometry, and are subsequently grown into large droplets along their trajectories in a supersaturation environment. A high speed CCD camera is used to record mobility-dependent particle positions and counts, which are then used to derive particle electrical mobility, and concentration. This eliminates the need for voltage scanning required in traditional SMPS, and ensures significant increase in measurement speed and counting statistics. A theoretical framework has been developed to obtain the transfer function of the instrument that facilitates characterizing its ideal performance over a range of operating conditions. A prototype has been developed, and its performance, including sizing accuracy, measurement resolution, and counting efficiencies are characterized.

The sizing accuracy of AMSS was successfully characterized by measuring monodispersed aerosol classified with Differential Mobility Analyzer (DMA) and Polystyrene Latex standards over the size range of 12 to 170 nm. Experimental results show that AMSS has a 100% counting efficiency for particles as small as 12 nm. The resolution of the AMSS, defined as Zp,ch/(deltaZp), where Zp,ch is characteristic mobility and deltaZp is full width at half height of transfer function, ranged from 5 to 14 for particle diameters over the entire measurement range. Experimentally determined resolution agreed well with that predicted by theory, though there was some deviation observed at high mobilities. AMSS is capable of measuring an entire submicron size distribution spectrum in less than a second, thereby offering a great advantage over the traditional scanning mobility techniques in applications requiring high time resolution.

4C3

ISOLATION OF AMBIENT PARTICLES OF KNOWN CRITICAL SUPERSATURATION: THE DIFFERENTIAL CRITICAL SUPERSATURATION SEPARATOR (DSCS).

ROBERT OSBORN, Chance Spencer, Don Collins, Texas A&M University, College Station, TX

A field-deployable instrument has been developed that isolates from an ambient aerosol population only those particles that have critical supersaturations, Sc, within a narrow, user-specified, range. This Differential Critical Supersaturation Separator (DScS) is designed to supply one or more particle size and/or composition analyzers to permit direct examination of the factors that influence the activation properties of ambient aerosols. The DScS consists of two coupled parallel plate continuous flow diffusion chambers housed within a single enclosure. Particles are initially introduced near the centerline between a warm, water-soaked, plate and a cool, continuously circulated, water bath. Those particles that activate at the resulting supersaturation (S_low) in this chamber grow quickly and fall into the water bath due to gravitational settling. The remaining aerosol continues into the second chamber, which differs from the first only in the use of a salt solution in the lower bath. The imposed temperature differential establishes a peak supersaturation (S_high) slightly higher than that maintained in the upstream chamber, while the presence of a salt solution at the lower boundary results in a subsaturated region in roughly the lower half of the chamber. Those particles having critical supersaturations between S_low and S_high activate in this chamber and begin to fall due to gravitational settling. Prior to depositing in the lower bath, the droplets evaporate in the subsaturated environment and continue to travel towards the chamber exit. The activated particles in the lower half of the chamber and the unactivated particles in the upper half are extracted in separate flows that are subsequently dried. The chamber size was maximized to permit sample flow rates of about 1 L/min for measurement of particles having Sc between 0.3 and 0.35%. Furthermore, the Sc-resolved aerosol is diluted by only about a factor of 3. Calibration data collected when pure ammonium sulfate and sodium chloride aerosols were introduced into the DScS will be presented for operation at $0.15\% < Sc < 0.175\%$, $0.3\% < Sc < 0.35\%$, and $0.6\% < Sc < 0.7\%$.

4C4

CROSSFLOW MOBILITY CLASSIFIER. SURESH DHANIYALA, Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY

Particle size measurements are critical to accurate characterization of ambient aerosol. For laboratory measurements, monodisperse particles of desired sizes are often required for studies involving tandem differential mobility analysis, or for parametric studies of size-dependent phenomena. The current popular technique to generate monodisperse aerosol is the differential mobility analyzer (Knutson and Whitby, 1975). In the DMA, particles are size classified in an electric field with bulk flow through the instrument flowing axially (CDMA) or radially (RDMA) (Zhang et al., 1995). While the DMA is well characterized and can produce high-resolution particle sizing, the instrument is expensive and typically large in size. A new instrument design similar in concept to the DMA (four flows, electrical classification technique), but a different flow geometry will be present. This instrument, called the crossflow mobility classifier (CMC) is designed to be compact and relatively inexpensive, while enabling high-resolution particle size classification. The instrument design will be discussed and performance comparisons with commercial DMA columns will be presented for a range of particle sizes and operating conditions.

References:
E. O. Knutson and K. T. Whitby. Aerosol classification by electric mobility: apparatus theory and applications. J. Aerosol Sci., 6:443–451, 1975.
Zhang, S.H. Akutsu Y., Russell, L.M., Flagan, R. C., and Seinfeld, J.H. Radial Differential Mobility Analyzer, Aerosol Science and Technology, 23:357-372, 1995

4C5

EXPERIMENTAL AND NUMERICAL STUDY OF A MULTI-STAGE DMA. Weiling Li, Da-Ren Chen, Department of Mechanical and Aerospace Engineering, Joint Program in Environmental Engineering Science, Washington University in St. Louis, MO; and Meng-Dawn Cheng, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN.

A new DMA column with multiple extractions (multi-stage DMA: MDMA) has been developed and reported in last AAAR conference to perform fast particle size distribution measurements over a wide size range while remaining the function of monodisperse particle classification. The prototype MDMA has three sampling outlets, capable of classifying monodisperse particles of three different sizes simultaneously. The length of each stage is designed to cover a subsection of an entire particle size range to be covered. By scanning voltage in a small range (thus reducing the scanning time) the entire particle size range is covered. The modular stage design of MDMA allows users to construct their own stages of desired lengths (depending on the particle size range to be covered for each stage) and to vary the number of stages in MDMA. The design of MDMA head and base also allows the operation of high sheath flow for either a high sizing resolution or extending its lower sizing limit to 1 nm.

TDMA experimental setup has been performed to calibrate the performance of MDMA and to explore its limits. For the prototype MDMA the maximal sheath flowrates at the 1st stage (with shortest stage length), 2nd stage and 3rd stage are 75 lpm, 60 lpm, and 50 lpm, respectively, without losing high resolution and transmission efficiency of the instrument. Two different monodisperse aerosol flow extraction schemes have been experimentally investigated in this study. One scheme is to extract aerosol flow with the rate equal to evenly partition the polydisperse aerosol flowrate at each stage and the other is to extract aerosol flow with the rate the same as polydisperse aerosol flowrate. The experimental evaluation of the sizing resolution and transmission efficiency of MDMA has been performed under these two sampling flow operation schemes and at different flowrate ratio of polydisperse aerosol and sheath flows.

To interpret the experimental observation a numerical model based on the particle trajectory calculation has been developed to study the performance of MDMD. The model calculates the electrical and flow fields, as well as the aerosol trajectory including the diffusion effect. The model was validated by comparing with the experimental transfer function. Using the developed numerical model we have also investigated the effect of electrical field distortion in the region near the sampling outlets on MDMA transfer function, and the minimal distance between two adjacent aerosol sampling outlets. The distance is important to determine the maximal number of stages that could be stacked in MDMA when the total particle classification length is fixed.

In this talk we will present the experimental result from our MDMA calibration, and our effort in numerical modeling of MDMA performance.

4C6

OPERATING CHARACTERISTICS OF THE OPPOSED MIGRATION AEROSOL CLASSIFIER.

Harmony Gates and Richard Flagan, California Institute of Technology, Pasadena, CA

The opposed migration aerosol classifier (OMAC) is a new design of differential mobility classifier. Previous modeling studies suggested that the OMAC has the potential to reduce the operating voltage required to avoid diffusional broadening of the classification transfer function, thereby enabling the development of miniature, and inexpensive instruments for measurements of the size distribution of aerosol particles in the low nanometer size regime. A prototype OMAC has been constructed and calibrated. While the instrument does function as planned, difficulties with materials of construction limited the resolution of the first prototype instrument. We will report on the characteristics of the new instrument, as well as ongoing efforts to improve resolution and integrate particle detection into the classifier.

4C7

CREATING WIDE RANGE PARTICLE SIZE DISTRIBUTION DATA BY MERGING TSI SCANNING MOBILITY PARTICLE SIZER™ AND AERODYNAMIC PARTICLE SIZER DATA.

TIM JOHNSON, Hee-Siew Han, Doug Plate, TSI Incorporated, Shoreview, MN; Evan Whitby, Chimera Technologies, Inc., Forest Lake, MN

The particle size distributions of atmospheric aerosols are generally in three modes: nuclei, accumulation and coarse particle modes. The size range for these aerosols normally varies from a few nanometers to several micrometers. In order to measure particle size distributions over such a wide range, a combination of several instruments is normally used. One of most widely used combinations is the Scanning Mobility Particle Sizer™ (SMPS) spectrometer for submicrometer particles and the Aerodynamic Particle Sizer (APS) for particles up to 20 µm.

A data merging algorithm for combining SMPS and APS data was developed. The SMPS measures particle electrical mobility diameter and APS measures particle aerodynamic diameter. To merge these distributions, particle shape factors and density information is used to convert the aerodynamic diameter data to an effective mobility diameter. The data merge algorithm then can use this composite data and fit a curve to the data. The combined data set can then be displayed as either mobility diameter or it can all be converted to aerodynamic diameter.

Several ways of modifying the input data are available to improve the fit of the data sets. An efficiency files can be applied to the APS data and the end channels of either distribution can be excluded if desired to improve the fit between the data sets. Several curve fitting functions can be manually selected or can be automatically applied to get the most appropriate fit to the data. Averaging of data can be done within the samples of a data file and across multiple data files. Specific samples can be excluded from a data set when bad data is detected. A batch mode to group sets of data by time interval, or other sorting criteria, can be used to process large sets of previously collected data. Various ways of displaying, printing, saving, and exporting the data are available.

In order to verify the accuracy of the algorithm, aerosols with known densities and shape factors, such as Arizona Road Dust were used. Other generated aerosols and atmospheric aerosol distributions were also measured with the SMPS and the APS systems and used to evaluate the data merge algorithm.

4D1

ELECTROSTATIC-DIRECTED DEPOSITION OF NANOPARTICLES ON A FIELD GENERATING SUBSTRATE. D. Tsai, R. Phaneuf, S. H. Kim and M.R. ZACHARIAH

We demonstrate a new assembly method to position metal nanoparticles delivered from the gas phase onto surfaces using the electrostatic force generated by biased p-n junction patterned substrates. Aligned deposition patterns of metal nanoparticles were observed, and the patterning selectivity quantified. A simple model accounting for the generated electric field, and the electrostatic, van der Waals, and image forces was used to explain the observed results.

4D2

HYDROGEN PRODUCTION VIA NANOSTRUCTURED PHOTOCATALYTIC TITANIA THIN-FILMS. RAFAEL MCDONALD, Pratim Biswas; Environmental Engineering Science Program, Washington University in St. Louis, St. Louis, MO

The photosplitting of water using solar energy is a potentially clean and renewable source of hydrogen fuel that is environmentally benign and easily distributed. UV-light incident on titanium dioxide electrodes immersed in water have been shown to produce oxygen and hydrogen(1). It has been shown that titanium dioxide photocatalysts(2) have optimal conversion efficiencies in the nanoparticle sizes, as quantum effects become more important. The optimum particle size has been experimentally determined for the degradation of various organics(2, 3), but this optimal particle size has not been determined for the splitting of water. Additionally, there are no reports in the literature indicating how other aspects of the morphology (surface roughness, fractal dimensions, etc.) of the films may affect efficiency of water splitting. Models currently exist that predict the effect of gas-phase deposition conditions on thin film characteristics(4), but many of these conditions have yet to be experimentally verified.

In this work, we demonstrate the effect that different process conditions have on the physical (particle size, morphology, crystal structure) and mechanical (adhesion) characteristics of the thin film. Titania films were created in either a two- or three-port diffusion flame reactor. A stainless steel support was passed through the flame and the particles deposited onto it. Process conditions, including flow rates and collection methods, were varied, and the effect on the morphology of the film was explored by AFM, SEM and BET. An algorithm was used to determine the fractal dimensions of the films from the AFM images, and correlated to the film deposition conditions. Distinct variations were observed in the resultant fractal dimensions based on the process parameters. Photocurrents were then measured to ascertain the effect that these different physical properties have on the catalytic activity of the films.

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4D3

FLAME SYNTHESIS OF LANTHANIDE-DOPED FLUORESCENT SILICA GLASS NANOPARTICLES. BING GUO, Ian M. Kennedy, University of California, Davis, CA

A gas phase flame synthesis process was used to synthesize lanthanide-doped fluorescent silica glass nanoparticles. Vapors of hexadimethylsiloxane and beta-diketonate of the lanthanide were mixed with the H2 fuel gas to form nanoparticles in the flame. Four lanthanide metals, namely Eu, Tb, Dy and Tm were doped into silica nanoparticles. The silica glass particles showed photoluminescence at different visible wavelengths depending on the lanthanide dopant in them. All of the nanoparticles exhibited long fluorescence life time. Doping into silica drastically improved the fluorescence from Tb, Dy and Tm, comparing to the lanthanides in their oxide form. The silica/lanthanide particles are chemically stable in biologically relevant conditions, which allows them to be used as fluorescent markers in immunoassays or as tracers in studying cell uptake of nanoparticles.

4D4

SOLVENT EVAPORATION AND PHASE SEPARATION EFFECTS ON MESOPOROUS SILICA PARTICLES PRODUCED BY EVAPORATION-INDUCED SELF ASSEMBLY IN DROPLETS. Shailendra Rathod, Brett Andrzejewski, TIMOTHY WARD, Gabriel Lopez, University of New Mexico, Albuquerque, NM

Evaporation-induced self assembly (EISA) of amphiphilic molecules (surfactants) in droplets is a versatile approach for the synthesis of spherical mesoporous particles with monodisperse well-ordered pores. Such particles are of interest as catalyst supports for metallic nanoparticles, and as controlled release or delivery vehicles. Self-assembly and liquid crystalline phase transformations of the amphiphile is driven by the concentration that occurs with solvent evaporation. Organic or polymeric additives may influence the phase behavior of the amphiphile, or may undergo their own phase transformations providing new particle architectures. Using the surfactant cetyltrimethylammonium bromide (CTAB) in an acidic ethanol/ water solution of tetraethylorthosilicate (TEOS), we have found that the organic additive trimethylbenzene (TMB) may act as a simple swelling agent in the hydrophobic domains of the amphiphile mesostructure, or may induce new mesophases. The nature of these influences is strongly related to the competitive dynamics of solvent/organic evaporation, structural organization, and silica condensation. Some hydrophilic polymers, such as polyacrylic acid, can be concentrated in the center of droplets during evaporation, leading to a polymeric core that, after calcination, provides thick-walled hollow particles of ordered mesoporous silica. Measurement of dye uptake and release by mesoporous particles is being done to evaluate the diffusion characteristics of the mesoporous silica. In addition multicomponent evaporation modeling is providing some insight into the internal gradients that influence radially-graded particle architectures.

4D5

ANALYSIS OF FE/NB NANOCOMPOSITES PRODUCED BY THE SODIUM FLAME AND ENCAPSULATION PROCESS.

Jacob A. Nuetzel, Richard L. Axelbaum, Ron S. Indeck

The Sodium Flame and Encapsulation (SFE) process was employed to produce an iron-niobium composite nanopowder. Computational fluid dynamics software was used to model the reactor and optimize run conditions. Ferrocene was chosen as the iron precursor because of its stability, and because it could be added to the SFE process without major modification to the SFE reactor or run conditions. Heated ferrocene vapor was delivered in a carrier of argon gas along with niobium chloride vapor. The mixture was injected into the reactor as a turbulent jet where it reacted with sodium vapor supplied from an outer coflow. In the vicinity of the high temperature sodium/halide reaction zone, the ferrocene vapor decomposes into iron particles, which combine with niobium particles to form composite nanoparticles. The resulting particles are then, by virtue of the SFE process, encapsulated in situ with the sodium chloride byproduct before exiting the reactor for collection. Powder morphology and composition were analyzed using X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersive spectroscopy. The magnetic properties of the composite powder were obtained via vibrating sample magnetometer and magnetic force microscopy. The magnetic properties were consistent with single domain iron, namely high saturation magnetization and low coercivity.

4D6

NANOSIZED YTTRIUM IRON GARNET BY FLAME SYNTHESIS.

Ranjan K. Pati, Osifo Akhuemonkhan, Sicong Hou, and SHERYL H. EHRMAN, Department of Chemical Engineering, University of Maryland, College Park, MD; Ichiro Takeuchi, Departments of Physics and Materials Science and Engineering, University of Maryland, College Park, MD

Yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) and doped YIG compounds are of interest for telecommunications and data storage applications because of their magnetic and magneto-optic properties. A variety of preparation techniques such as sol–gel, co-precipitation, combustion and glycothermal synthesis have been reported to prepare nanocrystalline powders of YIG. It is well known that deviations from stoichiometry have a strong influence on the magnetic properties of the ferrite materials. Additionally, the magnetic properties of a given particle also depend in a sensitive manner on size and shape. Here we report synthesis of nanosized YIG by flame spray pyrolysis of aqueous solutions of yttrium nitrate and iron nitrate. The material is characterized by thermogravimetric analysis (TGA), x-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer, Emmett and Teller (BET) surface area measurement and Fourier transform infrared (FTIR) spectroscopy. X-ray diffraction study of the material shows the formation of mainly the garnet phase with the presence of orthoferrite and iron (III) oxide. The particle size of as prepared powder ranges from 10 to 15 nm and the surface area is 48 m^2/g, obtained from TEM and BET respectively. Preliminary magnetic characterization indicates the material is ferromagnetic.

4D7

MOBILITY CHARACTERIZATION AND THE KINETICS OF CARBON NANOTUBE GROWTH. S.H. Kim and M.R. ZACHARIAH

We demonstrate the use of mobility classification tof CNT's grown in a continuous aerosol process. The separation process occurs at atmospheric pressure and involves electrostatic mobility separation which classifies fibers on the basis of equivalent projected surface area. This implies that one can for diameter controlled CNT's, obtain an on-the-fly determination of the CNT length distribution during CNT synthesis, or alternative y have a method to produce size separated CNT's. The method should be generic to any fiber based material.

We use the method to study with TDMA method the growth kinetics of CNT's. By varying the temperature of the growth we were able to extract Arrhenius growth parameters. We found an activation energy for growth ~ 80 kJ mol-1 from both acetylene or ethylene, which is considerably lower than previous works for substrate grown CNT's (Ea=110~150 kJ mol-1). Furthermore we observed that our aerosol CNT growth rates about two orders of magnitude higher than substrate grown CNT's.

4E1

EXPOSURE OF VOLUNTEERS TO CONCENTRATED ULTRAFINE PARTICLES IN LOS ANGELES. Henry Gong Jr., William S. Linn, Kenneth W. Clark; Los Amigos Research/ USC Keck School of Medicine, Los Angeles, CA Bhabesh Chakrabarti, Philip M. Fine and CONSTANTINOS SIOUTAS, USC Viterbi School of Engineering, Los Angeles, CA

Seven healthy and 12 asthmatic adults were exposed to filtered air (FA) and to concentrated ultrafine particles (CUFP) of <0.2 um aerodynamic diameter) using a large scale ultrafine particle concentrator, in a region of Los Angeles heavily impacted by automobile and diesel truck emissions. Exposures lasted 2 hours with intermittent exercise. Concentration range was 71 -277 ug/m3 by mass and 59,000 to 279,000 particles/cm3 by number. Statistically significant ($p<0.05$) or suggestive ($p<0.1$) changes indicating unfavorable effects of CUFP were found, including decrease in forced vital capacity (largest mean change of - 3% vs FA), in arterial O2 saturation by pulse oximetry (-1%), increase in diastolic blood pressure and decrease in heart rate variability at rest (-21% for SDDN). Healthy subjects appeared equally or more responsive than asthmatics. These results suggest that ambient ultrafine particles are acutely toxic to the cardiorespiratory system, to an equal to greater extent than larger ambient particles.

4E2

AEROSOL CHEMICAL CHARACTERISTICS IN FERTILIZER MANUFACTURING FACILITIES. YU-MEI HSU, Chang-Yu Wu, Dale A. Lundgren, University of Florida, Gainesville, FL; Wesley J. Nall, Polk County Health Department, Winter Haven, FL; Brian K. Birky, Florida Institute of Phosphate Research, Bartow, FL

Of the carcinogens listed by the National Toxicology Program (NTP), strong inorganic mists containing sulfuric acid were identified as a “known human carcinogen”. The current OSHA 8-hour Time Weighted Average (TWA) of Permissible Exposure Level (PEL) of sulfuric acid mist is set at 1 milligram per cubic meter. The new ACGIH (American Conference of Governmental Industrial Hygienists) Threshold Limit Value (TLV)-TWA of the thoracic particulate fraction is 0.2 milligram per cubic meter. Phosphate fertilizer manufacture was listed in the report as one of many occupational exposures to strong inorganic acids. The current data were collected in 1951-1976 with many samples obtained from outside the USA. Reduced pH environments are known to enhance the depurination rate of DNA and the deamination rate of cytidine. Sulfuric acid also irritates the human airway, and possibly this irritation may damage the epithelium, causing subsequent carcinogenic effects of other substances. In the respiratory system, the deposition fraction depends on particle size. Characterization of the aerosol composition and size distribution at modern facilities is a necessary step to the establishment of the best policy for worker protection. Such information is critical for health risk assessment and is useful in identifying the key sources.

In this study, sampling was conducted at eight plants in Florida. Depending on the design of the manufacturing process, sampling locations were selected for those with potentially high sulfuric acid mist concentration, including: sulfuric acid pump tank, belt or Byrd filter floor, sulfuric acid truck loading/unloading station, attack tank, and granulation plant on a scrub day. Pre-sampling was conducted on the designated facilities using Dichotomous samplers for 12 hours to determine aerosol mass loading levels that were needed to design the sampling time for the cascade impactor sampling, which will provide detailed information of size resolved aerosol composition. NIOSH method 7903 was also used to determine total acid mist concentration. Ion chromatography (Dionex 1500) was used to analyze water-soluble ion species.

For the Byrd/Belt filter floor, fluoride was the dominant species for the fine mode (max: 35.7 micrograms per cubic meter) while phosphate was the major one for the coarse mode (max: 85.8 micrograms per cubic meter). For the attack tank, fluoride and ammonium were the dominant species for the fine mode (max: 455.2, and 65.4 micrograms per cubic meter, respectively), while fluoride and phosphate were the dominant species for the coarse mode (max: 85.9, and 47.9 micrograms per cubic meter). At the sulfuric acid pump tank, sulfate was the dominant species, and the maximum concentration of sulfate was 58.1 and 61.1 micrograms per cubic meter for the fine mode and the coarse mode, respectively. In general, sulfate, fluoride, ammonium, and phosphate were the major species in fertilizer facilities. The concentration of total sulfate, including ammonium sulfate, calcium sulfate, and sulfuric acid, were lower than 0.2 milligram per cubic meter at all locations.

4E3

THE DETERMINATION OF AMMONIA IN MAINSTREAM TOBACCO SMOKE. CAI CHEN, James F. Pankow, OGI School of Science & Engineering, Oregon Health & Science University, Beaverton, OR

Internal tobacco industry documents released during litigation in the 1990s indicate that a variety of ammonia-related compounds have been widely used in cigarette products. This is of interest because increased ammonia levels in tobacco smoke will lead to increased proportions of the smoke nicotine being in the free-base form. (Free-base nicotine can evaporate from tobacco smoke particulate matter (PM) and deposit quickly in the respiratory tract.) A method was developed to determine ammonia in mainstream tobacco smoke (MTS) samples, both in the gas phase and in the PMMTS phase. For each cigarette smoked, the method employs the separate collection (in Teflon bags) of the 1st three MTS puffs and the remaining puffs. Gas phase ammonia was then trapped in H_2SO_4 in an impinger; PMMTS was dissolved in 2-propanol. Samples were analyzed for ammonia by ion chromatography (IC). Concentrations of ammonia in the gas phase and in PMMTS were measured for 10 brands of cigarettes and two brands of cigars. The method detection limit (MDL) for gas phase ammonia was approximately estimated as 1.43E+5 ng/m3; the MDL for PMMTS phase nicotine was approximately estimated as 5.74E-3 ng/ug.

4E4

EVALUATION OF PRE-TODDLER EXPOSURE TO INDOOR PM USING PRE-TODDLER INDOOR PARTICULATE ENVIRONMENTAL ROBOT (PIPER), OR LEGOS ARE NOT JUST FOR KIDS.

GEDIMINAS MAINELIS, Kathleen Schmeelck, Rutgers University, Dept. of Environmental Sciences, New Brunswick, NJ; Paul J. Lioy, Stuart L. Shalat, Environmental and Occupational Health Sciences Institute, Piscataway, NJ.

Numerous studies have shown strong correlations between elevated outdoor particulate matter (PM) levels and a variety of health effects. In addition, studies show that people spend about 80-90% of their time indoors and are exposed to both ambient and indoor particles. Compared to adult population, children express even greater vulnerability to many health effects caused by air pollution. Currently, PM levels indoors are measured by stationary samplers at a height of approximately 1m. However, children under one year of age (pre-toddlers) spend significant amounts of time very close to the floor, and they can stir-up significant quantities of particle sediment while crawling and playing. Thus, we hypothesized that the existing PM measurement methods underestimate pre-toddler exposure to airborne particles.

Since pre-toddlers spend a great deal of time on the floor crawling or rolling, which precludes the use of bulky sampling equipment, their personal exposure to PM is difficult to assess. As a solution to this issue, we used LEGO kits and designed a mobile and autonomous robotic measurement platform which mimics the physical dimensions and mobile activity patterns of pre-toddlers. The platform was equipped with IOM personal inhalable sampler which collected particles onto Teflon (PTFE) filter at a flow rate of 2 L/min for gravimetric mass measurement. In a separate set of experiments, the robotic platform was equipped with a real-time particle mass concentration monitor (model pDR-1000, Thermo Electron Corp., Franklin, MA, USA). Inlets of both samplers were positioned approximately 20 cm from the floor to mimic a child's breathing zone.

Using video data from previous children exposure studies, we determined typical pre-toddler movement patterns and programmed the robotic measurement platform to adequately mimic pre-toddlers' movement. During the measurements in a number of households, the robotic platform and its instrumentation were continuously operated for 4 hours and the measured particle concentrations were compared to those obtained by identical stationary monitors measuring particles at 1.1 m height (according to the US EPA specifications). Observed airborne inhalable particle concentrations measured by the robotic measurement platform ranged from 50 to 165 µm/m^3 and were consistently 2-3 times (100-200%) higher than those simultaneously measured by standard height stationary samplers. Similar results were obtained when using real-time particle monitors.

Thus, the preliminary data indicate that current indoor PM measurement procedures inadequately represent pre-toddler exposure to airborne particles which is enhanced by children's specific activities and time spent close to the floor.

4E5

DEPOSITION MEASUREMENTS FROM A TURBULENT IMPINGING JET LADEN WITH FLUORESCENT PARTICLES.

WES BURWASH, Edgar Matida, Carleton University, Ottawa, Ontario, Canada; Warren Finlay, University of Alberta, Edmonton, Alberta, Canada;

Impinging jets have numerous industrial and research applications. To date, single phase impinging jets have been more thoroughly investigated [1][2] when compared to their particle laden counterparts [3][4]. In order to improve numerical models of deposition, a better understanding of particle deposition in canonical geometries is necessary. In the current work, a particle laden air jet is formed with a round nozzle and impinged normally onto a flat surface (vertical and downward orientation). An aerosol of solid fluorescent particles (5 micron diameter) is created using a nebulizer [5] and injected into a flow of dry air, resulting in a steady nozzle flow of 111L/min and a Reynolds number based on the nozzle diameter (D=15mm) of Re = 10,000. The particle deposition efficiency and distribution on the flat surface are measured experimentally using fluorometry and imaging techniques. Three test cases are investigated, during each of which the nozzle is positioned at a different non-dimensional distance (L/D = 2, 4 and 6) from the impaction surface. The total deposition efficiencies are similar (16.5%-17.8%) and there is a distinguishable ring-like deposition form in all test cases, with lower deposition levels at the stagnation point. The maximum density peaks of the rings are 254, 347 and 685 particles/(mm squared), occurring at different distances from the stagnation point, 2.1D, 0.8D and 0.1D, for each test case L/D = 2, 4 & 6, respectively. This low deposition in the stagnation region may be attributed to particle bounce and re-entrainment into the flow [3]. The novel approach developed in this report can be applied in future numerical and experimental work aimed at better understanding of particle deposition involving turbulent complex flows.

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4E6

EVALUATION OF AN AEROSOL TIME-OF-FLIGHT MASS SPECTROMETER FOR INDUSTRIAL MONITORING, PART II. STEPHEN CRISTY, BWXT Y-12, Oak Ridge, TN

An aerosol time-of-flight mass spectrometer (ATOFMS) is being evaluated to determine its usefulness to detect, size, identify, and quantify respirable airborne particles in real time in laboratory and manufacturing facility environments.

The ATOFMS was purchased with a “standard” non-aerodynamic focusing inlet. Using this inlet, particles containing beryllium (Be) were detected in concentrations down to 0.05 µg Be/m3 air. Although this detection is below our action limit, the ATOFMS in the standard configuration detects few particles below 200 nm in size. Although Be particles found in our Be laboratory have been larger than one micrometer in size, an aerodynamic focusing lens with a range of 30 to 300 nm was purchased to investigate the existence of smaller particles.

Our initial experience with the focusing lens showed a large increase in particles detected over the overlapping ranges of 200 to 600 nm. Testing with 300 nm polystyrene spheres (PSL’s) showed that 168 times as many particles were detected using the focusing lens compared to the standard lens. However the ability to size particles was lost. In testing the performance of the focusing lens, it was raised in 1.1 mm steps to 10 mm above the factory set position while monitoring 300 nm spheres. At each step the velocity of particles increased and the spread of velocities decreased. Up to the seventh step the number of particles detected increased. The lens was set at 8 mm above the factory position and a size calibration was successfully made using six sets of PSL spheres ranging in size from 100 nm to 600 nm.

Although sizing was restored, 30 and 50 nm PSL’s were not detected due to insufficient scattering of the sizing laser light to produce detectable pulses from the photomultiplier (PMT) detectors. An amplifier [1] was added to the PMT output resulting in increased detection of smaller sized particles, but 50 nm PSL’s were not detected.

The results from use of single element solutions and an electrostatic classifier will be discussed with the implications for sizing and quantification. Comparisons of field data using the standard lens vs. aerodynamic focusing lens will also be made. Some data from a 100 to 3000 nm focusing lens is hoped for.

1. Design from Kimberly Prather and group, UC San Diego. Drawings from Tom Baraniak, Carleton College.

4E7

NANOPARTICLE OCCUPATIONAL HEALTH, SAFETY, AND ENVIRONMENT CONSORTIUM. MICHELE L OSTRAAT, DuPont, Particle Science Research and Technology, Wilmington, DE

A consortium of international industrial, academic, government and non-governmental organizations has recently formed to obtain information on occupational health, safety, and environmental issues associated with aerosol nanoparticles and workplace exposure monitoring and safety. Three main technical goals of the consortium are 1) the development of a method to generate a well-characterized aerosol of solid nanoparticles in air and to evaluate instrumentation to measure solid nanoparticles in air; 2) the development of an air sampling method that can be used on a day-to-day basis in research and development laboratories or in manufacturing settings; and 3) the ability to measure filtration or penetration/permeation and protection of personal protective equipment and clothing materials with respect to specific engineered nanoparticles or nanomaterials.

This consortium will work towards developing knowledge of workplace exposure monitoring capabilities and strategies through the design and development of portable aerosol monitoring instrumentation for conducting assessments of worker exposure to airborne engineered nanoparticles and nanomaterials. Additionally the consortium will conduct studies to obtain knowledge of the barrier performance characteristics of various protective equipment and clothing fabrics to aerosols of nanoparticles or nanomaterials. To accomplish these objectives, aerosol synthesis and characterization systems will be built to evaluate aerosol instrumentation for measuring solid aerosol particles > 3 nm with particular focus in the 3 – 100 nm size range.

Although engineering controls, respiratory protective devices and protective clothing fabrics are generally considered to provide adequate protection for exposures to fine-sized particulates, it is unclear whether respiratory protective devices and protective clothing fabrics are effective barriers for nanoparticulates < 100 nm. Unfortunately, the currently available methodologies utilized in industrial hygiene practices to measure particle exposures may not be sufficiently sensitive to measure occupational or ambient aerosol concentrations, whether in terms of particle mass, particle numbers or surface area. Therefore, the consortium has identified the ability to develop a sensitive system to assess barrier effectiveness or permeation of personal protective equipment including clothing fabrics, filters and respirators as an important objective.

Of additional significant interest to this consortium is the development of a personal air sampling monitor. In order to be useful, this personal air sampling device must be portable, require little or no power, and be operable under a wide range of particle handling conditions and chemistries. With the interdisciplinary nature of aerosol sciences and the numerous issues that need to be resolved, this arena is ideal for collaborative interactions between industry and academia.

5A1

PRODUCTION AND DISTRIBUTION OF PM2.5 AT A RURAL NEW YORK SITE DURING ICARTT 2004. JAMES SCHWAB, Min-Suk Bae, John Spicer, Olga Hogrefe, Yongquan Li, Kenneth Demerjian, Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, NY

There is a powerful synergy that emerges from the combination of a long-term database of continuous and integrated measurements and an intensive period of much more detailed measurements at the same site. This presentation will explore this synergy in the context of long-term and intensive data from our research site in Addison, in New York's Southern Tier region. The ASRC field station at Pinnacle State Park in Addison was established in 1995 and has been measuring ozone and ozone precursor gases for the past ten years. In 1999 we added a second focus on the measurement of PM2.5 mass and chemical composition. More than 20 gaseous, aerosol, and meteorological parameters, and a suite of up to 56 non-polar hydrocarbon species are measured continuously during routine operation. During the ICARTT 2004 summer intensive we augmented this measurement capability with the addition of a set of research instrumentation for a period of four weeks (or longer for some of the instruments). The research instrumentation included an Aerodyne AMS, a Particle-Into-Liquid-Sampler (PILS), an Aerodyne TDLAS, a full array of instruments to measure particle number and size, a continuous sulfate particulate analyzer, and a seven wavelength channel ultraviolet rotating shadow band radiometer. The Addison site is the western-most fully instrumented site in the ICARTT network of surface stations, and provides a comprehensive characterization of the aerosol composition and distribution as it travels east toward the rest of the ICARTT measurement locations. Detailed chemical measurements of aerosol composition, and continuous measurements of aerosol scattering and optical depth also allow the determination of aerosol optical properties and radiative effects. This presentation will discuss the production and distribution of aerosols at this rural transport site, and the implications of these measurements for atmospheric chemistry and air quality in the northeastern United States.

5A2

OVERVIEW OF AEROSOL MASS SPECTROMETRY AT CHEBOGUE POINT DURING ICARTT 2004. DOUGLAS WORSNOP, Megan Northway, John Jayne, Manjula Canagaratna, Tim Onasch, Aerodyne Research, Billerica, MA; James Allan, Mike Cubison, Hugh Coe, University of Manchester, UK; Jose Jimenez, Peter DeCarlo, Alex Huffman, Qi Zhang, University of Colorado, Boulder, CO; Eben Cross, Paul Davidovits, Boston College, Chestnut Hill, MA

A large set of aerosol and gas instrumentation was deployed at the Chebogue Point (Nova Scotia) site during July/August of 2004 as part of the ICARTT mission designed to measure properties of the outflow of the Northeastern United States. We report here an overview of aerosol measurements deployed by Aerodyne Research (AMS; MAAP), University of Manchester (HTDMA, VTDMA SMPS) and the University of Colorado (Thermal Denuder). This combination of instrumentation, together with that of other groups, provides a comprehensive picture of the physical and chemical properties of sub-micron diameter ambient aerosol.

Overall two distinct types of aerosol were observed: a mixture of sulfate and organic in air coming from the southwest (i.e. from the northeastern U.S.) and an organic dominated aerosol from the northwest (Canada). Both aerosol types appear to be processed, accumulation mode (200-400nm diameter). The organic aerosol appears to be highly oxidized, as measured by the $CO2+$ (m/z 44) marker measured with the AMS. For example, there is a clear correlation of $CO2+$/organic fraction with ozone level, indicative of a photochemical source – with the level of oxidation lower for the northwesterly Canadian flow. Aerosol hygroscopic growth factors and volatility measurements also vary with chemical composition. Beam width and light scattering probes within the AMS provide further aerosol characterization. Correlations of these and other aerosol measurements with meteorology and gas phase chemistry will be discussed.

5A3

FINE PARTICLE COMPOSITION MEASURED DURING ICARTT – AN OVERVIEW OF INORGANIC IONS AND WATER SOLUBLE ORGANIC CARBON.

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The Particle-Into-Liquid Sampler (PILS) was deployed on NOAA's WP-3D aircraft during the summer of 2004 in support of the Intercontinental Transport and Chemical Transformation – New England Air Quality Study. Throughout the duration of the study, semi-continuous measurements of fine (PM1.0) inorganic ion components (sodium, ammonium, potassium, calcium, magnesium, chloride, nitrate, and sulfate) and water-soluble organic carbon (WSOC) were made on the NOAA WP-3D aircraft. Intensive sampling of the urbanized metropolitan areas of the Northeast (e.g. Boston-New York-Washington corridor), as well as biomass plume studies, were also conducted. Within this measurement domain, a range of aerosol sources were sampled, including fresh power plant plumes, relatively fresh and aged urban plumes, and aged biomass plumes. On average, sulfate was found to be a significant fraction of observed PM, comprising approximately 41% of volume, and highest concentrations tended to be at lowest altitudes. Net charge of observed ions was generally near-neutral, although a number of observations describe conditions where the aerosol was apparently highly acidic – generally found to be at lower altitudes and in spatial regions known for power generation. WSOC was found to be well correlated with CO, especially during instances of plumes that were dominated by biosmoke. In contrast to the typical background and power plant plumes, during biomass events (high [WSOC]), analysis of charge balances on the inorganic aerosol show that an unmeasured anion is present, possibly an organic acid associated with NH4+. In this paper, we will present an overview of the measurements, compare the bulk chemical data to fine particle volumes, further investigate spatial distributions, and identify unique plumes encountered during the mission.

5A4

MAJOR SOURCES OF SUBMICRON AEROSOL MASS ABOVE THE NORTHEASTERN UNITED STATES INFERRED FROM AIRBORNE AEROSOL MASS SPECTROMETER MEASUREMENTS DURING ICARTT.

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The Aerodyne Aerosol Mass Spectrometer (AMS), which measures non-refractory components of aerosol particles with aerodynamic diameters between roughly 40 nm and 1.5 microns, provides mass spectra as well as organic, sulfate, ammonium, and nitrate mass distributions. Results will be shown from the Intercontinental Transport and Chemical Transformation - New England Air Quality Study (ITCT-NEAQS 2004) portion of the ICARTT study during July-August 2004, where an AMS was deployed aboard the NOAA WP-3D aircraft above the Northeastern United States and 30-second averaged samples were collected. For the first time, a pressure controlled inlet was used to maintain a constant mass flow rate into the AMS for airborne sampling. Unfortunately, the particle transmission efficiency for this inlet system was size dependent and the field data had to be significantly adjusted for quantitative analysis.

A wide variety of air masses were sampled during the intensive period, including clean continental, fresh and aged urban, biomass burning, and power plant plumes. Despite the issue with particle transmission, several conclusions could be drawn from the dataset. In general, the non-refractory submicron aerosol mass was composed of predominantly sulfate and organic material with a lower mass fraction of ammonium and minor amounts of nitrate. However, there was a wide variety of aerosol compositions at low altitudes and a trend of increasing organic mass fraction as a function of altitude. The dominant source at altitudes above 3 km was biomass burning from the Alaskan forest fires. The next most common contributor to submicron aerosol mass was sulfate from power plant sources. In power plant plumes that were transected during the day, fresh particle formation was observed in both the sulfate mass and particle volume distributions. Urban sources tended to play a less important role in submicron aerosol mass during this field study compared to biomass burning and power plant plumes. Most of the organic material was oxidized, even fairly close to urban sources, which is consistent with the organic material being aged and secondary in nature.

5A5

CHARACTERISTICS OF AN URBAN/INDUSTRIAL AEROSOL PLUME FROM THE EAST COAST OF THE UNITED STATES DURING ICARTT.

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In situ measurements of particle size distributions, bulk and single particle composition, and reactive and trace gas species were made aboard the NOAA P-3 aircraft as part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) field program in summer 2004. A plume of pollution originating from industrial and urban sources along the heavily populated Atlantic coastline of the northeastern United States was studied as it propagated over Atlantic coastal waters toward the northeast over a three-day period. Ratios of gas-phase precursors to particle mass decreased over the period, consistent with to gas-to-particle conversion. For this mix of urban and industrial sources, increases in particle mass with increasing plume age were dominated by particulate sulfate formation. A significant contribution to particle mass from forest fire sources was also observed. Particle size distributions evolved with time from complex, multimodal distributions having significant numbers of particles with diameters < 0.1 µm, to a unimodal distribution with a mass mean diameter near 0.5 µm.

5A6

SUBMICRON AEROSOL COMPOSITION AND CHARACTERIZATION OVER THE MID ATLANTIC USING AN AMS ON THE UK FACILITY FOR AIRBORNE ATMOSPHERIC MEASUREMENTS (FAAM) DURING ITOP (INTERCONTINENTAL TRANSPORT OF OZONE AND PRECURSORS), A PART OF THE ICARTT CAMPAIGN..

JONATHAN CROSIER, Paul Williams, Keith Bower, James Allan, Hugh Coe, SEAES, University of Manchester, UK; John Methven, Department of Meteorolgy, University of Reading, UK; Andreas Stohl, Norsk institutt for luftforskning (NILU), Kjeller, Norway; Douglas Worsnop, John Jayne, Aerodyne Research Inc, Billerica, MA; Jose-Luis Jimenez, University of Colorado, Boulder, CO

An Aerodyne Aerosol Mass Spectrometer (AMS) was deployed on the UK Facility for Airborne Atmospheric Measurements (FAAM, a BAe Systems model 146-301) during the Intercontinental Transport of Ozone and Precursors (ITOP) experiment, a European component of ICARTT. The AMS measures the mass concentrations of speciated, non-refractory chemical components in submicron aerosol online with a high time resolution. Size resolved information is also available where concentrations are significant. ITOP focussed on the long-range transport of pollutants from the North American continent over the Atlantic Ocean. The UK aircraft was based in the Azores and sampled mid Atlantic free tropospheric air. This was the first deployment of the FAAM aircraft in which inter-comparisons with other aircraft (NASA DC8, DLR Falcon) were available to validate data. The 'jump mass spectrum' mode of operation for the AMS was used to allow increased signal to noise at higher time resolution and new tools to process and validate these data were developed. Pseudo-Lagrangian sampling was also attempted in collaboration with the NASA DC8, NOAA P3 and DLR Falcon platforms. Several Lagrangians were achieved with air masses sampled by multiple platforms.

The FAAM aircraft sampled a variety of different airmasses during ITOP, including what appears to be anthropogenic pollution from the Ohio Valley, a known major source of sulphur dioxide, as well as biomass burning aerosol resulting from an Alaskan fire Plume and an African outflow. Distinct differences were found in the aerosol composition of the different air masses. The Ohio valley outflow (determined using back trajectory analyses) had highly elevated levels of sulphate that were above typical ambient UK mass concentrations, with small amounts of associated ammonium, although not enough to neutralise the particles. Large amounts of highly oxidised organics were also measured in what appears to be an internal mixture. The non-refractory component of the Alaskan fire plume particles was dominated by the organic fraction, which was composed of more hydrocarbon-like species. The presence of small amounts of nitrate in the fire plume was also correlated with high levels of NOx. A characterisation of the clean free-tropospheric North Atlantic air as a function of altitude was also

5B1

CLOUD DROPLET ACTIVATION: SOLUBILITY REDEFINED.

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It is well known that partially soluble compounds can affect the activation of aerosol into cloud droplets by contributing solute. In theoretical studies of cloud droplet activation, such compounds are assumed to provide as much solute as allowed by their solubility in pure water. Yet, experiments (for example, Raymond and Pandis, JGR, 2001) that study the cloud activation of single-component organic aerosol indicate that even slightly soluble compounds behave as if they were completely dissolved in water. Although a variety of mechanisms could be used to explain this phenomenon, we explore the possibility that the curvature of the solute "core" introduces a thermodynamic instability that eventually leads to the complete dissolution of the solute, within the typical timescale of activation experiments. To explore this possibility, we study the activation kinetics of low solubility organics, such as glutaric acid, glutamic acid, norpinic acid, pinic acid and pinonic acid. A dissolution kinetics and cloud droplet activation model was developed to study the droplet growth kinetics with and without the dissolution instability in order to verify if these compounds indeed can become activated, as indicated by available experimental data. If indeed such effects are important, then organics can contribute much more solute than previously thought, and the concept of solubility of organic species within activating cloud droplets needs to be redefined as well. We will provide an appropriate definition of what would then constitute as an "insoluble" and "soluble" aerosol species.

5B2

DIRECT MEASUREMENT OF THE RELATIONSHIP BETWEEN HYGROSCOPICITY AND ACTIVATION EFFICIENCY.

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Among the factors contributing to the overall uncertainty in the indirect effect of aerosols on climate is the still inadequately understood relationship between particle size, composition, and critical supersaturation. Applying the results of laboratory studies of the activation efficiency of relatively simplistic aerosols to predict CCN concentration for an ambient aerosol for which only an incomplete description of its size distribution and composition is available is undoubtedly challenging, as is reflected in the varied success of several recent CCN closure efforts. Whereas an understanding of the link between composition and critical supersaturation is ultimately needed, insight into the factors controlling activation can be gained through an improved understanding of the relationship between hygroscopic growth under subsaturated conditions and cloud droplet formation under supersaturated conditions.

In many respects, aerosol hygroscopicity represents a bridge between composition and critical supersaturation. Whereas critical supersaturation may be strongly dependent upon the presence of trace amounts of certain classes of compounds such as surfactants, the hygroscopicity of a particle population can be approximated from the volume fraction weighted average of the hygroscopic behavior of its constituents. This link between composition and hygroscopicity has been the focus of a number of laboratory and field investigations. In contrast, there has been little effort to quantify the relationship between hygroscopicity and critical supersaturation, which was the motivation for this study.

A humidified tandem differential mobility analyzer (TDMA) was coupled with a Droplet Measurement Technologies CCN counter to directly characterize the relationship between hygroscopicity and activation efficiency for both urban and rural continental aerosols. The size- and hygroscopicity-resolved aerosol separated by the TDMA was detected by both a CPC and a CCN counter. The activation efficiency of the aerosol is simply defined as the ratio of the particle concentration measured by the CCN counter to that measured by the CPC. The parameters describing the curve relating activation efficiency to hygroscopicity for an array of particle sizes and CCN counter supersaturations are contrasted with those expected for an aerosol composed of mixture of an inorganic salt and an insoluble core. Limitations in the experimental approach employed and implications for the treatment of aerosol-cloud interactions in models will be discussed.

5B3

NANOSIZE EFFECT ON THE DELIQUESCENCE AND EFFLORESCENCE OF SODIUM CHLORIDE PARTICLES.

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The deliquescence and efflorescence relative humidity values of 6- to 60-nm NaCl particles were measured using a Tandem nano-Differential Mobility Analyzer. The deliquescence relative humidity (DRH) increases when the dry particle mobility diameter decreases below 40 nm. The efflorescence relative humidity (ERH) similarly increases. For example, the DRH and ERH of 6-nm particles are 87% and 53%, respectively, compared to 75% and 45% for bulk NaCl. Power law fits describing the nanosize effect are: DRH(dp) = 94.513 dp^(-0.0581) and ERH (dp) = 58.895 dp^(-0.0703), which are calibrated for 6 < dp < 60 nm with under 1% RH uncertainty. To investigate any possible effects of impurities on the results, two different and independent methods are used to generate the aerosol particles, namely by vaporizing and condensing granular sodium chloride and by electrospraying a high purity sodium chloride aqueous solution. The DRH and ERH values are the same within experimental uncertainty for the particles generated by the two methods. A qualitative model suggests that the physical explanation for the nanosize effect is that the free energy balance increasingly favors smaller particles without water (crystalline particles) because the surface area and hence surface free energy per particle is less for small, anhydrous than for larger, aqueous particles.

5B4

MICRO-PHYSICAL CONSISTENT MODELING OF THE DELIQUESCENCE AND EFFLORESCENCE HYSTERESIS.

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A difference between deliquescence and efflorescence RH values (i.e., the hysteresis effect) is commonly observed for aqueous salt particles. As the direct aerosol effect is very sensitive to the water uptake properties of the particles, the study of the hysteresis effect is of high importance. Current aerosol dynamic models take account of the deliquescence and efflorescence hysteresis based a priori knowledge of the presence of solid phases at a certain relative humidity and overall composition. They either assume crystallization of a solid in a multicomponent solution once the RH drops below the DRH of the solid salt, or do not assume solidification at all and consider all aerosol particles to be liquid droplets.

In this talk, we present a modeling framework based on classical theory of nucleation kinetics to simulate the transformation from a metastable phase into a thermodynamically more favorable phase. We apply classical nucleation theory in the active set algorithm in order to predict explicitly the physical state of the aerosol particles and the deliquescence and efflorescence hysteresis. Our micro-physical consistent model is capable of modeling the phase transition and multistage growth of atmospheric aerosols in various relative humidity regimes. We present computational results to illustrate the model performance to simulate aerosol deliquescence, crystallization, solid to solid phase transitions, and acidity transitions.

5B5

HYGROSCOPICITY OF SECONDARY ORGANIC AEROSOL FORMED BY OZONOLYSIS OF CYCLOALKENES AND PHOTOOXIDATION OF BIOGENIC HYDROCARBONS.

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Water uptake by atmospheric aerosols affects the particle size and phase and therefore influences many physicochemical characteristics of the aerosol. These include particles respiratory tract deposition, optical properties, lifetime, reactivity, especially with respect to heterogeneous chemistry, as well as their ability to act as cloud condensation nuclei. At present, limited data exist on the hygroscopic properties of ambient and laboratory-generated secondary organic aerosol (SOA).

A series of experiments was performed at the Caltech Indoor Smog Chamber Facility to investigate the water uptake properties of aerosol formed by oxidation of several families of organic precursors, including simple cycloalkenes and atmospherically relevant biogenic compounds. For the cycloalkene family (C5-C8), SOA was nucleated in dark ozonolysis experiments in a dry chamber (RH ~5%). The water uptake of the nucleated aerosol was measured using a hygroscopicity tandem differential mobility analyzer (H-TDMA) set at a constant high RH (85-90%) during the aerosol growth. For the biogenic parent compounds, which included monoterpenes, sesquiterpenes, and oxygenated terpenes, SOA was formed by photooxidation, using HONO as the hydroxyl radical source, with the chamber at approximately 50% RH. Oxidation products of sesquiterpenes were allowed to nucleate, but all other biogenic systems were photooxidized in the presence of aqueous ammonium sulfate seed aerosol. In these experiments with biogenic parent hydrocarbons, the water content of the aerosol formed was measured by drying the particles in the H-TDMA during aerosol growth.

For both the cycloalkene dark ozonolysis experiments and biogenic photooxidation experiments, the particle water uptake was also measured at several relative humidities ranging from 5 -92% after the aerosol volume, as measured by the DMA, had reached its maximum. Hygroscopic growth factors for the pure organic portion in the seeded experiments were determined using size-resolved organic mass fraction derived from the Aerodyne Aerosol Mass Spectrometer and assuming volume-weighted water uptake. The biogenic oxidation products, especially of the sesquiterpene parents, were found to be very slightly hygroscopic. The water content of the aqueous biogenic SOA at a given particle size was also found to decrease as the aerosol growth proceeded, even for nucleated particles, which may be an indication of formation of larger, more hydrophobic species such as oligomers.

5B6

HYGROSCOPICITY OF MULTI-COMPONENT ORGANIC AERSOLS USING AN ENVIRONMENTAL SCANNING ELECTRON MICROSCOPE.

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Atmospheric aerosols are ubiquitous throughout the atmosphere and have far-reaching influences on the global radiation budget, visibility degradation, and human health. Because of these effects, significant research in the past two decades has focused on individual particulate constituents and their interactions with water. Previously, the interaction between water and the inorganic fraction of atmospheric aerosols has been well characterized, and the role of single-component and two-component organics in aerosols is becoming more fully understood. What remains is to investigate the water interactions of particles containing several inorganic and organic constituents to develop a more realistic simulation of the complex nature of ambient particulates.

To accomplish this goal, aerosols were collected by electrostatic plate collection at a rural site in central Pennsylvania and in a controlled laboratory setting. The aerosols were imaged using an Environmental Scanning Electron Microscope, or ESEM (FEI model Quanta 400). The ESEM allows us to work in a controlled relative humidity atmosphere which can be brought to supersaturation by cooling the sample support. In this manner, we were able to absorb, condense, and evaporate water directly onto and off of the aerosol surface and image the interactions. We were then able to analyze the deliquescence and efflorescence behavior of aerosols, while observing particle morphology and growth rate.

Previous researchers have characterized the properties of aerosols utilizing various techniques including TDMA, FTIR, and EDB. These techniques, however, are limited by their inability to account for morphological changes or the effects of repetitive deliquescence/ efflorescence. Recent work with ESEM has provided results consistent with those of the other methods, while allowing the sample to be imaged in-situ. In these earlier studies, samples were ground to submicron sizes using a mortar and pestle or between two glass slides before being impacted on carbon substrates or liquid droplets of aqueous sodium chloride were permitted to dry on the substrate. Arguably, these sample preparation techniques may provide unrealistic particle morphologies or increased interactions with the substrate. By employing an electrostatic impactor to collect dry particulates from an air stream, these problems may be avoided and a more realistic interaction is observed.

Aerosols from 100 nanometers to 100 microns were used to investigate aerosol-water interactions on a range of scales. Results of the aerosol hygroscopicity and morphology imaging will be presented along with some discussion of the advantages and disadvantages of using the ESEM technique to study aerosol water uptake.

5C1

COMPACT MULTIPLEXING OF MONODISPERSE ELECTROSPRAYS USING MICROFABRICATION.

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The development and testing of a compact multiplexed system of quasi-monodisperse electrosprays is presented. The system was microfabricated by deep reactive ion etching of silicon wafers, yielding arrays with a density of 250 sources per square centimeter. An optimal electrode configuration for the system reliable performance was identified based on an extractor electrode mounted at a distance from the spray sources that is comparable to the distance between sources. The electrode has the dual function of limiting cross-talk between neighboring sources and minimizing space charge feedback from the spray cloud. Testing with ethanol demonstrated that the system can be optimized to produce uniform droplets from all parallelized electrosprays, each one operating as an isolated spray in the quasi-monodisperse cone-jet mode, as demonstrated by the dependence of current and droplet size on flow rate and by size distribution measurements. Ease of operation and uniformity in size from spray to spray requires strategies either to increase the pressure drop in the flow path and/or to uniformize the electric field at the spray sources, by minimizing edge effects.

5C2

EFFECT OF SOLUTES/NANOPARTICLES ON CHARGE LIMITS OF DROPLETS.

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We have critically examined charge instability induced breakups of droplets containing solutes and suspended nanoparticles. Droplets were suspended in an electrodynamic balance, and a high precision light scattering technique based on optical resonances was used to determine the size and the size change of a droplet at a charge instability induced breakup. The charge level and the charge loss at a breakup were obtained from the dc voltages required to gravitationally balance the droplet prior to and following the breakup. We have examined pure diethyl phthalate (DEP), diethylene glycol (DEG), and triethylene glycol (TEG) droplets, and to examine the effect of solutes and nanoparticles we have conducted experiments on droplets containing lithium chloride (LiCl) salt and polystyrene nanoparticles at varying concentrations.

The results from pure droplets of DEP, DEG, and TEG show that breakups due to the charge instability occur at the Rayleigh charge limit. The observed charge losses during breakups range from about 21% for DEP droplets to about 41% for TEG droplets. While a DEP droplet loses about 2.3% of its mass, no mass losses, within the detectable limit of 0.03%, are observed during breakups of DEG and TEG droplets. The results from TEG and DEG droplets containing LiCl solute show that droplets explode at significantly higher charge levels than the Rayleigh limit, and droplets can remain stable at charge density levels greater than twice the Rayleigh limit. The results from droplets containing polystyrene nanoparticles show that the presence of suspended particles in DEP droplets has no effect on the charge instability induced breakups. On the other hand, TEG and DEG droplets containing polystyrene nanoparticles explode at significantly higher charge levels than the Rayleigh limit. As the volume fraction of nanoparticles in a TEG or a DEG droplet increases, the droplet charge density level at which a breakup occurs increases, and at higher concentrations of nanoparticles, a droplet can remain stable at charge density levels greater than three times the Rayleigh limit. The experimental results suggest that electrical properties of the host droplet dictate the effects of solutes and suspended nanoparticles on the charge stability.

5C3

HIGHLY CHARGING OF NANOPARTICLES THROUGH ELECTROSPRAY OF NANOPARTICLE SUSPENSION.

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Recent development of nanoxerography requires highly charged aerosol nanoparticles to avoid noise deposition occurred due to random Brownian motion. However, it has been known that it is difficult to charge aerosol nanoparticles with more than two elementary charges. The goal of this work is to develop a simple technique for obtaining highly charged monodisperse aerosol nanoparticles by means of electospray of colloidal suspension. Highly charged aerosol nanoparticles were produced by electrospraying (ES) and drying of colloidal suspension of monodisperse gold nanoparticles. Size and charge distributions of the resultant particles were measured by scanning mobility particle sizer (SMPS) and tandem differential mobility analyzer (TDMA). We demonstrated that electrospraying of nanoparticle suspensions and subsequent drying produced highly charged aerosol nanoparticles having the same sizes as the original nanoparticles. Measurements of size and charge distributions by using a tandem DMA system and transmission electron microscope (TEM) analysis were done and confirmed the validity of the method. The geometric mean number of elementary charges is 4.6 for 4.2 nm, 23.5 for 10.5 nm, and 122 for 25.0 nm, respectively. The number of elementary charges is proportional to Dp1.95. The method described here constitutes a convenient, reliable, and continuous tool for preparing highly charged aerosol nanoparticles from nanoparticles produced by either wet chemistry or gas-phase methods.

This work was funded by the Creative Research Initiatives Program supported by the Ministry of Science and Technology, Korea.

Suh, J., Han, B., Okuyama, K. and Choi, M. (2005). Highly Charging of Nanoparticles through Electrospray of Nanoparticle Suspension, J. Colloid Interface Sci. 287: 135-140.

5C4

MOLECULAR DYNAMICS SIMULATION OF ION EMISSION FROM NANODROPLETS OF IONIC LIQUIDS.

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The work reported here is motivated by a desire to fully understand the physics of colloid thruster propulsion technology. Colloidal thruster technology is based on the electrostatic acceleration of small droplets that are generated by feeding a conducting fluid through a small capillary and applying a large acceleration potential. Experiments have shown that best results are achieved when the system is operated in the “cone” mode, which is achieved when the volumetric flow rate lies between certain limits. In this limit of very low flow rate, the electrostatic field causes a very narrow jet of charged liquid to form at the tip of the cone. The jet then breaks down into fairly monodisperse and small droplets (order of 20 nm) via the classical Rayleigh mechanism. The droplets are subsequently accelerated to high velocities after leaving the nozzle; specific impulses of a few thousand seconds have been demonstrated. In addition to the droplet mode of operation, it has been demonstrated that with suitable propellant and operating conditions, that the direct emission of ions from the cone tip and from drops can contribute substantially to the specific impulse and thrust. It is an understanding of this direct emission mode that we seek. Because high electrical conductivity coupled with low volatility is a desirable combination, in recent years ionic liquids have been explored for use in colloid thruster applications. Ionic liquids are salts that are liquid at room temperature. By varying the molecular structure of the base ions and using additive of various kinds, the properties can be adjusted over a wide range of values. Here we use molecular modeling to study the dynamics of small droplets of ionic liquids. Clusters of the base ions are simulated using several force field models. Before an electric field is applied minimization methods are used to determine the equilibrium structure of the droplet. An electric field is then applied and resulting motion of droplet and individual ions observed. The results are compared with Iribarne-Thomson theory.

5C5

MODIFIED KELVIN-THOMSON EQUATION CONSIDERING ION-DIPOLE INTERACTION: COMPARISON WITH EXPERIMENTAL ION-CLUSTERING THERMODYNAMIC DATA.

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The classical Kelvin-Thomson (CKT) equation, which was derived by Thomson about a century ago, has been the fundamental of classical ion-induced nucleation theory. In the CKT equation, the effect of charge on Gibbs free energy change for the formation of the cluster (or equilibrium vapor pressure over an ion cluster) is taken into account by considering the electrostatic potential energy of the cluster. However, CKT theory doesn't consider the interaction of condensing ligands with the ions. The ion clustering enthalpy and entropy changes predicted by CKT equation for small ions are known to be significantly less negative than those observed. Here we present a modified Kelvin-Thomson (MKT) equation, which considers the effect of dipole-ion interaction by taking into account the extra energy needed for dipole molecules to escape from the ion cluster.

We show that the clustering enthalpies and entropies for protonated clusters (with ligands = H_2O, NH_3, CH_3OH, and C_5H_5N) calculated based on the MKT equation are in much better agreement with experimental data than those predicted based on the CKT equation. The Gibbs free energy changes for the evaporation of common precursor gas molecules (H_2O, NH_3, H_2SO_4, HNO_3) from corresponding charged clusters/droplets are also calculated and compared with available measurements. The predicted Gibbs free energy changes are in excellent agreement with observed values for small ion clusters (containing less than ~ 5 ligands) for all four precursor gases but are generally higher (within a few kcal/mol) than observed values for relatively large clusters. Since the measurements of Gibbs free energy changes for containing > 5 ligands are very limited and the uncertainty in the measured values for large clusters is not known, we can't decide at this point if MKT equation systematically overpredicts the values of Gibbs free energy changes for larger clusters. Both Thomson effect and dipole-charge interaction effect significantly reduce the evaporation of polar molecules from charged clusters/droplets. The relative importance of dipole-charge interaction effect increases as temperature decreases. The dipole-charge interaction reduces the supersaturation required for ion-induced nucleation, and the contribution of ion nucleation to atmospheric particle formation should be reassessed since the dipole-charge interaction effect is not considered in earlier studies.

5C6

STUDY OF ELECTRO-BROWNIAN COAGULATION OF AEROSOL NANO-PARTICLES.

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Though a role of electricity in aerosol dynamics is not completely understood, there is great interest in this particular phenomenon for such diverse reasons as environmental technology, atmospheric physics, electrostatic propulsion for space vehicles, electrostatic atomization, environmental aerosol medicine, etc. Additional electrical charging during particle formation can drastically enhance or diminish the coagulation rate and determine aerosol dynamics.

We would like to present some new results in theory of electro-Brownian coagulation describing dynamics of charged aerosol particles at simultaneous Knudsen numbers, up to nanoscale size, including a range: $0.1 < Kn < 10$.

New data concerns:

(1) deriving a new equilibrium charge-size distribution function in a bipolar charged aerosol ensemble,
(2) critical revising the Fuchs "boundary sphere" method and developing an alternative paradigm based on ideas of the neutron scattering theory,
(3) deriving general formulas for the electro-Brownian coagulation of charged aerosol (nano-) particles, including the electro-Brownian coagulation kernels and the "enhancement" factor in both laminar and turbulent regimes;
(4) deriving analytical formulas for an asymptotic presentation of the coagulation kernels;
(5) a criterion of preventing (reducing) the coagulation of charged particles.

A comparison of theoretical and experimental results showed their relatively good agreement, thereby confirming an adequacy of our approach and models. New data can be used for technological managing with aerosol coagulation, mean particle size, and size distribution, as well as for refining our undertsanding electro-dynamic aerosol phenomena in nature.

5D1

CHARACTERIZATION OF FINE PARTICLE EMISSION IN SMALL SCALE WOOD COMBUSTION..

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Small scale residential wood-fired heaters have been thought to be a significant source of pollutants especially of fine particles. It is proposed that domestic wood combustion accounted for more than half of the stationary combustion based primary PM2.5 emissions in Finland.

A three year research program was initiated in 2002 to study the fine particle emissions from a large variety of small scale wood combustor units. In the study a sampling standard development, flow reactor tests and theoretical particle formation model development were other tasks. Finnish fireplaces, baking oven, stoves, small boilers and burners, regional thermal power plants, pellet heaters and domestic oil burners were on the test list. With fireplaces mainly dry birch wood is used and in the stoker-burners wood chips and pellets have been used.

The exhaust gas is detected continuously with analyzing rack for hydrocarbons, NO, NO2, CO, CO2 and O2 for gas, by ELPI and SMPS aerosol analyzer for fine particles as well as fuel mass flow and the draught and temperatures of the exhaust. Particle mass is detected periodically by standard method (SFS 3866). The exhaust gas dilution were made by ejector diluters (Dekati), dilution tunnel (ISO 8178) or/and by hood method (EPA5G).

The fine particles from wood-fired combustion were composed mainly of ash (alkali), condensate organic material and soot. The principal factors of ash particle emissions were attributed to mass of released ash forming species, cooling velocity of exhaust gas and composition of ash (K, S, Cl, Ca). The amount of released ash depends on combustion temperature. Thus reducing the amount of ash in fine particles is not easy in small scale wood combustion. The organic fraction was low in continuous burning and it can be reduced also in batch combustion by controlling the location of air injection and mixing in the burning chamber.

In general the highest emissions were in incomplete combustions situations like firing phase and smouldering combustion and lowest in the continuous burning of wood chips and pellet. In the batch burning the average PM1 emission was about 100 mg/MJ, in the effective devices about 50 mg/MJ. In the continuous burning PM1 emission was 5 – 30 mg/MJ. The number emissions were 1 x 10^13 – 10^14 kpl/MJ and did not correlate with other emission compounds. The particle average size varied between 80 to 200 nm. The size distributions were unimodal and shape of particles were agglomerates, covered of organic material in incomplete situations.

5D2

IN-SITU MEASUREMENT OF PARTICLES FROM GRATE COMBUSTION OF BIOMASS.

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Fine airborne particles are associated with adverse health effects in the human population. The aim of this work was to increase knowledge about health and environmentally relevant properties of aerosols from biomass combustion.

In-situ techniques such as Scanning Mobility Particle Sizer (SMPS), Electrical Low-Pressure Impactor (ELPI), Aerodynamic Particle Sizer (APS) and Tandem Differential Mobility Analysers (TDMA) based on hygroscopic growth were applied. Results from these techniques were combined with measurements from filter samplers and impactors for collecting particles on substrates for subsequent chemical analysis. Emissions from local district heating plants (0.5-12 MW), based on moving grate combustion of woody fuels, were sampled with a dilution system and characterised.

The investigated biomass combustion sources emit high concentrations of fine and ultrafine particles (Pagels et al. 2003). The chemical composition is dominated by KCl and K2SO4; Zn, Cd and Pb were also quantified. Elemental carbon was identified in particles larger than 150 nm during periods of incomplete combustion. The particle concentration depends on the fuel ash content and the combustion efficiency. During favourable combustion conditions the aerosol is essentially internally mixed with hygroscopic growth factors significantly higher than reported for diesel exhaust and environmental tobacco smoke . The particles restructure from agglomerates to a more compact shape upon first exposure to moderately high relative humidity (Rissler et al. 2005). This results in an increase in effective density and fractal dimension. Hygroscopic growth of these particles reduces the respiratory dose by a factor of 3 compared to hydrophobic particles of the same size.

The biomass combustion particles mainly consist of soluble ash components and need to be treated differently in future health effect assessments compared to particles from incomplete combustion, e.g. from diesel engines, wood stoves and cigarette smoke.

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5D3

DIESEL AND SPARK IGNITION ENGINE ON-ROAD AND LABORATORY COMPARISONS.

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We have evaluated emissions from heavy-duty Diesel and light-duty, spark ignition (SI) vehicles on-road and in the laboratory. Emissions from the same or similar engines were evaluated in both places in an effort to duplicate the on-road results in the laboratory. All Diesel engines produced bimodal size distributions with the nuclei mode ranging in size from 6 to 11 nm and the accumulation mode from 52 to 62 nm during highway cruise and acceleration. On-road size distribution measurements nearly always showed a nuclei mode while laboratory measurements showed a nuclei mode under many, but not all conditions. We attribute this to less steady operating conditions on-road than in the laboratory, different dilution conditions such as cold ambient temperatures, and a stronger propensity of atmospheric dilution to form nuclei mode particle. The size distributions formed depend not only upon engine condition, fuel and lube oil composition, and exhaust system design, but also upon other factors such as engine operating history, and environmental conditions. Diesel laboratory studies of the composition of ultrafine and nanoparticles showed that nuclei mode particles consisted mainly of heavy hydrocarbons. More than 97 % of the volume of the volatile constituents of 12 and 30 nm particles disappeared on heating to 400°C, and that the volatility resembled that of C24-C32 n-alkanes implying a significant contribution from lubricating oil. The fraction of solid particles decreased as particle size decreased.

For the SI tests we were unable to measure a significant particle signature above background under steady highway cruise conditions,. Particle number emissions were much higher, both on-road and in the laboratory during acceleration, at high speed cruise, and during cold-cold starts. Fuel-specific number emissions range from 1.5E15 to 4.6E17 particles/kg of fuel. Mass emissions from composited cold-cold UDC tests ranged from 1 to 7 mg/km for the test fleet. The elemental carbon fraction varied from 30 to 60% of the total mass. Cold-cold start temperatures, driving cycles and vehicular condition influence SI emissions.

Source apportionment results showed that on a weekly weighted basis and on weekdays, the majority of observed particle number was attributed to heavy-duty Diesel traffic. Weekend production of particles was attributable to light duty automobiles. On a per vehicle basis, heavy-duty vehicles produced substantially greater numbers of particles. On a fuel-specific basis, heavy-duty vehicles produce slightly higher concentrations of particles than light-duty vehicles. The relative contribution of light-duty vehicles to particle number emissions increased as particle size decreased.

5D4

DILUTION OF TAILPIPE EXHAUST IN VEHICLE WAKE: EFFECTS OF SPEED, SHAPE OF VEHICLE, AND TAILPIPE LOCATION.

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The rate at which fresh combustion emissions are diluted with ambient air can greatly affect the evolution of the particle size distributions in emissions from sources like motor vehicles. In particular, the generation of ultrafine particles within vehicle emissions is influenced not only by the particle and gaseous concentrations in the exhaust, but also by the rate and extent of dilution. This project experimentally investigated the impacts of different vehicle shapes, vehicle speeds, tailpipe positions, and tailpipe emission velocities on the exhaust dilution behavior, focusing especially on the near-wake region immediately downstream of the tailpipe where the most rapid changes in the dilution ratio occur.

The dilution of emissions downstream of model vehicles (5:1 scale) was studied in a wind tunnel located at the Wind Engineering Research Center at Tamkang University, Taiwan. A light duty truck, a passenger car and a heavy duty tractor head (without the trailer) were used to represent three typical vehicle types. A tracer gas was released at a measured flow rate from the tailpipe, to simulate the injection of exhaust emissions into the surrounding air. To evaluate the spatial distribution of the tailpipe emissions, sixty sampling probes were placed in the test section downstream of the vehicle to sample tracer gas concentrations simultaneously. Since different mixing characteristics in the near wake (first few vehicle heights downstream) versus the far wake region (more than 10 vehicle heights downstream) have been reported in the few previous publications in this research area, we placed a large number of probes in the near-vehicle region to investigate the early stages of dilution. A number of vehicle speeds, exhaust emission velocities, and tailpipe positions and orientations were tested.

Results show what range of dilution ratios can be expected as a function of downstream distance (i.e., time). Data analyses show the vehicle shape quite strongly influences dilution profiles in the near wake region, but is much less important in the far wake region. The tractor generally results in higher dilution than automobile and light duty truck under similar conditions. Changes in tailpipe location and exhaust exit velocities also have significant effects in the near wake mixing profiles. The detailed spatial information obtained for the exhaust mixing behavior as a function of downstream distance (time) may prove valuable for studying ultrafine particle formation in vehicle exhaust.

5D5

BIMODAL PARTICLE SIZE DISTRIBUTIONS AND MORPHOLOGY OF SOOT IN A RELATIVELY SOOTY LAMINAR PREMIXED ETHYLENE FLAME.

BIN ZHAO, Kei Uchikawa, Hai Wang, University of Southern California, Los Angeles, CA; Murray V. Johnston, University of Delaware, Newark, DE

The evolution of soot particle size distribution functions (PSDFs) was investigated in a premixed ethylene-oxygen-argon flame at equivalence ratios of 2.5 by in situ probe sampling and Scanning Mobility Particle Sizer (SMPS) analysis. Soot particles were also characterized with thermophoretic sampling followed by transmission electron microscopy (TEM) analysis. For this relatively sooty flame, the PSDF consists of two lognormal distributions, one that peaks around 6 nm in mobility diameter and the other at mobility diameters greater than 15 nm. The mean particle diameter of the small particle-size mode remains relatively unchanged beyond a distance of 7.5 mm above the burner surface, whereas the mobility diameter of the second mode continue to increase in the flame as soon as it becomes discernible.

The bimodal PSDFs observed here appear to be fundamentally different from the bimodal distributions observed previously in lightly sooting flames [1-3], where the bimodality was attributed to the competition of particle growth and persistent particle nucleation. Indeed, TEM analyses show that the small-size mode of the PSDF is associated with nearly spherical primary particles, whereas the second, larger-size mode contains mainly soot aggregates of low fractal dimensions. Therefore the current bimodality is the result of particle aggregation, and the limited of mass growth primary particles can be explained by a drastically lowered flame temperature due to increased radiation from flame soot.

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5D6

EMISSIONS FROM SPARK IGNITION ENGINES: CHARACTERIZATION OF PARTICLE MORPHOLOGY.

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Automobiles powered by spark ignition (i.e., gasoline) engines can have substantial particulate matter (PM) emissions during cold start and rapid acceleration, and from malfunctioning engines in gross emitters. Not much research has been reported on the morphology of particles emitted by gasoline engines. This knowledge is essential in interpreting measurements with optical instrumentation, in the modeling of PM atmospheric chemistry, and in establishing a better understanding of PM toxicology.
A study was performed in the Kansas City area during January to March 2005 to determine the shape and morphology of particle emissions from various vehicles operated on chassis dynamometers using a standard three-phase driving cycle. Tailpipe emissions from 59 vehicles were diluted with a constant volume sampler (CVS) and fine particles were sampled onto nucleopore clear polycarbonate filters and imaged with Scanning Electron Microscopy (SEM). The particle images are being analyzed for fractal dimensions, diameter of primary particles, and three different shape descriptors. Particles are also being probed with energy dispersive X-ray spectroscopy to confirm their carbonaceous nature. The morphology of particles will be analyzed using two fractal analysis techniques to derive a density fractal dimension and a textural fractal dimension. These measures quantitatively describe the space filling quality and the roughness of the boundary of the two dimensional projection of the particle. Several shape descriptors will be used to describe different attributes of particle shape. Results will be reported as function of driving cycle phase and vehicle type, age, mileage, etc.

5E1

DELIVERY AND BIOLOGICAL EFFECTS OF INHALED PARTICLES. ANTHONY HICKEY, Daniel Cooney

The delivery of particles to the lungs has historically been dominated by discussion of the influence of aerodynamic size and distribution. These important physico-chemical characteristics have been clearly correlated with the deposition of xenobiotics and drugs. A convergence of the literature in the disciplines of industrial hygiene, environmental medicine and pharmaceutical sciences on this subject occurred in the 1960s and 1970s and has continued for several decades. Stokes' law has been shown to predict aerosol behavior accurately for particles above 1µ;m and can be extended to smaller sizes with the application of slip correction factors. Lung disposition of micron sized particles may be considered in terms of the kinetics of absorption, mucociliary and cell mediated clearance. In addition to site of deposition, some important particle properties such as crystallinity, hydrophobicity, wettability and solubility will impact on clearance mechanism. Research in environmental and drug aerosol deposition is converging yet again as the importance of nanoparticles in toxicology and therapeutics is being considered. These particles not only affect aerodynamic behavior, which can be predicted to some extent through modification of density and shape terms in Stokes' law, but are thought to have implications for lung disposition. The fate of nanoparticles may be hazardous in the case of diesel exhaust particles, for example, and advantageous for certain drugs and vaccines. This overview will consider current perspectives on the subject of delivery and biological effects of inhaled particles.

5E3

HEALTH EFFECTS OF COAL COMBUSTION-DERIVED PM: PRELIMINARY RESULTS FROM THE TERESA STUDY. ANNETTE C. ROHR, EPRI, Palo Alto, CA; Pablo A. Ruiz, Edgar Diaz, Meriam Lemos, Beatriz Gonzalez-Flecha, John Godleski, Petros Koutrakis, Harvard School of Public Health, Boston, MA

Background: Coal-fired power plants produce only small quantities of primary particulate matter (PM), and most of the concern over the health impacts of power plant emissions focuses on the secondary particles formed via atmospheric oxidation of emitted SO2. However, toxicological studies of these secondary particles are difficult to carry out. The TERESA (Toxicological Evaluation of Realistic Emissions of Source Aerosols) study involves the use of mobile laboratories at power plants to age emissions, followed by animal exposures. Three plants are included in the project to allow assessment of different coals and pollution control configurations. Objective: The goal of TERESA is to evaluate the toxicity of secondary particles derived from coal-fired power plant emissions. A secondary objective is to compare, using the same experimental design, the health impacts of mobile source emissions. Methods: Detailed methods are described in other submitted TERESA-related abstracts. Primary emissions were drawn from the stack into a mobile laboratory, where several atmospheric scenarios were simulated (primary particles only, secondary particles, secondary particles + secondary organic aerosol, and secondary particles + ammonia + secondary organic aerosol). Female Sprague-Dawley rats were exposed to these atmospheric mixtures for 6 hours. Control animals were exposed to filtered air. Pulmonary function and breathing pattern data were collected during exposure, and bronchoalveolar lavage fluid and blood were collected post-exposure for cytological and biochemical analyses. Oxidative stress in heart and lung tissue was evaluated using an in vivo chemiluminescence (CL) technique and the TBARS assay. Results: PM2.5 concentrations were 200-300 µ;g/m3 in all the secondary particle scenarios. We observed no differences in breathing pattern or pulmonary function between control and exposed animals. No differences in BAL or blood parameters were observed. There were also no differences for CL or TBARS. As an illustrative example, CL in heart tissue was 14 ± 4 (exposed) vs. 10 ± 1 (control) for secondary particles + SOA. In lung tissue, CL was 9 ± 1 (exposed) vs. 9 ± 1 (control). Conclusions: Results from the first TERESA plant, under several different simulated atmospheric scenarios, indicate no toxicological effects with exposure to secondary particles derived from coal combustion. Field experiments are now underway at a second plant burning low-to-medium sulfur coal and located in the Southeast. At this plant, a more extensive assessment of cardiovascular effects will be carried out using a compromised rat model implanted with telemeters for the evaluation of heart rate, temperature, and heart rate variability.

5E4

GENERATION OF REACTIVE OXYGEN SPECIES BY URBAN PARTICULATE MATTER. Chuautemoc Arellanes and SUZANNE E. PAULSON Atmospheric Sciences Department, University of California at Los Angeles, CA

Size-segregated measurements of the reactive oxygen species hydrogen peroxide (H2O2) in both the gas- and the aerosol-phase have been made at several sites around the Los Angeles Air basin. Aerosol-phase hydroperoxide levels were in the range 0.2-4 ppb, and 0.5-40 ng m-3, respectively. The aerosol H2O2 levels far exceed those predicted by gas-liquid partitioning, by more than two orders of magnitude. The observed aerosol mass loadings of H2O2 correspond to aqueous concentrations of 10-3 -10-1 M, well above the levels necessary to induce lung epithelial cell damage in laboratory studies. Rather than simply absorbing H2O2 from the gas phase, aerosol particles appear to be able to generate H2O2 in aqueous solution. The chemistry that leads to continuous production of H2O2, and its time and pH dependence are examined. Dependence of production of peroxides by aerosols on particle type and chemical composition will also be discussed.

5E5

CELLULAR AND CYTOKINE RESPONSE TO PULMONARY GENE DELIVERY BY ELECTROHYDRODYNAMIC SPRAYS. CORINNE LENGSFELD, University of Denver, Denver, CO; Yvonne Lentz, Tom Anchordoquy, University of Colorado Health Sciences Center, Denver, CO

Electrohydrodynamic sprays, unlike other aerosolization techniques such as jet and ultrasonic nebulization, do not significantly degrade the supercoiled structure of plasmid DNA. As a result, this atomization technique holds promise as a viable method for pulmonary gene delivery over a broad formulation range. However, large electrical potentials are required in electrosprays to create suitably sized aerosols for pulmonary delivery. To our knowledge, the potential harm of delivering highly charged droplets to the lung has yet to be explored. This study evaluates the influence of electrical field strength on DNA transfection efficiency, cellular immune response and plasmid structural integrity. METHODS: Using EpiAirway(TM), a differentiated in vitro model of human bronchial/tracheal epithelial cells, we evaluated cellular and cytokine responses as well as transfection efficiency after delivering non-complexed 5 kb, plasmid DNA and polyethylenimine (PEI)/DNA complexes either directly or indirectly to the cells. Aqueous solutions containing 0.1 mg/ml pGreen Lantern-1 were supplied at 0.2 ml/min to a stainless steel capillary. Voltages of 0, 3, 6, and 9 kV were applied to the conductive capillary with a ground distance of 3 mm. A total volume of 100 ul was applied to each membrane. At specified time points (0, 2, 5, 8, 12, 24, and 40 hours), the tissues were moved to new wells containing fresh medium. Samples of the underlying medium from each time point were collected and stored at 4C for use in LDH and cytokine assays. LDH levels were measured using a CytoTox 96 Cytoxicity Assay Kit and quantified with the Gemini EM Fluorescent Microplate Reader at a wavelength of 490 nm. TNF-alpha levels were measured using a Human TNF-alpha Immunoassay Kit and quantified at a wavelength of 450 nm. Forty hours after transfection, cells were harvested from the membrane using trypsin, gently rinsed and resuspended in PBS for analysis of green fluorescent protein expression using a Coulter Epics XL flow cytometer at 525 nm. RESULTS: Although we found little change in lactate dehydrogenase (LDH), a small yet statistically significant increase in tumor necrosis factor-alpha (TNF-alpha) activity was detected 72 hours after delivery for both non-complexed and complexed DNA. These heightened levels indicate some cellular immune response to the applied electric field. Structural integrity was sustained under all conditions unless a corona discharge occurred. Transfection results are pending final analysis, but preliminary structural evaluation suggests that the PEI/DNA complex is altered at higher voltages.

5E6

ULTRAVIOLET GERMICIDAL IRRADIATION FOR VIRUS INACTIVATION. Chih-Shan Li, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University Chun Chieh Tseng, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University

The increasing incidence of infectious diseases has prompted the application of Ultraviolet Germicidal Irradiation (UVGI) for the inactivation of viruses. This study evaluates UVGI effectiveness for both airborne and surface viruses in a laboratory test chamber by determining the effect of UV dosage, different nucleic acid type of virus (single-stranded RNA, ssRNA; single-stranded DNA, ssRNA; double-stranded RNA, dsRNA; and double-stranded DNA, dsDNA), and relative humidity on virus survival fraction after UVGI exposure.
For airborne viruses, the UVGI dose for 90% inactivation was 339-423 µW sec/cm2 for ssRNA, 444-494 µW sec/cm2 for ssDNA, 662-863 µW sec/cm2 for dsRNA, and 910-1196 µW sec/cm2 for dsDNA. For all four tested, the UVGI dose for 99% inactivation was 2 times higher than that for 90% inactivation, and the ratio of surface to airborne UVGI dose ranged from 1.94 to 6.14. Both airborne and surface viruses with single-stranded nucleic acid (ssRNA and ssRNA) were more susceptible to UV inactivation than were those with double-stranded ones (dsRNA and dsDNA). For all tested viruses at the same inactivation, the UVGI dose at 85% RH was higher than that at 55% RH, possibly because water sorption onto a virus surface provides protection against UV-induced DNA or RNA damage at higher RH. In summary, UVGI was an effective method for virus inactivation.

6A1

MEASUREMENTS OF AEROSOL RADIATIVE PROPERTIES AND EFFECTS USING AIRBORNE SUNPHOTOMETER AND SOLAR SPECTRAL FLUX RADIOMETER IN ICARTT 2004. PHILIP RUSSELL, Warren Gore, James Eilers, NASA Ames Research Center, Moffett Field, CA; John Livingston, SRI International, Menlo Park, CA; Peter Pilewskie, University of Colorado, Boulder, CO; Jens Redemann, Beat Schmid, John Pommier, Steven Howard, Bay Area Environmental Research Institute, Sonoma, CA; Ralph Kahn, Jet Propulsion Laboratory, Pasadena, CA; Allen Chu, NASA Goddard Space Flight Center, Greenbelt, MD

From 12 July through 8 August 2004, the NASA Ames 14-channel Airborne Tracking Sunphotometer (AATS-14) and Solar Spectral Flux Radiometer (SSFR) made nineteen science flights on a Jetstream 31 (J31) aircraft over the Gulf of Maine in the INTEX-NA (INtercontinental chemical Transport EXperiment-North America) and ITCT (Intercontinental Transport and Chemical Transformation of anthropogenic pollution) components of ICARTT (International Consortium on Atmospheric Transport and Transformation). This paper gives an overview of J31 ICARTT results, with emphasis on satellite validation and aerosol spatial variability. It also provides an introduction to the related paper by Redemann et al. on J31 determinations of aerosol radiative forcing efficiency in ICARTT.

AATS-14 measures direct solar beam transmission at fourteen discrete wavelengths (354-2138 nm). It provides instantaneous measurements of aerosol optical depth (AOD) spectra and water vapor column content, in addition to vertical profiles of aerosol extinction and water vapor density during suitable aircraft ascents and descents. SSFR uses separate nadir and zenith viewing hemispheric FOV sensors to measure up- and downwelling solar irradiance at spectral resolution ~8-12 nm over the wavelength range 300-1700 nm.

Objectives of the J31 measurements in ICARTT included providing AOD data for the evaluation of MODIS (MODerate-resolution Imaging Spectroradiometer) and MISR (Multi-angle Imaging Spectro-Radiometer) AOD retrievals, quantifying sea surface spectral albedo (which can contribute the largest uncertainty to satellite aerosol retrievals for small AOD over water), testing closure (consistency) among suborbital results, testing chemical-transport models using AOD profiles, determining cloud properties for studies of aerosol indirect effects, and assessing regional radiative forcing by combining satellite and suborbital results. Flight plans often included profiles above the NOAA Ship Ronald H. Brown and, several times, coordination with other mission aircraft – namely, the NOAA DC-3 and the NASA DC-8. Fourteen J31 flights were coordinated with a Terra or an Aqua satellite overpass. The Terra overpasses included several MISR local mode (high spatial resolution retrieval) events. Generally, retrievals of spatially coincident AOD from both MODIS and MISR during Terra overpass were not possible due to sun glint effects on the MODIS measurements. However, temporally and spatially coincident AATS-14, MODIS, and MISR AOD measurements were acquired during one overpass. In this paper, we compare the AATS-14 and satellite sensor spectral AOD retrievals by examining spatial and temporal variability measured by AATS-14 along the J31 flight paths within the satellite sensor suborbital retrieval boxes. We will also survey other more recent J31 ICARTT results as time permits.

6A2

AIRBORNE MEASUREMENTS OF SPECTRAL DIRECT AEROSOL RADIATIVE FORCING - A NEW AEROSOL GRADIENT METHOD APPLIED TO DATA COLLECTED IN INTEX/ITCT/ICARTT, 2004.

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As part of the INTEX-NA (INtercontinental chemical Transport EXperiment-North America) and ITCT (Intercontinental Transport and Chemical Transformation of anthropogenic pollution) field studies, the NASA Ames 14-channel Airborne Tracking Sunphotometer (AATS-14) and a pair of Solar Spectral Flux Radiometers (SSFR) took measurements from aboard a Jetstream 31 (J31) aircraft during 19 science flights (~53 flight hours) over the Gulf of Maine during 12 July – 8 August 2004. The J31 was one of the platforms designated by ICARTT (International Consortium for Atmospheric Research on Transport and Transformation) to study the impact of aerosols on the atmospheric radiation balance. AATS-14 measures the direct solar beam transmission at 14 discrete wavelengths (354-2138 nm), yielding aerosol optical depth (AOD) spectra, while the SSFR system yields down- and upwelling solar irradiance at a spectral resolution of ~8-12 nm over the wavelength range 300-1700 nm. The combination of coincident and simultaneous AATS and SSFR measurements yields plots of net spectral irradiance as a function of aerosol optical depth as measured along horizontal flight legs (gradient plots). From the slope of these plots we determine the change in net radiative flux per change in aerosol optical depth, dF/dAOD, or aerosol radiative forcing efficiency [W m-2 AOD-1]. This manner of deriving forcing efficiency is called the aerosol gradient method. Unlike ground-based measurements of direct aerosol radiative forcing which rely upon the advection of various air masses over a measurement site during an extended period of time, the airborne method has the advantage of being quasi-instantaneous. In INTEX/ITCT, we observed a total of 16 horizontal AOD gradients, with 11 gradients well suited for our analysis because of the small changes in solar zenith angle during the gradient measurements. More than half of the AOD gradients (at a wavelength of 499 nm) were greater than 0.1 and extended over distances less than 40 km. Within the 11 case studies we found a high variability in the derived instantaneous aerosol forcing efficiencies (forcing per unit optical depth) for the wavelength range from 350 to 700nm, with a mean of -103Wm-2. The instantaneous fractional forcing efficiencies, defined as the forcing efficiencies divided by the downwelling irradiance, yielded a mean of 22% for the 11 case studies. We present spectrally resolved aerosol forcing efficiencies between 350 and 1670 nm and compare the range of observed broadband forcing efficiencies to previously reported values from ground-based observations during ACE-Asia and INDOEX.

6A3

AEROSOL OPTICAL PROPERTIES AND F(RH) OVER NORTH AMERICA DURING INTEX.

ANTONY CLARKE, Steven Howell, Cameron McNaughton, Yohei Shinozuka, Vladimir Kapustin, University of Hawaii, Honolulu, HI

Extensive flights aboard the NASA DC-8 were undertaken over North America as part of the INTEX-A, ICARTT Missions during the spring of 2005. Aerosol physical, chemical and optical measurements were made over an altitude range of up to 10km in diverse regions in order to obtain characteristics of regional aerosol types. Distinct physical, optical and humidity responses were identified for forest fire, urban pollution and regional haze. Spectral differences in light scattering (nephelometer) and light absorption (absorption photometer) revealed group classification of common aerosol types. Thermal volatility applied to size selected samples provided data on the relative volume mixing of volatile and refractory particles (eg. black carbon or soot) components that also differed appreciably in different regions. These groupings were also associated with particular gas phase species.

The frequency distributions of light scattering response to humidity changes, f(RH), showed some regional differences and changes with altitude. The frequent lowering of f(RH) in continental outflow off the north-east coast, apparently due to increased organic mass fraction for near surface measurements made on the R/V Ron Brown (P. Quinn and T. Baynard, personal correspondence), was less pronounced on a Northeast regional basis. Our vertical profiles and flight leg measurements also indicated typically higher f(RH) values over 1-5km than in the 0 -1km altitudes while cases of lowest values were often evident at higher altitudes. However, column optical properties were frequently influenced by layers associated with the long-range transport of aerosol from Canadian forest fires over much of the eastern US that had a lower f(RH) than boundary layer air. These and related data will be used to link the aerosol optics to these microphysical characteristics and regionally representative aerosol types.

6A4

AEROSOL OPTICAL PARTICLE PROPERTIES DURING NEAQS 2004: SHIP-BASED MEASUREMENTS OF AEROSOL ABSORPTION AND SCATTERING. BERKO SIERAU, David S. Covert, University of Washington, Dept. of Atmospheric Sciences, Seattle, WA Patricia K. Quinn, Timothy S. Bates, Derek Coffman, NOAA-PMEL, Seattle, WA

In-situ, three wavelength measurements of aerosol light scattering, hemispheric backscattering and absorption coefficients of the New York/Boston urban pollution outflow were carried out aboard the NOAA research vessel Ronald H. Brown during the NEAQS-ITCT 2004 (New England Air Quality Study-Intercontinental Transport and Chemical Transformation Study) field campaign. Aerosol total and sub-micrometric scattering and sub-micrometric absorption were measured using multiwavelength nephelometers and multiwavelength, filter-based absorption photometers, respectively, operating on a common inlet at a relative humidity of approximately 60%. Intensive aerosol properties derived from these extensive properties are the Ångström exponents for the scattering and absorption coefficients, i.e. their wavelength dependence, and the hemispheric backscattering ratio. Combining the aerosol scattering and absorption coefficients yields the single-scattering albedo, a key parameters in estimating aerosol direct radiative forcing.

During NEAQS-ITCT 2004 most parts of the cruise track were characterized by relatively low scattering and absorption of < 40 Mm^(-1) and < 5 Mm^(-1), respectively. However, distinct pollution events were measured with air masses coming offshore from the Boston urban area and resulting in peak scattering levels of 100-150 Mm^(-1) and absorption levels of 10 Mm^(-1). Smaller scale pollution events, i.e. ship plumes, showed much higher absorption levels up to 20-30 Mm^(-1) and were frequently observed during the entire cruise. The single scattering albedo is strongly dominated by the absorption pattern, mainly due to the large scale and small scale pollution events. A classification of the submicrometer aerosol based on the wind direction measured at the ship, i.e. basically a classification into onshore and offshore trajectories, does not yield distinct sets of aerosol parameters in terms of the single scattering albedo and the absorption and scattering Ångström exponents.

The intensive and extensive aerosol parameters are important for relating in-situ optical properties to those sensed remotely, eg., ground optical depth from sun photometry or satellite measured radiance and extinction profiles from lidar. The suite of parameters and wavelength dependence provide constraints on model building and closure studies with physical and chemical aerosol properties. The single scattering albedo will be used in combination with the aerosol optical depth to estimate aerosol direct radiative forcing.

6A5

THE RELATIVE HUMIDITY DEPENDENCE OF AEROSOL EXTINCTION. TAHLLEE BAYNARD, Edward Lovejoy, Anders Pettersson, Rebecca Garland, Hans Osthoff, Margaret Tolbert, A. R. Ravishankara, NOAA Aeronomy Lab and/or CIRES, University of Colorado, Boulder, CO; Patricia Quinn, Tim Bates, NOAA PMEL, Seattle, WA

Understanding the links between emissions, aerosol composition, and aerosol optical properties is necessary to determine aerosol radiative forcing and predict future forcing. One particular issue that needs to be addressed is the response of aerosol optical properties to water uptake, which is a significant source of uncertainty in determining aerosol radiative forcing. Direct measurements of the relative humidity dependence of aerosol extinction using a cavity ring-down aerosol extinction spectrometer (CRD), developed in the NOAA Aeronomy Laboratory, have increased our understanding of aerosol optical properties. In this presentation, results obtained using the CRD instrument will be discussed with a special focus on field measurements during NEAQS-ITCT 2004 and the laboratory studies of the relative humidity dependence of aerosol extinction related to composition and size.

6A6

MEASUREMENT OF ANTHROPOGENICALLY INFLUENCED AEROSOLS AT A MARINE SITE.

ELISABETH ANDREWS, Anne Jefferson, University of Colorado, Boulder, CO Patrick Sheridan, Ellsworth G. Dutton, John A. Ogren, NOAA/CMDL, Boulder CO James Allan, University of Manchester, Manchester, UK

During the summer of 2004, NOAA's Climate Monitoring and Diagnostics Laboratory (CMDL) deployed a large suite of integrated aerosol and solar radiation instruments to Chebogue Point (CBG), Nova Scotia to conduct ground measurements as part of a large, multi-national campaign to investigate the transport of pollutants from the mid-west across New England and into the Atlantic. One of the goals of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) project is to answer the question "How do the chemical, physical, and optical properties of aerosols impact regional haze and climate?" CMDL's moveable rack system included measurements of aerosol optical properties such as light scattering, absorption, and hygroscopic growth. Additional CMDL instrumentation included a cloud condensation nuclei counter to provide an indication of the cloud-forming potential of the aerosols passing the Nova Scotia site and a scanning electrical mobility spectrometer to measure the size distribution of aerosols.

Here results are presented describing two different areas we have explored based on our Chebogue Point measurements. First we show the influence of fog on aerosol optical properties and radiative forcing. We sampled aerosol optical properties continuously, during both clear and foggy conditions. During fog events the aerosol was considerably more absorbing (aerosol single scattering albedo decreased by 20-30%) and smaller (the backscatter fraction increased by a factor of 2), likely due to preferential scavenging of large hygroscopic particles. The systematic variation of backscatter fraction and single scattering albedo counteract each other when incorporated into a simple radiative forcing model, resulting in little difference (less than 5%) in radiative forcing efficiency for fog and non-fog time periods at Chebogue Point. Second, we characterized the hygroscopicity of the Chebogue Point aerosol using a humidograph system. The median hygroscopic growth factor f(RH) (the ratio of light scattering at 85% relative humidity to light scattering at low relative humidity conditions) of the CBG aerosol was approximately 1.4, which is considerably lower than has been seen at other sites and is, in fact, similar to what is seen for smoke and dust events at a remote, mid-continental site in Oklahoma. Measurements of aerosol organic and sulfate suggest that the hygroscopicity was strongly influenced by the relative amount of these two components. The median value of the radiative forcing efficiency determined taking into account the hygroscopic nature of the aerosol was 20% lower for less hygroscopic aerosol ($f(RH)<1.6$) than for more hygroscopic aerosol ($f(RH)>1.6$).

6B1

LABORATORY MEASUREMENTS OF BIOGENICALLY-INDUCED PARTICLE FORMATION AND GROWTH.

TIMOTHY M. VANREKEN, James N. Smith, Alex Guenther, Peter Harley, and Thomas Karl, National Center for Atmospheric Research, Boulder, CO

A unique "biogenic aerosol facility" has been developed to promote the study of biogenic emissions and their influence on new particle formation and growth. The facility is comprised of two interconnected chambers: a biomass chamber and a reaction chamber. The biomass chamber is an open-ended PTFE bag that can be placed over a photosynthetically-active plant source (e.g., a young pine tree). This chamber is plumbed so that the accumulated VOC emissions from the plant can be passed to the reaction chamber. The reaction chamber is a one cubic meter PTFE bag with several sampling ports. For the experiments described here which focus on ozone chemistry, the chamber is kept dark by placing it in a light-tight stainless steel enclosure constructed for this purpose. In addition to controlling the VOC concentration within the reaction chamber by passing and/or recirculating clean air through the biomass chamber, additional equipment is in place to control the temperature, relative humidity, ozone concentration, and sulfur dioxide level; it is also possible to add seed aerosol to the chamber when desired. Measurement capabilities include trace gas measurements using Proton Transfer Reaction Mass Spectrometry (PTRMS) and various aerosol properties, including number concentration and size distribution, hygroscopicity, CCN activity, and composition. As a whole, this new facility represents a powerful tool for examining the mechanisms for biogenic secondary organic aerosol formation and growth in the atmosphere.

The capabilities of the biogenic aerosol facility are demonstrated by reproducing experiments in which pure monoterpene precursors are observed to form new particles in the absence of a seed aerosol. Additionally, a series of experiments are conducted exploring the dependence of new particle formation on the background concentrations of ozone, sulfur dioxide, and the VOCs emitted by the biomass sample (it has been proposed that sulfuric acid clusters, arising from the oxidation of sulfur dioxide, are a prerequisite for new particle formation). These initial experiments focus on a single plant species whose emissions have previously been characterized; future studies will examine additional species. These initial experiments will be discussed, emphasizing the dependence of the resultant aerosol on the gas-phase precursors.

6B2

MARINE PARTICLE NUCLEATION: OBSERVATIONS AT BODEGA BAY AND POINT REYES, CALIFORNIA.

JIAN WEN, Yongjing Zhao, Anthony S. Wexler, University of California, Davis, CA

Homogeneous nucleation has drawn more attention recently due to the potential for these small particles to grow into cloud condensation nuclei, thus affecting cloud formation as well as the global radiation budget. Nucleation has been observed at different locations around the world; however, the key questions of the chemical composition of the nuclei as well as the exact nucleation pathways remain unresolved. The aim of our study is to identify and characterize nucleation events at Bodega Bay and Point Reyes, California.

A TSI nano-SMPS was installed in a lab at Bodega Bay, about 50m from the coastline and 5m above sea level. Based on measurements conducted from June to December 2001 and from January to June 2003, we have observed two kinds of nucleation events, i.e. long-term (a few hours) and short-term (a few minutes) particle bursts. The long-term events mostly occur during daytime in the summer lasting from 0.5 hour to 8 hours. Narrow spikes (short-term events) that occur year-round, both day and night, last only a few minutes to a half hour, but contain particle number concentrations comparable to some of the long-term events. Wind direction and speed affect the occurrence and intensity of the particle burst. Nucleation mostly takes place during northwesterly onshore wind for both long- and short-term events. The theoretical estimations of condensational sink for precursor gases and the sea-to-air flux of precursor gas indicate that nucleation is more favourable at higher wind speed, which agrees with our observation at Bodega Bay. The seasonal and inter-annual variations of ultrafine particle number concentration N3-10nm appear to correlate with ocean upwelling, a characteristic of currents along the west coast of US that brings up nutrients from subsurface waters promoting plant productivity. Simultaneous measurements of nucleation at the coast and 1.6 km out suggest that nucleation is a coastal phenomenon supporting the contention that it is related to direct or biogenic emission of precursor gases from the coastal area during the sea upwelling periods.

Starting from April 2005, we are involved in the Marine Stratus Radiation Aerosol and Drizzle (MASRAD) campaign at Point Reyes, CA, about 30 km south of Bodega Bay. A TSI nano-SMPS and APS are installed at the site. The measurement results will be compared with those at Bodega Bay assisting us to determine if the nucleation observed at Bodega Bay is a local or regional phenomenon.

6B3

ROLE OF SULPHURIC ACID IN PARTICLE FORMATION EVENTS IN FINLAND.

Sanna-Liisa Sihto, Markku Kulmala, University of Helsinki, Helsinki, Finland; Veli-Matti Kerminen, Finnish Meteorological Institute, Helsinki, Finland; Ari Laaksonen, University of Kuopio, Kuopio, Finland; KARI LEHTINEN, Finnish Meteorological Institute and University of Kuopio, Kuopio, Finland.

Formation of nanometer sized aerosol particles, nucleation followed by condensational growth, has been observed frequently all over the globe (Kulmala et al., 2004). In Hyytiälä, in the finnish Boreal forest these nucleation events are frequent, at least 50-60 days per year, and characterized by an increase of particles in the lower size range of a differential mobility particle sizer (DMPS) (e.g. 3 nm) followed by the growth of a new nucleation mode up to Aitken or even accumulation mode size after 1-2 days.

This paper focuses on comparing detailed measurements of the particle size distribution with gas measurements, especially of sulphuric acid. The new particle nucleation mechanism has been speculated to be binary sulphuric acid - water, and later ternary sulphuric acid - water - ammonia as well as kinetic. Also ion induced and/or mediated mechanisms have been proposed. However, none of the above have been succesful in predicting all observed events. In all the proposed mechanisms sulphuric acid is playing a major role. It is this role that we wish to confirm and quantify.

Our approach consists of two methods: 1) Regression analysis of measured data sets and 2) Aerosol dynamics modelling. By comparing time series of aerosol size distributions and sulphuric acid concentrations, and by using theories of nucleation and initial steps of growth it is possible to neglect some of the proposed mechanisms for particle formation. Size distribution simulation is also a powerful tool: by using two recently developed approaches, the discrete method (Lehtinen and Kulmala, 2002) and a multicomponent sectional method UHMA (Korhonen et al., 2004) we may test which combinations of the nucleation and early growth expressions result in particle formation rates in accordance with the observations.

Korhonen et al., Atmos. Chem. Phys. 4, 757, 2004.
Kulmala et al., J. Aerosol Sci. 35, 143, 2004
Lehtinen and Kulmala, Atmos. Chem. Phys. 3, 251, 2002.

6B4

FORMATION AND INITIAL GROWTH OF ATMOSPHERIC AEROSOLS. MARKKU KULMALA, University of Helsinki, Helsinki, Finland; Kari Lehtinen, Finnish Meteorological Institute and University of Kuopio, Kuopio, Finland.

Formation and subsequent growth of atmospheric aerosol have recently been an active research topic (Kulmala et al., 2004a). Aerosol particles are ubiquitous in the Earth's atmosphere and influence our quality of life in many different ways. In urban environments, aerosol particles can affect human health through their inhalation Wichmann and Peters, 2000). In the global troposphere aerosol particles are thought to contribute to climate change patterns (Ramanathan et al., 2001). Understanding these effects requires detailed information on how aerosol particles enter the atmosphere and how they are transformed before being removed by dry or wet deposition. Key processes in this respect are the formation of new atmospheric particles and their subsequent growth to larger sizes.

In most studies the aerosol size distributions as well as formation and subsequent growth of nucleation mode aerosols have been observed using DMPS/SMPS + CPC systems, which have cut off sizes of (at least) 3 nm. Hence these studies are not suitable for detection of nucleation and initial steps of the particle growth. On the other hand, using ion spectrometers to reach ion spectra the sizes below 3 nm can be observed. One of the main advances of our recent work has been the simultaneous measurement of size distributions with DMPS and ion spectrometer systems, giving us e.g. useful information about the initial steps of particle growth (Kulmala et al., 2004).

It is the competition of growth and scavenging that determines the actual production rate of new observable particles (above 3 nm), regardless of the nucleation mechanism. Furthermore, this production rate is very sensitive to both the growth rate (as a function of size) as well as the size distribution of background aerosol particles (Kerminen et al., 2004). Therefore knowing the mechanism how initial steps of growth will occur is a crucial piece of information in any study of new particle formation. The formation of aerosol in the atmosphere can be kinetically limited by some of the intermediate steps of its formation processes. The equilibrium state is thus not necessarily the aerosol itself but can be, for example, thermodynamically stable neutral clusters. Although there is strong indication that the water-sulphuric acid-ammonia nucleation mechanism explains the formation of new atmospheric aerosols (diameter < 3 nm) in many circumstances, the atmospheric concentrations of these vapours are not sufficient to explain the observed growth rates of the particles (Kulmala et al., 2004a).

The initial steps of growth can occur via several ways: Condensation of nucleating vapours, Activation of soluble vapours, Heterogeneous nucleation, Ion mediated particle formation (or ion-induced nucleation with enhanced condensation rate), Self coagulation or Chemical reactions at the surface. In this paper, in addition to reviewing some global features of particle formation events the long time series obtained in our research station in Hyytiälä is explored in order to assess the importance of the above mentioned mechanisms.

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6B5

MEASUREMENTS OF HETEROGENEOUS ICE NUCLEATION BY MINERAL DUST. KIRSTEN KOEHLER, Paul Demott, Anthony Prenni, Christian Carrico, Sonia Kreidenweis, Colorado State University, Fort Collins, CO

Ice nucleation behavior of several mineral dust species has been investigated. Most dust particles are insoluble and relatively inefficient CCN, but have been observed to be good ice nuclei (IN). Arizona Test Dust was purchased commercially from Powder Technologies, Inc. It is insoluble, with a large fraction of submicrometer particulate matter. Although a milled product, it was designed to be representative of airborne dust in the southwestern United States. Owens (dry) Lake dust was obtained from the U.S. Geological Survey and has the unique property that, unlike sandy dusts, it contains a high fraction of soluble material. This former lake was dried out after water was diverted from it to Los Angeles, CA in 1913 and is now one of the largest sources of airborne particulate matter in the Western Hemisphere. It is expected to be representative of dust emitted from various dry lake beds.

Ice nucleation is measured using a continuous flow diffusion chamber. The particles are generated in two ways, wet and dry. For wet generation, the dust was suspended in high purity water and then atomized and subsequently dried. A fluidized bed was used for dry generation. The Arizona Test dust was significantly more effective at ice nucleation when generated by the dry method. For the same relative humidity with respect to ice (RHi), only 1% of the particles had nucleated ice following wet generation, whereas 10% nucleated ice in the sample that had been dry-generated. Since the Owens Lake dust contains soluble material, the particles are likely being more significantly altered from their natural state during the wet generation process. The dry generation process is expected to generate particles that are more representative of material suspended in the atmosphere.

Ice formation on the dust shows little dependence on temperature between -60 and -40oC, nucleating ~1% of particles at a similar RHi for any temperature. However, there is a strong dependency on particle size. The dry-generated Arizona Test dust exhibited similar behavior to that for other dust samples reported in the literature, nucleating at a similar RHi for similar size. The wet-generated Owens Lake dust required a higher RHi to serve as an IN. This increase in required RHi appears to be related to the soluble fraction of the particle. Hygroscopicity measurements have been implemented to estimate the soluble fraction using a humidified tandem differential mobility analyzer. All tested dusts nucleate ice at RHi conditions lower than required for homogeneous freezing of equal-sized sulfate particles at below -40°C. New studies will explore ice nucleation between 0 and -40°C.

6B6

OBSERVATIONS OF ULTRA-FINE PARTICLES OVER A FOREST.

S.C. PRYOR, Indiana University, IN; R.J. Barthelmie, L.L. Soerensen, Risoe National Laboratory, Denmark

During May-June 2004 we undertook measurements of the particle flux, physical particle size distribution and chemical composition over a Beech forest in Denmark. Highest number concentrations of sub-30 nm particles were observed when net radiation exceeded 300 Watts per meter squared, ambient particle surface area was less than 100 microns squared per cubic centimeter, and the condensational sink was below 3.5*10^-3 per second. The 10-30 nm particles show growth rates of 1.5-4.5 nm per hour, and based on measurements using a nano-MOUDI are comprised predominantly of ammonium, sulfate and associated water (Pryor et al. 2005). In contrast to recent research from the Waldstein forest in Bavaria (Held et al. 2004), during these ‘nucleation bursts’ the particle flux was upward implying a source at/below the canopy in accord with data from the Hyytiälä forest in Finland (Bigg 2001). During May-June 2005 we shall return to the Beech forest site to take additional data to address whether: (i) ammonia is a significant limitation on nucleation and/or growth and (ii) the nucleation events are occurring in the trunk space of the forest, within or above the canopy.

References:

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Pryor SC et al. (2005) Observations of ultra-fine particles above a deciduous forest. Geophysical Research Letters 32 doi: 10.1029/2004GL022261

6C1

MOLECULAR DYNAMICS OF THE COALESCENCE OF UNEQUAL SIZE AND COATED AEROSOLS.

T. Hawa and M.R. ZACHARIAH

The largest collision kernel is between a small particle with high mobility, and a larger particle which presents a large collision cross-section. However, most coalescence models are limited to the analysis of equivalent particle sizes. In this paper we focus on understanding the coalescence mechanisms of unequal sized nanoparticles. We have studied the coalescence of pairs of silicon nanoparticles of volume ratios between .053 - 1 with 10000 (at 1500 K) and 1600 (at 1000 K) silicon atoms using molecular dynamics (MD) simulation under constant temperature conditions. We found that the convection processes, and deformation of the smaller particle dominated the coalescence process for liquid-like particles. On the other hand, for near solid-like particles diffusion processes dominated the coalescence of nanoparticles. Coalescence processes become faster when the ratio of two particle sizes (smaller/larger) approaches zero. Most importantly we find that the Koch-Friedlander (KF) accurately predicts the coalescence time of two unequal sized particles when benchmarked against the MD simulation results, and that the characteristic coalescence times is independent of the volume ratio of the coalescing partners.

In this paper we also consider the role of surface passivation on the rate of nanoparticle coalescence. We have studied the coalescence of bare and H-coated silicon nanoparticles of sizes between 2-6 nm using molecular dynamics simulation at 1000 and 1500 K. We found that coalescence of coated particles consists of two steps. First chemical reaction between particles, and relocations of surface atoms near the reacting region occurs, which comprise an induction period. The second step consists of the nominal coalescence event, which depends on the surface tension and solid-state diffusion in the particle. The hydrogen passivation layer was found to remain on the surface during the entire coalescence event. We also develop a mathematical model to describe the dynamics of coalescence of coated particles.

6C2

MEASURING MICROPARTICLE ADHESION FORCE USING ELECTROSTATICS.

THOMAS SZAREK and Patrick F. Dunn, Particle Dynamics Laboratory, University of Notre Dame, Notre Dame, IN

This presentation discusses a unique measurement device designed to examine the adhesion force of microparticles of differing size and composition at various pressure and humidity conditions. Particles resting on the lower of two electrodes become charged as an electric potential is established between the plates. A particle will move towards the other plate when the electrostatic force exceeds the pull-off force. By knowing the electric field as a function of time, simple observation can be used to determine the required pull-off force. The adhesion force can be determined directly from the pull-off force. The device created allows the experimentalist to view a large number of particles at once so a statistically significant amount of data can easily be collected. Two Petri dishes, whose flat bottoms allow for a uniform electric field and whose rounded edges minimize sparking, were coated by sputtering a thin layer of aluminum on the bottom of the dishes such that the surface is conducting but still translucent. Particles resting on the surface can be viewed from underneath and their removal easily detected by observation using a camera with high optical magnification. The plates were rigidly mounted inside a vacuum tank at a known spacing. Additionally a computer code was developed to objectively determine the size of particles. Thus, polydispersed samples could be studied under the same atmospheric and charging conditions. The results from these experiments for both conducting and insulating particles at various pressure and humidity conditions will be presented.

6C3

A SELF-CONSISTENT GAS-KINETIC THEORY OF NANOPARTICLE TRANSPORT.

HAI WANG, Denis Phares, Charles S. Campbell, University of Southern California, Los Angeles, CA; Zhigang, Li, University of Delaware, Newark, DE

We present a careful comparison of available electric mobility data with a gas-kinetic theory [1,2] recently developed for the transport properties of nanometer size, spherical particles in the small Reynolds number ($Re < 1$) and large Knudsen number regimes ($Kn >> 1$). The data considered here include the measurements reported by Ude and de la Mora on polyethylene glycol particles and several earlier sets of electric mobility data obtained for silver, copper oxide, and protein nanoparticles. The radius of these particles ranges from 0.5 to 10 nm. The comparison confirms the theoretical prediction that the van der Waals interactions between the particle and fluid molecules are important to describing the transport properties of nanoparticles. In addition, the comparison shows that a specular-to-diffuse scattering transition exists for particles a few nanometers in radius, and that the transition radius and the rate of transition with respect to particle size appear to depend on particle material. The remaining uncertainties will be discussed and the need for additional data in the particle radius range of 1 to 10 nm will be emphasized.

1. Li, Z. and Wang, H. “Drag force, diffusion coefficient and electric mobility of small particles. I. Theory applicable to free molecular regime,” Physical Review E 68, 061206-1-9 (2003).
2. Li, Z. and Wang, H. “Drag force, diffusion coefficient and electric mobility of small particles. II. Applications,” Physical Review E 68, 061207-1-13 (2003).

6C4

MONTE CARLO SIMULATIONS OF STRUCTURAL TRANSITIONS IN BINARY AEROSOL NANODROPLETS.

GERALD WILEMSKI, Hongxia Ning, Department of Physics, University of Missouri-Rolla, Rolla, MO

Two very different types of structures have been predicted for binary aerosol droplets whose constituents have limited miscibility in the bulk liquid phase. These predictions were based on extensive density functional theory calculations by Li and Wilemski for a mock water—pentanol system. In vapors with high pseudo-pentanol (p-pentanol) vapor activities, the droplets are fairly uniform mixtures with an outer layer of nearly pure p-pentanol. In contrast, at low p-pentanol vapor activities, the droplet cores are nearly all p-water, and the p-pentanol is concentrated in an outer layer whose thickness depends mainly on the vapor composition. Over a moderately broad region of vapor activities, both the well-mixed and core-shell structures were found to coexist. This raises the interesting prospect of dynamical transitions from one structure to another that are triggered by random internal compositional fluctuations and mediated by systematic changes in the vapor composition. As a means of exploring efficiently the dynamics of these transitions, we have performed Monte Carlo simulations of binary nanodroplets whose equilibrium structures resemble those described above. We use a lattice Monte Carlo method in which the droplet molecules are idealized as beads that are constrained to move between discrete sites of an fcc lattice. Only nearest neighbor interactions are allowed. The identity of a bead determines how it interacts with each of the nearest neighbor sites. Simulations were generally run on lattices of more than sixty thousand lattice sites with the droplets typically containing more than ten thousand beads. Two models of binary droplets were considered. In the simpler version, the beads of each species occupy only a single site, and they differ only by their energetic interactions. The more complex model treats mixtures of single site and double site beads, i.e., dimers whose two beads are permanently linked. By suitably adjusting the interactions between the ends of a dimer and a single site bead and with the two ends of a different dimer, aqueous mixtures of strongly amphiphilic molecules can be modeled. The dynamics of transitions between different droplet structures and its dependence on the state of the vapor will be illustrated using results obtained from simulations with these two models.

6C5

GAS-NANOPARTICLE SCATTERING: A MOLECULAR VIEW OF MOMENTUM ACCOMMODATION FUNCTION.

Zhigang Li, University of Delaware, Newark, DE; HAI WANG, University of Southern California, CA

In recent gas-kinetic theory studies [1,2], we demonstrated that a transition from specular to diffuse scattering must occur for particles a few nanometers in radius. This transition states that the momentum accommodation factor is not a constant, and rather, it must minimally depend on the particle size. In this way, the drag and electric mobility of ultrafine aerosols, i.e., those with particles in the nanometer size range, are notably influenced by the transition in the collision dynamics. Historically the existence of this transition may be inferred readily by the contrast between the Chapman-Enskog theory, in which the specular scattering is assumed for molecular diffusion, and Millikan's observation that the drag on his oil droplet particles (>0.2 um) corresponds mostly to Epstein's solution of diffuse scattering. Both of these theories are successful in explaining the data for particles of their respective size ranges. Yet, the origin of diffuse scattering and consequently the transition between the two dominant gas-particle scattering modes was never understood. In this presentation, we examine the origin of diffuse scattering by molecular dynamics and show that the diffuse scattering is the consequence of gas molecule absorption or trapping on the particle surface. Trapping occurs because of gas-particle intermolecular interactions and particle's ability of energy accommodation. The trapped gas molecule undergoes surface diffusion and upon desorption the trajectory of the gas molecule is decidedly diffuse. These observations explain the transition from specular-to-diffuse scattering as the particle size becomes larger than the molecular size. We will also discuss the implication of this transition on the transport properties of nanometer size particles.

1. Li, Z. and Wang, H. "Drag force, diffusion coefficient and electric mobility of small particles. I. Theory applicable to free molecular regime," Physical Review E 68, 061206-1-9 (2003).
2. Li, Z. and Wang, H. "Drag force, diffusion coefficient and electric mobility of small particles. II. Applications," Physical Review E 68, 061207-1-13 (2003).

6C6

ENHANCED PHOTOLYSIS IN THE AEROSOL PHASE RELATIVE TO THE BULK-LIQUID PHASE. PAUL NISSENSON, Chris Knox, Donald Dabdub. University of California, Irvine. Irvine, CA; Leon Phillips. University of Canterbury, Christchurch, New Zealand.

Aerosol photochemistry may play a vital role in determining the concentration of important tropospheric species. This talk examines the differences in photolysis rates and intensity distributions between aerosols and bulk-liquid solutions using experimental and numerical techniques. In particular, molybdenum hexacarbonyl (Mo(CO)_6) in 1-decene is irradiated in both the aerosol and bulk-liquid phases. It is observed that Mo (CO)_6 photolyses significantly faster in the aerosol phase compared to the bulk-liquid phase. The primary hypothesis to explain this phenomenon is that the aerosols act as resonant cavitities that produce intensity enhancements. Previous works show that droplets experience large intensity enhancements for certain combinations of droplet size and wavelength, but do not examine the internal ntensity distribution averaged over a full spectrum of wavelengths. Equations from Mie Theory are used to calculate the average intensity distribution within aerosol droplets. Questions of particular interest are: Is there a significant intensity enhancement in the aerosol phase relative to the bulk-liquid phase when averaging over a full wavelength spectrum? How does the intensity between the aerosol interface and the rest of the aerosol differ?

6D1

USING FUNDAMENTAL THERMODYNAMICS TO EVALUATE THE FORMATION OF ORGANIC PARTICULATE MATTER IN THE ATMOSPHERE BY ACCRETION REACTIONS. KELLEY BARSANTI, James Pankow, OGI School of Science & Engineering, Oregon Health & Science University, Portland, OR

The theoretical method developed by Barsanti and Pankow (2004) has been extended in this work to allow evaluation of the extent to which any type of accretion reaction may contribute to organic particulate matter (OPM) formation in the atmosphere. This work builds on previous considerations of OPM formation by individual accretion reactions, in which predictions were made using estimated Gibbs free energy of formation (Gf°) values to calculate equilibrium constants (K) for each accretion reaction of potential interest (Barsanti and Pankow 2004, 2005). In this work, levels of OPM were computed for a range of K values, under a range of ambient conditions (e.g., varying initial reactant and background OPM levels). This approach yielded a series of curves from which, given any accretion-product K value, initial reactant concentration, and background OPM level, the predicted level of OPM can be easily determined. This approach will allow for evaluation of atmospheric OPM formation by any type of accretion reaction of interest, assuming a knowledge of the underlying thermodynamics.

For reactants and accretion products of interest in the atmosphere, few physical property data are available. Thus, group contribution methods (GCMs) have been used to obtain Gf° values. GCMs have been recommended to estimate physical property data based on their relative accuracies and computational efficiencies; however, such methods are not completely reliable (Poling et al., 2001). Errors in estimated Gf° values may lead to significant errors in calculated K values. Conclusions regarding the level of accuracy required for free energy data obtained from physical property estimation methods and/or experimental measurements will be considered.

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Barsanti, K.C., Pankow, J.F. (2005, submitted), Atmospheric Environment.
Poling et al. (2001), Properties of Gases and Liquids, 5th edition.

6D2

THERMODYNAMIC MODELS OF AEROSOLS CONTAINING DICARBOXYLIC ACIDS, THEIR SALTS, AND INORGANIC COMPOUNDS.

SIMON L. CLEGG, School of Environmental Sciences, University of East Anglia, Norwich, U.K.; John H. Seinfeld, Dept. Chemical Engineering, California Institute of Technology, Pasadena, CA

Soluble organic compounds, including the dicarboxylic acids and their salts, affect atmospheric aerosol water uptake and the cloud nucleating properties of aerosols. Models of the thermodynamic properties of the inorganic components of atmospheric aerosols are relatively well developed. However, this is not true of models of inorganic/organic mixtures, due to the lack of thermodynamic data for the dicarboxylic acids and their salts (including even their solubilities in water), and the lack of a model formalism suitable for representing the properties of aqueous mixtures, containing both electrolyte and non-electrolyte components, to very high concentration or low ambient relative humidity.

Recent laboratory experiments, by a number of different groups, have established the deliquescence properties of some dicarboxylic acids (such as malonic, succinic, and glutaric acids) and their mixtures with inorganic salts including NaCl and (NH4)2SO4. In a series of modelling studies we have addressed the problems of: (1) quantifying the interactions between salts and dissolved acids and their effects on water activity and solid/liquid equilibrium; (2) integrating the thermodynamic description of organic acid behaviour into a larger scheme that includes the inorganic components of aerosols.

We have focused on systems including malonic and succinic acids in order to test different modelling approaches and, ultimately, to enable these compounds and other acids to be included in atmospheric thermodynamic codes. The modelling approaches used are those proposed by Clegg et al. (2001) (successfully applied by Parsons et al. (2004) to (NH4)2SO4/malonic acid mixtures), and by Clegg and Seinfeld (2004). The latter method - an extension of the Zdanovskii-Stokes-Robinson approach - represents the water content of mixed inorganic/organic solutions well, but is not ideally suited to calculations of organic acid dissociation and its effects on aerosol acidity.

We will discuss the application of both methods to the available data, using the models to interpret observations, including the formation of dicarboxylic acid salts which in some cases differ from those generally assumed to occur. The requirements for new experiments to provide key thermodynamic data will be discussed.

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S. L. Clegg and J. H. Seinfeld (2004) J. Phys. Chem. A, 108, 1008-1017.

6D3

THE ORGANIC CHEMICAL COMPOSITION OF SOURCE AEROSOLS BY THERMAL EXTRACTION-GC/MS.

MICHAEL HAYS, Richard Lavrich, US EPA, Research Triangle Park, NC

Molecular marker source apportionment [Chemical Mass Balance (CMB)] will be one of the benefits of developing thermal extraction/gas chromatography/mass spectrometry (TE/GC/MS) for determining organic aerosol composition. Evaluating the fine particulate matter (PM2.5) chemical composition at the source and receptor using the same analytical method will free the source contribution estimates from any systematic bias. The focus thus far has been to develop TE/GC/MS for only ambient organic aerosols. We have chosen to chemically characterize PM2.5 source emissions using TE/GC/MS. In doing so, we examine matrix bias, reproducibility, recovery, and accuracy of the TE/GC/MS method applied to jet engine and diesel vehicle exhaust, biomass burning, and World Trade Center/Ground Zero source emissions. We are finding that (i) the source matrix interference is minimal; (ii) the method accuracy and replication for most detected marker species are satisfactory; but (iii) the reliability of TE/GC/MS analysis for heteroatomic molecules may be compromised. Together with our experimental results, we will present important future research directions and a brief history of TE/GC/MS applications to organic aerosols.

6D4

LABORATORY INVESTIGATION OF THE OXIDATION KINETICS OF ORGANIC MOLECULAR MARKERS USED FOR SOURCE-APPORTIONMENT: MEAT COOKING EMISSIONS.

EMILY WEITKAMP, Kara Huff-Hartz, Amy Sage, Allen Robinson, Neil Donahue, Carnegie Mellon University, Pittsburgh, PA;

A large fraction of fine particulate matter is organic. Currently large uncertainties exist regarding the nature and dynamics of aging of the organic fraction, especially under atmospherically relevant conditions. Of particular concern is the chemical stability of molecular markers used for source apportionment. The stability of these compounds has not been evaluated for the long time scales associated with the transport dominated conditions of the Eastern United States. To address these concerns, experiments are being conducted in the smog chamber at Carnegie Mellon University. The objectives of the experiments are to measure the oxidation kinetics of individual condensed-phase organic compounds in mixtures of varying complexity from simple binary mixtures to real organic aerosols.

In this talk, we present measurements of the oxidation kinetics of molecular markers commonly used for meat cooking emissions: unsaturated alkenoic acids and cholesterol. To understand the effects of mixture composition on oxidation rate, aerosols of model meat mixtures of increasing complexity were investigated, from simple 2 component mixes to real meat cooking extracts. Aerosol was generated in the smog chamber and exposed to O3. Gas phase compounds were added to the chamber and their concentrations were measured using on line GC-FID to link measured kinetic rates back to well-known gas phase species. Filters of condensed phase species were collected periodically over a 4-hour experiment, solvent extracted, derivitized and analyzed via GC-MS. A relative rate approach was used to determine oxidation rate constants. Results show a decrease in reaction rate with an increase in aerosol complexity. For example, the oleic acid half-life was approximately 7 times longer in a 14-component mixture than in a 4-component mixture. Similarly, the cholesterol half-life was more than 20 times slower in the 14-component mix than in the 4-component mix. Experiments have also been performed with real meat extract. The implications of these results on source apportionment estimates are discussed.

6D5

INVESTIGATION OF THE PHYSICAL PROPERTIES OF GROUP SPECIATED FINE PARTICLE WATER-SOLUBLE ORGANIC CARBON AEROSOLS.

Rodney J. Weber, AMY P. SULLIVAN, Poulomi Sannigrahi, Ellery D. Ingall, Georgia Institute of Technology, Atlanta, GA

The chemical complexity of the organic aerosol makes complete speciation nearly impossible. In addition, this complexity makes it challenging to relate atmospherically relevant physical properties of the organic aerosol to specific chemical fractions. However, by successive isolation of chemical groups it may be possible to simplify this complexity and yet provide a comprehensive analysis of the pertinent chemical and physical properties of the ambient aerosol. This paper describes results of analysis of ambient water-soluble organic carbon (WSOC) that have been isolated by a new method involving Solid Phase Extraction (SPE) using XAD-8 resin followed by Size-Exclusion Chromatography. The method is described in a companion paper.

This paper will report on results investigating specific properties of the isolated chemical fractions of ambient aerosol collected near different sources. For example, C-NMR has been used to investigate the prevalence of various functional groups and a diode array spectrophotometer has been used to determine the chemical fractions responsible for visible light absorption.

6D6

TEMPERATURE DEPENDENCE OF THE YIELD AND KINETICS OF SECONDARY ORGANIC AEROSOL FORMATION DURING THE LIMONENE OZONOLYSIS.

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Secondary organic aerosol (SOA) is generated by the ozonolysis of (R)-(+)-limonene in a 10 m3 Teflon smog chamber, in the presence of an OH radical scavenger (2-butanol) at temperatures between 13 oC and 40 oC. Limonene is a monoterpene with two double bonds that is emitted by vegetation but also during the use of cleaning products. The degree of oxidation of the double bonds and the corresponding phase of the oxidized products affect the kinetics of SOA formation. In a first set of experiments at constant temperature, the temperature dependence of the SOA yield of the limonene-ozone reaction and the partitioning of its products was investigated. In a second set of experiments the temperature-dependence of the gas-aerosol partitioning of the SOA products was measured by changing the temperature of the smog chamber after SOA formation at constant temperature.
The limonene SOA mass decreases by 2% for every 1oC increase in temperature for reacted limonene concentrations of 60 ppb. These measurements were used for the parameterization of the SOA yield of the limonene ozonolysis as a function of temperature.
Several oxidation products of limonene, limonaketone, limononic acid, keto-limononic acid, limononaldehyde, and keto-limononaldehyde, were synthesized. The kinetics of the ozonolysis of limonaketone, limononic acid, and limononaldehyde were measured as well as the relative vaporization oxidation products.

6E1

EXPERIMENTAL APPROACHES FOR ASSESSING AND OPTIMIZING AEROSOL DELIVERY.

WILLIAM D. BENNETT

Aerosolized therapeutics are used to treat or prevent a variety of lung diseases. It may be desirable to optimize total aerosol deposition, target delivery of these aerosols to specific regions of the lung, and enhance their retention at those targeted sites. Experimentalists have a number of techniques available to assess and optimize the dose of inhaled aerosols to the respiratory tract of humans. Generally, these methods involve inhalation of surrogate particles intended to mimic the drug-particle of interest, though in some cases the fate of the drug itself may be ascertained. Total deposition of inhaled particles in the respiratory tract can be determined by use of stable, monodisperse aerosols and light scattering photometry at the mouth to assess inhaled and exhaled aerosol concentrations. This technique may also be adapted to assess regional deposition within the lung by considering sequential boluses delivered to variable inhalation depths. However, gamma scintigraphy, either planar or 3D SPECT (single photon emission computerized tomography) imaging, has been more commonly used to assess both total and regional deposition of inhaled aerosols. Combining radiolabeled gas and particle imaging can also provide information on the ability to deliver aerosol to regions of the lung with poor ventilation. An added advantage to the use of radiolabeled aerosols is that the retention of the deposited particle may also be determined if the label remains tightly associated with the particle or molecule of interest. This technique may also allow for assessing new methodologies for enhancing bioavailability of deposited drug molecules on the airway surface. For example, we might assess the effectiveness of mucociliary inhibitors and absorption enhancers proposed to increase drug targeting to subepithelial tissue in the bronchial airways. Imaging by positron-emission tomography (PET) allows for some inhaled drugs to be chemically labeled with positron emitters (i.e. incorporation of the radiotracer directly into the drug molecule) that can be imaged for assessment of regional deposition and retention in the lung. Finally, measurement of blood or urine markers for some inhaled drugs can be used to assess deposited dose and bioavailability. With this array of methodologies, investigators have been able to successfully determine the optimal aerosol delivery conditions, e.g. particle sizes, structures, and breathing conditions, for their particular therapy of interest. Furthermore, based on results from these experimental assessments of drug dosimetry, new technologies have emerged to further enhance drug delivery to the lungs.

6E3
MOUTH-THROAT DEPOSITION OF AEROSOL BOLUSES INHALED DURING FLOW ACCELERATION. WARREN H. FINLAY, Biljana Grgic, University of Alberta, Canada

We have previously performed in vitro measurements on deposition of aerosols in the mouth-throat region during steady flow. In the present experiments, this work is extended to examine the effect of unsteady flow acceleration on mouth-throat deposition. This was done by inserting short bursts of aerosols (i. e. boluses) into flow entering an idealized mouth-throat geometry (the "Alberta geometry") that we have used extensively in the past for steady flow deposition measurements. The boluses were inserted at 30 l/min. centered at a flow acceleration of 4 l/sec^2 using a Respiratory Aerosol Probe (Pari, Germany). Monodisperse dioctylphtalate particles of diameter 5 micrometers were used, generated using a condensation aerosol generation (Topas, Germany). For comparison, boluses with the same properties were inserted into steady flow at 30 l/min.

Because of the flow acceleration, boluses of short duration (20 ms half-width) were used in order to have the entire aerosol delivered at nearly the same flow rate and result in meaningful data. However, short duration of aerosol delivery results in very small aerosol mass being delivered. This yielded exceedingly small amounts of aerosol being collected for analysis of deposition, necessitating a high number of repeats of the bolus delivery that was almost beyond the realm of possibility. However, data was successfully obtained and the results indicate that mouth-throat deposition is significantly higher for unsteady vs. steady flow (35% vs. 26%). A possible explanation for this is the realization that flow acceleration leads to higher particle velocities by the time the particles reach their impaction sites, leading to the particles depositing at an effectively higher flow rate. Data supporting this explanation is presented.

6E4
PARTICLE SIZING OF EXHALED MAINSTREAM TOBACCO SMOKE. JOHN McAUGHEY, Phil Biggs and Richard Baker, British American Tobacco, Southampton, UK

Mainstream tobacco smoke is a complex organic-based, dynamic liquid droplet aerosol, generated from a combination of combustion (at up to 950oC), with pyrolysis and distillation (at less than 600oC) of plant material (Baker, 1999). Particle diameters from 180-860 nm have been reported in various review articles (Ingebrethsen, 1986, McRae, 1990, Bernstein, 2004). A review of the published literature and unpublished internal data indicates that, on average, 60 to 80% of the mainstream smoke particulate matter is retained in the lungs after inhalation. However, there remains a lack of data reconciling particle retention with the physical properties of the smoke. It is recognised that retention will be determined by a combination of aerosol, cigarette, puff, inhalation and physiological parameters. Of the aerosol properties, particle diameter is important in determining retention. It is known, however, that the dynamics of tobacco smoke will cause its continued growth by coagulation and by hygroscopicity during inhalation. It has further been suggested that smoke retention at high particle concentrations may be influenced by behaviour of the particle cloud rather than that of individual particles.

In this work, particle size data are reported for inhaled versus exhaled mainstream tobacco smoke. Measurements were conducted using a fast electrical mobility spectrometer at 10 Hz resolution in the range from 10-1000 nm (Model DMS-500, Cambustion, UK). Fresh cigarette smoke on inhalation was typically 150-200 nm median diameter, with exhaled median smoke diameters in the region of 300–400 nm. Typical periods for the combined puff, inhalation and exhalation cycle were of the order of 6-8 seconds. These data will be discussed in the context of published retention data and current computer models of particle retention.

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6E5

THE REGIONAL LUNG DEPOSITION OF INHALED, NEBULIZED AEROSOL DEPOSITED FROM A SHALLOW BOLUS WITH BREATH HOLDING COMPARED TO CONTINUOUS, RAPID, SHALLOW BREATHING.. KIRBY ZEMAN and William Bennett. Center for Environmental Medicine, Asthma and Lung Biology, University of North Carolina, Chapel Hill, NC

Aerosol dosimeters and inhalers that are designed to deliver inhaled particles for preset inhaled volumes and for variable periods of time during the inhalation phase are presumed to be a useful strategy for targeting the bronchial airways and limiting systemic exposure to therapeutic compounds by absorption through alveolar tissue. Delivering particles into the theoretical volume of the conducting airways should produce a high regional deposition predominately in those airways.

We designed a system to trigger nebulization of a modified DeVilbiss 646 jet nebulizer for delivery of small boluses (40ml) to shallow volumetric front depths (VFD) in the lung. The boli of insoluble Tc99m-labelled sulfur colloid aerosol (6.5 um MMAD) were injected into the inhaled tidal volume (500 ml starting from FRC) to a mean VFD of 60% anatomic dead space, followed by a 5 second breath hold and forced expiration. By gamma camera scintigraphy taken immediately after the inhalation of several breaths, the regional deposition of the boli particles in 20 subjects was compared by unpaired t-test to the regional deposition obtained by continuous aerosol (5 um MMAD) delivery during the inhalation phase of periodic breathing (500 ml tidal volume at 25 breaths/minute) in another group of 17 subjects. This latter technique was chosen to maximize deposition by inertial impaction in the bronchial airways while minimizing residence time and thus deposition by sedimentation in the deep lung.

Our indicators of bronchial versus acinar deposition showed no difference between the two methods, bolus vs. continuous breathing, respectively: 1. C/P, the central-to-peripheral lung counts normalized to their Xe133 equilibrium scan, 1.85 versus 1.77 (NS); 2. the total lung clearance (%) of labeled particles through 2 hours, 24 versus 31, p=0.14; 3. the total lung clearance (%) through 24 hours 61 versus 59 (NS); and the fraction of all deposited particles that was deposited in the mouth, 0.31 versus 0.33 (NS).

There may be little advantage to incorporating shallow bolus injection into the design of delivery systems for particles in this size range. Aerosol delivery systems that are principally designed to control breathing patterns and aerosol size characteristics are likely to be efficient for targeting therapeutic agents to the bronchial airways.

6E6

FABRICATION OF SUB-MICRON DIAMETER AEROSOL FIBERS BY PHYSICAL VAPOR DEPOSITION. ANDREW R. MARTIN, Warren H. Finlay, Department of Mechanical Engineering, University of Alberta, Edmonton, Canada; Doug Vick, Michael J. Brett, Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Canada.

The tendency of elongated, cylindrical particles entrained in a shear flow to align with their major axes parallel to the direction of fluid motion is of particular importance to the dosimetric assessment of inhaled fibrous aerosols. Aerodynamic alignment with inhaled air streamlines allows fibers to penetrate deep into the lung, whereas compact particles of similar mass would be filtered out in the upper respiratory tract. For researchers interested in the delivery of inhaled pharmaceutical aerosols, such considerations have raised the possibility of loading particles with increased drug mass (by increasing length), without appreciably enhancing deposition in the mouth, throat, and upper airways. For toxicologists, the potential health risks of long, insoluble fibers are well known: fibers longer than alveolar macrophage diameters (~ 10-20 um) are poorly cleared from the distal regions of the lung, thus raising the possibility of carcinogenic activity.

Currently, much of our understanding of the respiratory tract deposition of inhaled fibers is based on mathematical models built around theoretical equations. Unlike for spherical particles, little empirical data exists with which to evaluate such analytical or numerical predictions. The limited amount of data is not surprising given ethical concerns over requiring human subjects to inhale potentially dangerous fibrous aerosols, and the difficulty of generating monodisperse (in both diameter and length) fibers for methodical, in vitro testing.

We are exploring the promise of a physical vapor deposition (PVD) process known as glancing angle deposition (GLAD), developed at the University of Alberta, as a method for fabricating monodisperse, sub-micron diameter aerosol fibers. The GLAD technique enables controllable growth of porous thin films consisting of discrete columnar structures. Separation of these structures from their substrate in an aqueous suspension, and subsequent nebulization, yields aerosol fibers of a specified size and shape. At this point, silica and TiOx fibers have been generated; therefore, to facilitate chemical assay in deposition experiments, the tips of these fibers have been tagged with the UV-absorbent compound tris-8-hydroxyquinoline aluminum (Alq3) by vacuum deposition. Combined, these processes show promise for generation of recoverable, monodisperse aerosol fibers for in vitro deposition experiments.

7A1

OBSERVATION OF BIOGENIC NUCLEATION EVENTS AT LOW TIDE IN NOVA SCOTIA, CANADA. James Allan and and Michael Cubison, University of Manchester, United Kingdom, SUSANNE HERING, Aerosol Dynamics, Berkeley, CA, John Ogren, NOAA, Boulder, CO, Jose-Luis Jimenez and Peter DeCarlo, University of Colorado, Boulder, CO, Allen Goldstein and Dylan Millet, University of California, Berkeley, CA.

Evidence of new particle formation was found for the approximately one-half of the days of a six-week study period in the summer 2004, at Chegogue Point, a rural site located on the coast near Yarmouth, Nova Scotia, Canada. Concentrations, as measured by a water-based and butanol-based condensation particle counters, reached as high as 100,000 cm-3. Mobility size distributions show that most of the periods of high concentration were dominated by particles in the sub-10 nm size range. These high number concentration events coincided with low tide, and are believed to be associated with the biogenic release of iodine, as has been observed at Mace Head by O'Dowd and coworkers. Occasional spikes in of particles in the 20-40 nm size range were observed coincident with ferry crossings. The overall profile of particle number concentrations was characterized by sharp spikes of one to three hours duration overlaying a slowly varying background. The background aerosol varied from 500 to 5000 cm-3, and correlated with carbon monoxide concentrations, indicative of transport from an urban source region. Although some of the tidal nucleation events were of several hours duration, there was no evidence of particle growth.

7A2

APPLICATION OF THE CACM AND MPMPO MODULES USING THE CMAQ MODEL FOR THE EASTERN UNITED STATES. JIANJUN CHEN, Robert Griffin, Huiting Mao, University of New Hampshire, Durham, NH

The Caltech Atmospheric Chemistry Mechanism (CACM) and the Model to Predict the Multi-phase Partitioning of Organics (MPMPO) were updated with a detailed treatment of the oxidation mechanism and secondary organic aerosol (SOA) formation potential of α-pinene, ß-pinene, and d-limonene. The updated CACM and MPMPO modules were incorporated into EPA's CMAQ model. The revised CMAQ model is used to simulate air quality over the Eastern United States, with a particular focus on New England (NE) for the period August 3-4, 2004. Much of NE featured clear or partly cloudy skies with high temperatures in the range of 27 to 32 ºC during the daytime of August 3, 2004. A cold front pushed through NE during August 4, 2004. For these two days, 24-hour-average organic and PM2.5 concentrations were approximately 7 µg/m3 and 13 µg/m3, respectively, at Thompson Farm, a rural site in Southeastern New Hampshire. The model results (e.g. ozone, PM2.5, and individual PM2.5 chemical components) will be compared against various observational datasets (e.g. AIRMAP, IMPROVE, SEARCH, and EPA's AIRs), as well as CMAQ model predictions using the CB4 gas-phase mechanism and the incorporated SOA approach based on the SORGAM module. Emphasis will be placed on SOA predictions. The contributions from anthropogenic and biogenic precursors to total simulated SOA will be quantified. The sensitivity of SOA predictions to the primary organic aerosol emissions will be evaluated. The difference in SOA predictions with or without UNIFAC activity coefficient calculations will also be examined.

7A3

A PARCEL MODEL STUDY OF SELECTED AIRBORNE MEASUREMENT CASES DURING THE ICARTT 2004 FIELD CAMPAIGN - CLOUD PROCESSING OF GASES AND AEROSOLS.

WANMIN GONG, W. Richard Leaitch, Nicole Shantz, Anne Marie Macdonald, Katherine L. Hayden, Kurt G. Anlauf, Desiree Toom-Sauntry, Amy Leithead, Shao-Meng Li, Sangeeta Sharma, J. Walter Strapp, Meteorological Service of Canada, Toronto, Ontario, Canada M3H 5T4

While in-cloud processes are perceived to play an important role in determining atmospheric composition, they are poorly understood and confidence in the modelling of in-cloud processes is relatively low. Particularly there is a lack of suitable observations for evaluating current model parameterizations of in-cloud processes. As part of the ICARTT 2004 campaign, an aircraft study of Chemical transport and Transformation by Cloud (CTC) was conducted. Measurements of trace gases, aerosol particles, cloud droplets, and bulk cloud water were made from the NRCC Convair 580 aircraft between July 20 and August 18, 2004 over southwestern Ontario, northern Ohio, and eastern Michigan.

In the present study, an aerosol microphysics parcel model, coupled with size resolved cloud chemistry, is used to simulate several towering cumulus cases from the aircraft study to assist with data analysis and to investigate interactions between microphysics and chemistry. In particular, sensitivity tests are conducted to examine the effect of aerosol composition, size distribution, and mixing state on aerosol activation and its subsequent impact on cloud chemistry. This study will also assist with the development of improved parameterizations of cloud processing of gases and aerosols in large scale air quality models.

7A4

EVALUATION OF A NEW CLOUD DROPLET FORMATION PARAMETERIZATION WITH IN SITU DATA FROM ICARTT.

CHRISTOS FOUNTOUKIS, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA; Nicholas Meskhidze, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA; Athanasios Nenes, Schools of Chemical and Biomolecular Engineering and Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA; William Conant, Environmental Science and Engineering, California Institute of Technology, Pasadena, CA; John H. Seinfeld, Environmental Science and Engineering and Chemical Engineering, California Institute of Technology, Pasadena, CA

Developing accurate parameterizations of aerosol-cloud interactions are crucial for reducing the uncertainty in assessments of the aerosol indirect effect. Parameterization assessments should not only be carried out by comparing with the predictions of comprehensive numerical models but with observational data as well. The latter can serve as a source of unconstrained constants that exist in the parameterization, such as water vapor accommodation coefficient.

In this work we analyze the cumuliform and stratiform cloud data collected during the ICARTT (International consortium for atmospheric research on transport and transformation) mission (Cleveland, OH; August, 2004) and use them to evaluate the modified NS parameterization (Fountoukis and Nenes, 2004; Nenes and Seinfeld, 2003). In situ data sets of aerosol size distribution, chemical composition and updraft velocities are used as input for the parameterization, and the evaluation is carried out by comparing predicted cloud droplet number concentration with that obtained from the observations. The clouds sampled were formed in a diverse set of air masses that span from heavily polluted to clean continental conditions. In addition to cloud droplet number, we also assess the parameterization's ability to capture observed spectral width of the cloud droplet distribution, which is important for predicting the formation of drizzle and precipitation.

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7A5

MIXING STATE OF CCN IN THE NORTHEASTERN UNITED STATES.

JEESSY MEDINA, Athanasios Nenes, Georgia Institute of Technology, Atlanta, GA; Laura Cottrell, Robert Griffin, University of New Hampshire, Durham, NH

Ground measurements of cloud condensation nuclei (CCN) were made during July and August of 2004 as part of the NEAQS ITCT-2K4 (New England Air Quality Study - Intercontinental Transport and Chemical Transformation 2004) mission at the Thompson Farm sampling site maintained by the University of New Hampshire. Two continuous-flow streamwise thermal gradient CCN instruments (built by Droplet Measurement Technologies, Inc.) were used for the measurements. The first instrument operated counted CCN concentrations of ambient sample air, while the second counted CCN concentrations of sample air, first classified by a differential mobility analyzer. The supersaturation spectra included 5 settings that ranged from 0.2% to 0.6% every 5 minutes each. To further constrain the measurements, chemical composition of the aerosol was obtained from an Aerodyne Aerosol Mass Spectrometer. By combining both measurements together, the CCN mixing state, as well as insight into the chemical composition and closure can be assessed.

7A6

CLOUD PROCESSING OF THE CHICAGO URBAN PLUME.

W. RICHARD LEAITCH, Anne Marie Macdonald, Kurt G. Anlauf, Desiree Toom-Sauntry, Katherine L. Hayden, Wanmin Gong, Amy Leithead, Shao-Meng Li, J. Walter Strapp, Meteorological Service of Canada, Toronto, Ontario, Canada M3H 5T4

The Chemical transformation and Transport by Clouds project (CTC) was undertaken by Canadian government and university scientists from July 22 to August 18, 2004 as part of the ICARTT 2004 intensive field study. The objective of CTC is to try to improve our knowledge of how clouds based in the boundary layer process chemicals. The main field activity of CTC was to conduct measurements of trace gases, aerosol particle physics and chemistry, and cloud microphysics and dynamics during ICARTT. The measurement platform was the National Research Council of Canada Convair 580, and several flights were conducted below and in clouds. Two broad types of cloud were studied (convective towers and boundary layer stratocumulus). On August 10, two flights were conducted crossing the urban plume from Chicago and the surrounding area at two locations
successively downwind. The plume was first sampled on the eastern side of Lake Michigan, and about five hours later it was sampled on the western side of Lake Erie. On both flights, sampling of the plume was conducted in and below boundary layer cloud. The results of the measurements and the application of a detailed parcel model to this case are used to consider how particle activation in cloud and in-cloud chemistry impacted the evolution of this plume.

7B1

SOA PRODUCTION FROM ISOPRENE: AQUEOUS-PHASE MECHANISMS.

ANNMARIE G. CARLTON, Barbara J. Turpin, Department of Environmental Science, Rutgers University; Katye Altieri, Sybil Seitzinger, Institute of Marine and Coastal Sciences, Rutgers University

Glyoxal and methylglyoxal are water-soluble gas-phase oxidation products of isoprene and aromatic compounds. Lim et al., (2005) predicted that aqueous-phase oxidation of these compounds in cloud droplets produces glyoxylic and oxalic acid. These products remain, in part, in the particle phase after droplet evaporation. The result is SOA formation through cloud processing. Lim et al. (2005) estimated this process contributes 1.6 Tg yr-1 to global biogenic SOA production.

In this work, laboratory experiments were conducted to test and refine the mechanistic model used by Lim et al. (2005). Batch photochemical aqueous-phase oxidation experiments were conducted with hydrogen peroxide plus glyoxal or methlyglyoxal in 1 liter borosilicate reaction vessels with a monochromatic UV source (254 nm). Control experiments were conducted 1) without UV and 2) without hydrogen peroxide. Time series samples were taken over one hour at pH values typical of cloud and fog droplets. Samples were analyzed by high performance liquid chromatography (HPLC) and electro-spray ionization-mass spectrometry (ESI-MS) for precursors and products. Results are largely in agreement with Lim et al. (2005), showing that products of aqueous-phase photooxidation include oxalic, glyoxylic, pyruvic, acetic and formic acids. In addition, evidence was found for the formation of several carboxylic acid dimers. This evidence is presented in a companion paper (Altieri et al.). The presence of dimers suggests that SOA formation is greater than that predicted by Lim et al (2005). Experimental results were used to further elucidate the products of the aqueous-phase oxidation pathways and to improve our understanding of in-cloud SOA formation pathways. Yields and implications for in-cloud SOA formation will be discussed.

7B2

ORGANIC NITRATE PRODUCTION FROM A-PINENE OXIDATION BY O3 IN PRESENCE OF NO AND ITS INFLUENCE ON SOA FORMATION.

JIEYUAN ZHANG, Neil Donahue, Carnegie Mellon University, Pittsburgh, PA

The emission rate of biogenic volatile organic compounds (BVOCs), such as isoprene, monoterpenes, and sesquiterpenes, is very large. The oxidation of these BVOCs produces organic peroxy radicals (RO2), key intermediates with multiple reaction pathways. The reaction of peroxy radicals (RO2) with nitric oxide (NO) sits in the very center of atmospheric chemistry. Organic nitrates produced by this reaction will influence secondary organic aerosol (SOA) formation dramatically because nitrate volatility will differ from that of compounds produces in the absence of NO. We shall combine a theoretical estimate of nitrate yields for these systems with experimental data for a few test cases.

For the theoretical estimate, we set up a nitrate yield model using both quantum chemical calculations of the potential energy surface and existing yield data for relatively small carbon numbers (C5-C8). The model successfully reproduces multiple features of existing data quantitatively, including both high and low pressure asymptotes to nitrate production as well as the observed shifting of pressure falloff curves with carbon number. Consequently, we present a new parameterization of nitrate yields, providing interpolation equivalent to existing parameterizations but dramatically improved extrapolation behavior. Extrapolation of the data shows that the nitrate yields from large carbon number precursors (larger than C10) becomes independent of carbon number, with a high pressure limit around 0.45 below 1 atmosphere.

We shall then present data from a high pressure flow reactor showing nitrate yields from α-pinene oxidation by O3 in presence of NO. The products are detected by Fourier transform infrared spectrometer (FTIR) and proton transfer react mass spectrometer (PTR-MS). The same system was studied in a smog chamber to get the SOA composition and yield by GC-MS and a scanning mobility particle sizer. Combing the experimental results at both conditions, we shall discuss the organic nitrate production from α-pinene oxidation by O3 in presence of NO and its influence on SOA formation.

7B3

SECONDARY ORGANIC AEROSOL FORMATION FROM ISOPRENE OXIDATION.

JESSE H. KROLL, Nga L. Ng, Shane M. Murphy, Roya Bahreini, Richard C. Flagan, John H. Seinfeld, California Institute of Technology, Pasadena, CA

We describe chamber studies of the formation of secondary organic aerosol (SOA) from the oxidation of isoprene (2-methyl -1,3-butadiene). Isoprene is one of the most abundant non-methane hydrocarbons emitted into the troposphere (with a source strength of ~500 Tg/year), so even small SOA yields may have a large impact on SOA formed both locally and globally. Reactions are carried out in Caltech's dual 28 m3 Teflon chambers (at 20 deg C and 50% RH), in the presence of ammonium sulfate seed particles; aerosol growth is monitored by a differential mobility analyzer (DMA) and an Aerodyne aerosol mass spectrometer (AMS). Isoprene oxidation is initiated by introduction of ozone (for ozonolysis experiments), introduction of both ozone and nitrogen dioxide (for nitrate radical + isoprene experiments), or introduction of an OH precursor followed by UV irradiation (for photooxidation experiments). Aerosol growth, with yields on the order of a few percent, is observed for both photooxidation and nitrate radical experiments, though not for ozonolysis experiments. Photooxidation experiments are carried out under a range of experimental conditions in order to establish the dependence of SOA growth on NOx level. In order to better understand the mechanism of SOA growth, the oxidation of known isoprene oxidation products (methacrolein, methyl vinyl ketone, and 3-methyl-furan) is also studied. The roles of organic nitrate formation and oligomerization reactions on SOA growth are examined, and the implications of this work for tropospheric SOA production are discussed.

7B4

AN UPGRADED ABSORPTIVE SECONDARY ORGANIC AEROSOL PARTITIONING MODULE FOR THREE-DIMENSIONAL AIR QUALITY APPLICATIONS.

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The secondary organic aerosol (SOA) module used in the Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (MADRID) was formulated based on empirical SOA formation data from environmental chambers. The MADRID aerosol treatment has been implemented within the Community Multiscale (CMAQ) model to provide an alternative treatment for simulating the formation and fate of particulate matter in the atmosphere.

Anthropogenic SOA precursor gases are represented by two aromatic compounds and biogenic SOA precursors are represented by five monoterpenes and a sesquiterpene. The secondary organic aerosol algorithm, representing of 24 surrogate condensable compounds forming SOA via absorptive partitioning, has been optimized to require reasonable computational resources compatible with three-dimensional simulations over large domains and long periods. As an improvement to the science represented in MADRID, two additional anthropogenic precursors have been added to represent SOA formation from long-chain alkanes and PAH species.

The presence of water in an organic particulate matter mixture affects the characteristics of the absorbing medium (e.g., molecular weight) and the activity coefficients of the condensing compounds. The role of water on the partitioning of SOA has been investigated and the relative humidity (RH) dependence of the partitioning coefficients has been parameterized in the model. The new RH dependence algorithm has been implemented in the CMAQ-MADRID air quality model.

An eleven-day episode during the 1999 Southern Oxidant Study is used as a case study to explore the potential importance of alkane and PAH precursors, especially in urban areas. The effects of relative humidity, both in the amount of SOA formed and in the temporal distribution of SOA concentrations, are also investigated.

7B5

HETEROGENOUS PARTICLE PHASE PRODUCTS FROM ALPHA-PINENE OZONE OXIDATION.

NADINE CZOSCHKE, Myoseon Jang, University of North Carolina

The α-pinene ozone atmospheric oxidation produces a range of semivolatile oxygenated products. These products are able to either self nucleate or condense onto preexisting particulate matter to form secondary organic aerosol (SOA). It has been shown in our laboratories that the presence of an inorganic acidic seed aerosol enhances the mass of SOA produced from a given α-pinene oxidation. The mechanism for producing this increased mass is believed to be several categories of heterogeneous acid catalyzed reactions such as aldol condensation and hydration/acetal formation. Several groups have also shown the presence of oligomeric compounds in SOA, especially under conditions involving an inorganic acidic seed aerosol. This presentation will highlight some of the structures of the products from these heterogeneous reactions that can be seen with analysis using an ion trap MS as well as changes in the product distribution in the presence of different inorganics.

The analyzed products are from indoor chamber experiments in a 2 m3 Teflon film chamber. Ozone oxidation of α-pinene was carried out in the presence of inorganic seed aerosols either with or without an acid catalyst. Sodium chloride is used as the neutral seed aerosol and a mixture of ammonium sulfate and sulfuric acid is the acidic seed aerosol. The products are analyzed using the spectra from a Varian ion trap mass spectrometer. PFBHA derivitization was used to aid in the identification of the oxygenated products of the heterogeneous reactions.

7B6

OZONOLYSIS OF A-PINENE: TEMPERATURE DEPENDENCE OF SOA YIELDS.

RAVI KANT PATHAK, Neil Donahue, Spyros N. Pandis, Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, USA; Charles Stanier, Chemical & Biochemical Engineering and IIHR Hydroscience and Engineering University of Iowa, Iowa City, IA, USA

Despite a number of smog chamber studies of the α-pinene/O3 system, the role of temperature on α-pinene secondary organic aerosol SOA yields remains poorly understood. In this study, the temperature dependence of the SOA yields during the ozonolysis of α-pinene was investigated. Experiments were performed with and without ammonium sulfate aerosol seeds at RH<10% and temperatures between 15oC and 40oC in a 10 m3 temperature controlled smog chamber. The initial mixing ratio of α-pinene was varied from 10 to 50 ppb and an excess of ozone together with OH-scavenger were used in all the experiments.

The lack of inert seeds during low α-pinene concentration experiments leads to experimental artifacts mainly due to losses of semi-volatile compounds to the walls of the chamber. The α-pinene SOA yields show a modest dependence on temperature between 15oC and 40oC. For example, SOA yields for 50 ppb of reacted α-pinene as were 14.1%, 12.3%, 11.8%, and 10.3% at 15oC, 20oC, 30oC and 40oC, respectively. The yield at 15oC was 8.4% for 20 ppb α-pinene and 4.8% for 10 ppb of α-pinene.

The existing parameterizations of SOA yields for this system are unable to predict α-pinene yields accurately at lower temperatures and their estimates differ from our measurements by a factor of 2 in general. In this study, we propose a new four-product parameterization based on our measurements at four temperatures between 15oC and 40oC and also the measurements by other researchers (Hoffmann et al., 1997; Griffin et al., 1999; Cocker et al. 2001).

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7C1

EVALUATION OF ION MOBILITY SENSOR (IMS) FOR FIRE DETECTION.

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As a part of a smart fire detection sensor package for commercial aircrafts, ion mobility sensor (IMS) was designed by researchers in NASA for particle concentration sensing. Fire detection and management in aircrafts is an important issue for airlines. Besides the demand of high accuracy to detect all real fires, false alarm is another concern for a fire detection system used onboard. It is because the emergency landing due to false alarm presents the safety issue for landing airports meanwhile significantly reduces the profit of airline companies. A new fire detection package has thus been designed recently to better address the issues. During the recent FAA fire detection workshop, this fire sensor package demonstrates its amazing ability of 100% true fire detection and 100% false fire rejection compared with that of existed commercial fire detectors. The sensor package includes different sensors to detect different gaseous species and particle concentration. The readings from different sensors are fed in an on-board CPU to intelligently predict the incipient of true fires. Ion mobility sensor (IMS) is the unit in the package for detecting the presence of particles. The IMS detection of the particle concentration is based on the ion-depletion principle. Bipolar air ions are produced by radioactive material and separated by an electrical field. Ions of one polarity are then trapped in an electrostatic well once separated. The ion concentration reduces when particles are past through the ion well and acquire ions. The ion concentration is detected by releasing ions from the well and with a current sensor downstream of the well. The difference of ion concentration with and without particles serves as the indication for particle concentration detection.

In this study, the performance of the prototype IMS has been evaluated experimentally and numerically. In the experimental study the effects of flowrate and relative humidity on the IMS signal were first investigated. The information can be used to calibrate the IMS signal when operated in different environmental conditions. The second part of this testing is to challenge IMS with particles of defined particle size and concentration. Monodisperse particles of different sizes are generated using the atomizer-DMA-classification technique as test aerosol. The concentration of monodisperse particles was varied with a co-axial dilutor downstream of the aerosol generation system. A CPC (TSI model 3022) was used to monitor the concentration of test particles prior to the introduction to IMS. The quantitative reduction of IMS ion signal was then related to CPC readings. The collected data provide the scientific evaluation of IMS performance. A semi-empirical model based on Fuchs' charging theory was also developed to interpret the data collected. In this talk we will present both the experimental and modeling aspects of this study.

7C2

LASAG (LOS ALAMOS SOLID AEROSOL GENERATOR).

MURRAY E. MOORE, Los Alamos National Laboratory, Los Alamos, NM

Abstract:
At the Los Alamos National Laboratory a new aerosol wind tunnel facility has been constructed. Aspects of this facility are similar to that described by Witschger, et. al. (Journal of Aerosol Science, Vol. 28, No. 5, pp. 833-851, 1997). The dominant analytical approach they describe includes an aerosol generator for solid aerosol particles (specifically spherical glass bead aerosols). The Los Alamos facility needed such an aerosol generator, and after the evaluation (and subsequent rejection) of a commercial product, and checking the availability of other aerosol generators, a concept idea for a new type of generator was developed by Dr. Murray E. Moore of Los Alamos. Several prototypes were tested until a satisfactory working design was finalized. A U.S. patent application is pending for the design of this aerosol generator.

Although developed as an aerosol generator for analytical purposes, this device could be used for entraining a variety of solid particulates into an air stream, for a range of applications. These could include pharmaceuticals for therapeutic treatment, pollens or beneficial microbes for agricultural applications, metallic powders for rapid prototyping or even solid dyes or paints for commercial and recreational purposes.

The LASAG (Los Alamos Solid Aerosol Generator) has inherent cost advantages since the prototype was built from off the shelf parts arranged in a proprietary fashion, with the total cost of parts at about $200 USD (depending on the size scale of the prototype). (The finished parts for a manufactured or molded version of the device might cost more.)

If the size of the generator were increased at a given scale factor, the system would produce more aerosol particles. For a given size of the LASAG, there is a maximum amount of solid particulate that can be generated, but the system can be tailored to generate a lesser amount with the same size device. With the particular prototype that is currently in use, the measured mass output of aerosol was about 10 grams per hour in an air flow of about 15 LPM.

The LASAG design virtually guarantees the absence of clogging of the device by solid material. One commercially available generator, in particular, was rejected from consideration due to mechanical clogging by large size glass bead aerosols (over about 25 microns diameter). Except for the external source of filtered air, the LASAG is a non-pressurized system, operating at a nominal gauge air pressure. Bulk feed solid particulates are added at ambient conditions, enhancing the ability to control the feed material.

7C3

SIZE DETERMINATION AND MONITORING OF STABILITY OF MACROMOLECULES USING NANOAEROSOL MEASURING TECHNIQUES.

WLADYSLAW W. SZYMANSKI, Christian Laschober, Georg Reischl, Institute of Experimental Physics, University of Vienna, Vienna, Austria; Guenter Allmaier, Institute for Chemical Technology and Analysis, Technical University of Vienna, Vienna, Austria

The increasing need for real time measurement of biopolymers with regard to their size combined with observation of biochemical processes requires innovative experimental approaches and tools. Although mass spectrometric methods can accurately determine molecular weights of biopolymers, the measurement must be performed under high vacuum conditions which may adversely affect some biocompounds. Moreover, with the increasing mass of macromolecular complexes the classical MS approach makes the determination of the actual electrostatic charge on species in question extremely difficult. Since nanometer-sized aerosols are comparable with macromolecules based on their mass, an electrostatic mobility analysis technique was used. A must requirement for this approach is a device providing known charge conditioning on the species, which was done using radioactive source and corona discharge. Comparative measurements will be discussed showing the advantages of the latter technique with regard to yield of singly charged species. Using the electrostatic mobility analysis technique the stability of selected noncovalent homo-protein complexes such as e.g. streptavidin, or catalase at different pH values was monitored and their size and size changes as a function of acidity determined. Sizing of chemically well-defined specimen including the intact human rhinovirus, which can be considered as supramolecular noncovalent biocomplex was also successfully performed. Furthermore, after a limited temperature exposure of the virus the release of the so-called capsid proteins was monitored and shift in the size of the virus was measured. This data can be seen as a first documentation of virus characterization using nanoaerosol technique. It demonstrates that intact biospecies not only can be generated by means of this technique but also meaningfully investigated.

7C4

ONLINE MEASUREMENT OF AGGREGATE SURFACE AREA AND VOLUME DISTRIBUTION BY ELECTRICAL MOBILITY ANALYSIS.

ANSHUMAN AMIT LALL and Sheldon K. Friedlander, Department of Chemical Engineering, University of California, Los Angeles, CA

Differential mobility analyzers are usually calibrated for spherical particles, and provide number, area and volume distributions for spherical particles. However these instruments cannot be directly used to obtain the surface area and volume distributions for aggregates. Aggregates are important in technological applications, such as the manufacture of fine powdered materials, and in air pollution and atmospheric sciences. Thus nanoparticle chain aggregates of low fractal dimension are another important limiting case, in addition to spheres; a method is described which makes it possible to relate aggregate surface area and volume distributions to the electrical mobility diameter. This is accomplished by equating the migration velocity of an aggregate to that of a sphere. Particles of equal migration velocities will trace similar paths in the mobility analyzer and have the same mobility diameter (neglecting the Brownian diffusive spread). By equating the migration velocities of a sphere and aggregate, the number and size of the primary particles composing the aggregate can be related to the diameter of a sphere with the same migration velocity.

The method holds for idealized aggregates with low fractal dimension and uniform primary particles in the free molecule size range. The calculation of aggregate surface areas and volumes requires two theoretical \modules\, one for the drag on the aggregates and the other for aggregate charging efficiency. Two modules selected from the literature were used. The results indicate that the surface area distributions of aggregates with parallel orientation relative to aggregate motion are somewhat under-predicted when calculated directly from the mobility diameter. However, the volume distributions are greatly over-predicted, up to a factor of ten compared with values based on the mobility diameter. The affect of aggregate orientation on surface area and volume estimates was also examined.

The method was tested for silver aggregates generated by an evaporation-condensation method. The calculated aggregate number distributions and volume were tested against the experimental data for volume equivalent spheres. For comparison, the aggregate number-size distributions (dn/dlogdm vs dm) were converted to number-volume distributions (dn/dlogv vs v). The aggregates were sintered to obtain spheres with the same volume as the original aggregates assuming that the aggregate volume does not change upon sintering and neglecting coagulation. Thus the number of aggregates in a given volume range (number-volume distribution, dn/dlogv) should not change after sintering to the spheres. The aggregate number-volume distribution based on theory was in good agreement with measured values for sintered volume equivalent spheres. The theoretical volume of aggregates with a given mobility diameter was in good agreement with the values reported in the literature (Park et al., 2004) for diesel aggregates.

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7C5

A METHOD FOR AIRBORNE MEASUREMENTS OF WATER-SOLUBLE ORGANIC CARBON: PILS-TOC RESULTS FROM THE NOAA WP-3D DURING ICARTT.

AMY P. SULLIVAN, Richard E. Peltier, Rodney J. Weber, Georgia Institute of Technology, Atlanta, GA; Charles A. Brock, Joost de Gouw, John S. Holloway, Carsten Warneke, Adam Wollny, NOAA Aeronomy Laboratory and CIRES-University of Colorado, Boulder, CO

On-line airborne measurements of carbonaceous aerosol can provide unique information on its spatial distribution and sources, help assess the importance of the organic carbon fraction on aerosol optical and cloud nucleating properties, and facilitate the study of aerosol plume chemical evolution and aerosol chemical processing. To gain new insights into sources and the chemical transformation of carbonaceous material, a quantitative method has been developed for rapid (3 seconds to 1 minute), sensitive (0.1 micrograms C per cubic meter of air) on-line measurement of bulk organic carbon that is soluble in water (WSOC). In this approach ambient particles are collected into a continuous flowing liquid via the Particle-into-Liquid-Sampler (PILS), insoluble particles are filtered, and the dissolved carbonaceous material quantified with a Sievers Total Organic Carbon (TOC) analyzer [Sullivan et al., 2004]. This paper will present the measurement methodology and results from airborne measurements of the WSOC from biomass, urban, and power plant plumes during the NOAA ITCT 2K4 mission conducted in the northeastern U.S.

Sullivan, A.P., R.J. Weber, A.L. Clements, J.R. Turner, M.S. Bae, and J.J. Schauer, A method for on-line measurement of water-soluble organic carbon in ambient aerosol particles: Results from an urban site, Geophys. Res. Lett., 31, L13105, doi:10.1029/2004GL019681, 2004.

7C6

PARTICLE SENSORS FOR THE TWENTY-FIRST CENTURY: MONITORING, CHARACTERIZATION, EXPOSURE ASSESSMENT AND BEYOND.

MICHAEL APTE, Lara Gundel, Yanbo Pang, Lawrence Berkeley National Laboratory, Berkeley, CA; Justin Black and Richard White, University of California, Berkeley, CA

Epidemiological studies rely on information from both sides of the dose-response equation: risk factor measures and health outcome data, and resolution of their relationships depends upon the quantity, accuracy, specificity and precision of both. Major limitations for existing PM exposure measurement technologies include expense (hardware, operation and analysis); size and weight; operating noise; and ability to track multiple particle characteristics simultaneously. These limitations impact the practicality of conducting population-based PM exposure-related health studies. Advances in PM sensors have not kept up with those of microelectronic innovation; in fact, although expensive electronic monitors exist, most PM monitoring relies upon 19th century technology. This presentation describes the development and testing of two new instruments:

A portable, low-cost, battery-operated instrument has been developed for sampling environmental tobacco smoke and ambient particles. The second-hand smoke sampler (SHSS) collects particles and gas phase constituents for separate analyses. Respirable particles pass through a selective inlet and are collected by thermophoresis onto reflective surfaces. After sampling, the absorbance spectra of the collected particles are used to determine the aerosol mass concentration of both ETS and black carbon particles. The SSHS sampler also integrates four gas-phase passive samplers that are analyzed for nicotine and 3-ethenylpyridine using thermal desorption gas chromatography with a nitrogen-phosphorous detector. An electronic control system activates one of the three pairs of gas and particle collection sites every eight hours for up to a week, enabling collection of time-resolved gas and particle phase data for three distinct daily periods over the week.

The second instrument is a down-scaled microelectromechanical system (MEMS) version of LBNL's prototype Miniaturized System for Particle Exposure Assessment (MSPEA, AAAR 2003) that used a quartz crystal microbalance to measure deposited particle mass and differentiated optically among various PM types in real time (Diesel exhaust, secondhand tobacco smoke, and woodsmoke). The MEMS-PEA has down-scaled aerosol mass sensing by an order of magnitude in size, compared to the MSPEA, by integrating the collection, mass sensing and optical elements in a three-layer compact and rugged stack assembly that is prepared by microfabrication. In addition to monitoring and characterizing airborne particles, the sensor has potential applications in aerosol manipulation, picogravimetry, ventilation, and industrial process control, particle exposure systems for bioassays, diagnostics, toxicity assays, genomics research, manipulation of bacterial and particle-bound viral fragments, and drug development and delivery.

7D1

CLOUD FORMATION ON POLYMERIZED ORGANIC AEROSOL.

MARKUS PETTERS, Sonia Kreidenweis, Kirsten Kohler, Qiang Wang, Anthony Prenni, Paul DeMott, Colorado State University, Fort Collins, CO; Jefferson Snider, University of Wyoming, Laramie, WY

High-molecular-weight organic particles have abundant sources to the atmosphere through secondary formation from both biogenic and anthropogenic precursors (SOA aerosol). During the last few years, measurements by several different groups have shown surprisingly similar water uptake characteristics for both SOA and humic like particles. For laboratory-generated SOA aerosols, Baltensperger et al. (2005) show that hygroscopic growth increases over the first 7 hours of the experiment, but then remains constant for over 20 hours, despite evidence that oligomerization continues during the entire period. Conversely, cloud condensation nuclei activity of polymerizing SOA aerosol decreases with time (VanReken et al., 2005). These observations are at odds with the classical theory of hygroscopic growth, i.e. Kohler theory, that is used widely in the Atmospheric Science community. In particular, Kohler theory predicts that cloud condensation nuclei activity and hygroscopic growth below 100% relative humidity are not independent of each other. To overcome this apparent contradiction, we suggest a modified version of Kohler theory that can explain these observations.

7D2

MODELING AEROSOL FORMATION AND COMPOSITION FROM B-PINENE OZONOLYSIS USING GAS PHASE KINETICS AND GAS-PARTICLE PARTITIONING THEORY.

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A semi-explicit mechanism was developed and used to describe the formation and composition of gas and secondary organic aerosol from the gas phase ozonolysis of ß-pinene. The model was tested against experimental results obtained from large outdoor Teflon film chambers at the University of North Carolina (UNC) smog chamber facility. The model couples gas phase reactions with partitioning processes and possible particle phase reactions for a wide range of conditions. Partitioning was treated as an equilibrium between the rate of particle uptake and rate of particle loss of semi-volatile terpene reaction products. The model was found to provide reasonable predictions of secondary aerosol mass production. Gas and aerosol reaction products over time were also simulated over a variety of different conditions. Model sensitivity was tested and discussed with respect to effects of temperature, presence/absence of OH radicals scavenger, effect of condensed phase association reactions, humidity, water uptake, and reactant concentrations.

7D3

COMBINED NUCLEATION EXPERIMENTS ON N-NONANE USING A TWO VALVE EXPANSION CHAMBER AND A SUPERSONIC NOZZLE.

DAVID GHOSH, Judith Wölk, Reinhard Strey, Universität zu Köln, Köln, Germany; Yoojeong Kim, Worcester Polytechnic Institute, Worcester, MA; Murad Gharibeh, Shinobu Tanimura and Barbara E. Wyslouzil, The Ohio State University, Columbus, OH

The condensation behavior of n-nonane has been investigated using a two piston expansion chamber and a supersonic Laval nozzle. In the scope of this work the condensible species, n-nonane has been treated as a thermally perfect, calorically imperfect vapor. In the two valve expansion chamber the nucleation rates were measured within1 K of 221 K, 226 K and 231 K. In the supersonic Laval nozzle, the temperature range was 180 K – 215 K and we estimated that the maximum nucleation rate Jmax is 5x10^(16) /cm^3/s. Comparing the experimental data to the predictions of classical nucleation theory reveals much higher experimental rates for both sets of experiments. Finally, a scaling analyses using Hale's scaled nucleation model [1,2] shows that the experiments conducted in the supersonic Laval nozzle and the two piston expansion chamber are consistent with each other as well as the low pressure measurements conducted by Peters et. al. [3].

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7D4

PROTECTION SCHEMES DURING PUMP-DOWN FOR CRITICAL SURFACE IN VACUUM ENVIRONMENTS.

JUNG H KIM, Christof Asbach, Se-Jin Yook, David Y.H. Pui, University of Minnesota, Minneapolis, MN; Heinz Fissan, IUTA, Germany; Kevin J. Orvek, Intel Corporation, Hudson, MA; Arun Ramamoorthy, Pei-Yang Yan, Intel Corporation, Santa Clara, CA

This presentation addresses a study of particle formation during vacuum pump-down and methods that can be incorporated to protect critical surfaces (like semiconductor wafers or masks) from those particles. Particle formation during pump-down was re-examined with temperature measurements. Particles were intentionally produced with hard pump-down for studying protection schemes. For the first step, a face-down approach for a critical surface was used to investigate the effect of protection from particle contamination. It was very effective to hold a critical surface face-down for protection with the use of high gravitational settling velocity in vacuum environment. However, the face-down approach did not sufficiently protect the critical surface. For the second step, a bottom protective plate was introduced below the critical surface to improve the protection efficiency. The bottom plate played a great role in protection of the critical surface with preventing particle formation near the critical surface by keeping the surrounding gas temperature high enough to avoid particle formation as well as with potential blocking of incoming particles toward the critical surface. Higher gas temperature intrinsically avoids formation of residue particles by the condensation process during pump-down.

7D5

THE EFFECT OF CONDENSATION ON THE BOUNDARY LAYER THICKNESS IN SUPERSONIC FLOW. SHINOBU TANIMURA, Barbara E. Wyslouzil, Department of Chemical and Biomolecular Engineering, The Ohio State University, Columbus, OH; Mark Zahniser, Joanne Shorter, David Nelson, and Barry McManus, Aerodyne Research Inc., Billerica, MA

We used a tunable diode laser absorption spectrometer and a static pressure probe to follow changes in the temperature, vapor phase concentration of D2O, and static pressure during condensation in a supersonic nozzle. Using the measured static pressure ratio p/p0 and mass fraction of condensate g as inputs to the diabatic flow equations, we determined the area ratio (A/A*) Wet and the corresponding centerline temperature of the flow during condensation. From (A/A*)Wet we determined the boundary layer displacement thickness during condensation (d#) Wet. We found that (d#)Wet first increases relative to the value of d# in a dry expansion (d#)Dry, before becoming distinctly smaller than (d#)Dry downstream of the condensation region. After correcting for the temperature gradient across the boundary layers, the temperature determined from p/p0 and g agreed with the temperature determined by the laser absorption measurements within our experimental error (±2 K) except when condensation occurred too close to the throat. The agreement between the two temperature measurements let us draw the following two conclusions. First, the differences in the temperature and mole fraction of D2O determined by the two experimental techniques, first observed in our previous study [Paci et al., J. Chem. Phys. 121, 9964 (2004)], can be explained sufficiently by changes in d# caused by the condensation of D2O except when the phase transition occurs too close to the throat. Second, the extrapolation of the equation which expresses the temperature dependence of the heat of vaporization of bulk D2O liquid, is a good estimate of the heat of condensation of supercooled D2O down to 210 K.

7D6

SUPERSATURATION IN THE WYOMING CCN INSTRUMENT. JEFFERSON SNIDER, University of Wyoming; Markus Petters, Colorado State University

Two University of Wyoming thermal diffusion cloud condensation nuclei (CCN) instruments were intercompared using test aerosol composed of sodium chloride and ammonium sulfate. The objective of this work is the determination of maximum chamber supersaturation within the thermal diffusion CCN chamber. This required an analysis of error (random and systematic) coming from calibration of the light scattering and plate temperature measurement systems used by the Wyoming instruments. Our assessment was conducted at four nominal supersaturations (0.2, 0.4, 0.8 and 1.6%). With the exception of the smallest nominal supersaturaton (0.2%), relative error associated with the scattering detection calibration is +-20%. This has contributions from a random and systematic component. Determinations of the maximum chamber supersaturation, derived from determinations of the test particle size that produces 50% activation, are associated with a +-15% relative uncertainty. Determinations of the maximum chamber supersaturation coming from these studies are ~40% smaller than that inferred from measurement of the plate temperatures via thermal gradient diffusion chamber theory. Using spherical nearly-monodisperse test particles, mobility classified at 73% relative humidity, we demonstrate that most of the 40% bias is not the result of test particle asphericity, or of the presence of air or water occlusions within the test particles, as had been conjectured previously.

7E1

MEDICAL AEROSOLS AND THE MODERN CLINICIAN.

GERALD SMALDONE, Pulmonary/Critical Care, State University of New York at Stony Brook,NY

This presentation summarizes the experience of the Stony Brook laboratory in defining the major factors affecting aerosol deposition primarily during delivery of drug via nebulization. Oropharyngeal deposition, progression of lung disease, regional deposition and use of facemasks in drug delivery and device safety are described. Systems incorporating patient feedback provide control of factors affecting deposition and the control of dose to the lung can now be expected. New devices designed with a medical realization of therapeutic need are beginning to be developed. The interface between the patient and the device represents a new area of practical research. Facemasks have been shown to be important in terms of drug delivery with differing behavior observed between MDI/valved holding chambers and nebulizers. Recently completed clinical trials have demonstrated the usefulness of aerosol therapy targeted to the lungs in reducing systemic toxicity with enhanced efficacy. A prime example is aerosolized cyclosporine, used to prevent rejection in lung transplantation. For larger patient populations, the pursuit of therapies to reduce the incidence of Ventilator Associated Pneumonia (VAP) can affect the outcome of illness in the intubated patient in the Intensive Care Unit. The widespread use of systemic antibiotics in the ICU may be responsible for increased incidence of superinfection, systemic toxicity, emerging bacterial resistance and increasing costs. Respiratory infections in intubated patients may originate in the proximal airways at sites of inflammation in the region of the endotracheal tube. Topical therapy with aerosols, targeted to those patients with emerging tracheobronchitis may prevent deep lung infection. Finally, patients with Pulmonary Fibrosis may benefit from aerosolized interferon gamma (IFN-gamma), a potential immuno-modulator in the treatment of pulmonary tuberculosis (TB) and in idiopathic pulmonary fibrosis (IPF). IFN-gamma plays a key role in modulating the effects of T-lymphocytes on alveolar macrophages. In preliminary studies with New York University, we have administered IFN-gamma to patients with TB and IPF. In spite of advanced fibrosis, gamma camera images and BAL data indicate significant deposition throughout the lungs and decreases in TGF-beta levels.

7E3

MODELS FOR AEROSOL DEPOSITION IN THE HUMAN LUNG: WHOLE LUNG VS. LOCAL SCALE MODELS.

WERNER HOFMANN, University of Salzburg, Salzburg, Austria

Current particle deposition models may be grouped into two categories referring to the region of interest in the lung, i.e. either deposition in the whole lung (whole lung approach), or deposition in a localized region of the lung (local scale approach). Because of the complexity of the airway system, airflow and particle deposition in whole lung models are decoupled and thus treated independently. Particle deposition in individual airways is then indirectly related to the airflow by analytical equations for particle deposition efficiencies under specified flow conditions. Different conceptual models vary with respect to lung morphometry and mathematical modeling techniques, such as deterministic symmetric generation models, stochastic asymmetric generation models, deterministic asymmetric multiple-path models, or one-dimensional cross section models. Although comparisons with experimental data in human subjects indicate that all currently available models correctly predict total and regional deposition, they cannot be validated by comparison with experimental in vivo data at the single airway level, as these data are presently not obtainable.

In the local scale approach, only deposition in selected components of the branching airway system is considered, e.g. in bronchial airway bifurcations. This geometric limitation permits the combined solution of the fluid dynamics and particle transport equations by numerical methods, providing information on particle deposition efficiencies and localized deposition patterns within selected structural elements of the human lung. While the computational methods employed in these anatomical structures are generally the same, using commerically available computational fluid dynamics (CFD) program packages, it is primarily the anatomical and physiological complexity which distinguishes the simulations for the various regions. As with the whole lung model, the primary limitation of the numerical models is that they cannot be validated by comparison with experimental in vivo data at the corresponding antomical level, e.g. in single airway bifurcations, only in highly stylized geometric models.

While one could envision a time, in which CFD calculations could technically be performed for the whole human respiratory tract, such an approach may be completely irrealistic, because the morphological information necessary for these simulations will not be obtained at the required spatial resolution in the near future. Thus for the time being, a system´s approach is the most appropriate methodology for the whole lung and the CFD approach for different localized regions of the lung. However, CFD calculations may aid whole lung deposition models by providing more realistic deposition efficiencies or by combining CFD simulations for the large bronchi, where the anatomical information can be obtained by present imaging techniques, with stochastic or multiple path model calculations for all distal parts of the lung.

7E5

CHARACTERIZATION OF A NOVEL CONSTANT-OUTPUT POWDER AEROSOL GENERATOR. MATTHEW J. SHAW, J. David Luedeke, Jason A. Curran, Battelle Memorial Institute, Columbus, OH

Aerosolizing powders for use in laboratory studies can be difficult. The ideal powder aerosol generator would be compatible with numerous powder types, be simple to use, require minimum quantities of starting material, be easily cleaned, and, perhaps most importantly, be able to generate constant and reproducible outputs of powder aerosol over extended periods of time. Historically, several types of powder aerosol generators have been designed and used, including those making use of powder-packed cylinders with scrapers or brushes, fluidized beds, turntables with venturi eductors, vibrating membranes, jet mills, and even simple string wound on a fishing reel. All of these generator types have reportedly been used in numerous laboratories, either as individual techniques or in an assortment of combinations, with varying degrees of success.

An alternative to these powder aerosol generation systems is the Vilnius Aerosol Generator (VAG). The VAG utilizes a unique combination of inlet air jets, a vibrating membrane, and an air-driven stirring “turbovane” to break up and aerosolize the test powder, coupled with a light-scattering photometer and computer system for real-time feedback control. In the current study, tests were performed using the VAG to generate numerous powders, including Arizona Test Dust, Bacillus atrophaeus spores (with and without fluidizer), silica powder (with and without a fluorescent tag), and lactose, a common carrier material used to administer inhalation pharmaceuticals. Test results with these powders, expressed in terms of generator output range, repeatability, and temporal stability, characterize the performance of the VAG as a powder aerosol generator suitable for a range of laboratory studies in which gram-quantities of powder are required to be aerosolized in a controlled, repeatable manner with good temporal stability.

7E6

SIMULATION OF ASYMMETRICAL AEROSOL DEPOSITION IN AN IDEALIZED MOUTH WITH A DRY-POWDER INHALER MOUTHPIECE INLET. Edgar Matida, MARCEL ILIE,Carleton University,Ottawa,Canada Warren Finlay,University of Alberta,Edmonton,Canada Mohammad Golriz,Umea University.Umea,Sweden

Aerosol drug delivery into the lungs [1] through the oral cavity has become an established method in the treatment of lung diseases and has great potential for other non-lung diseases. Compared against more traditional devices (such as nebulizers and pressurized metered dose inhalers, MDIs), dry powder inhalers (DPIs) [2] have relatively very complex outlet flows, which undesirably will increase particle deposition in the mouth cavity.

In the aerosol deposition simulation involving complex geometries, it is common practice to use RANS (Reynolds Averaged Navier-Stokes) equations to solve the primary flow and Lagrangian random-walk eddy interaction models (EIMs) to track individual particles in the computational domain. Since RANS simulations give the mean values of flow velocity, turbulence kinetic energy and dissipation, EIMs provide, through modeling, the instantaneous flow velocity values at the particle location.

In the present work, total aerosol deposition in an idealized mouth geometry having a commercial DPI mouthpiece is simulated using the RANS/EIM approach and compared against experimental results [3]. The DPI mouthpiece consists of a double-helical structure (two internal guide walls) rotating 300 degrees over 13.5 mm of length, which generates a highly turbulent swirling flow. The primary flow is solved using the shear stress transport turbulence model at an inhalation flow rate of 90.0 L/min.

Thousands of particles (d=4.1 microns) are released in the computational domain. The aerosol deposition results show an overprediction of total deposition efficiency, TD=91%, when compared to experimental values obtained in the measurements, TD=67%. Simulated deposition patterns show non-uniform deposition characteristics (particles deposited more on the anterior part of the mouth, particularly on the right side from a patient’s perspective) due to the asymmetric swirling flow coming out of the DPI mouthpiece. While further experiments are needed to determine whether the simulation of localized particle deposition follows actual deposition, and despite the fact that some discrepancies in total deposition efficiencies occur, it is conjectured that the design of inhalation devices can be significantly improved when both numerical simulation (along with additional corrections [4] when necessary) and particle deposition experiments are combined.

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8PA1

FORMATION AND EVOLUTION OF NANOPARTICLES IN THE VEHICULAR EXHAUST ON AND NEAR HIGHWAY. HUA DU and Fangqun Yu Atmospheric Sciences Research Center, State University of New York at Albany, Albany, New York

Traffic is a significant source of nanoparticles which may have adverse health effects on humans. It is important to understand the key parameters and processes controlling the formation and properties of engine-generated nanoparticles on and near highway. Our previous study showed that for vehicles running on fuels with typical fuel sulfur content of ~400ppm, H2SO4-H2O binary homogeneous nucleation can form very high concentration of volatile nanoparticles in vehicle exhaust under some atmospheric conditions. In this study, we investigate the evolution of nanoparticles formed right behind tailpipes on and in the vicinity of highway. We develop a scheme that characterizes exhaust dilution processes (tailpipe to road, road to roadside, and roadside to ambient) as a function of major parameters including wind speed, vehicle speed, and number of lanes. The simulations based on our nucleation and growth model show that H2SO4-H2O nucleation happens within ~ 0.1 s of plume age and organic compounds contribute significantly to the growth of these fresh nanoparticles before the exhaust leaves the highway. Two groups of organic compounds (one associated with lubricating oils and the other associated with unburned fuels) are considered in our calculations. Due to the large Kelvin effects, these organic compounds can only condense on nanoparticles bigger than certain sizes. Our simulations also indicate that, under some conditions, the organic compounds condensed on the nanoparticles earlier evaporate and the nanoparticles shrink as the exhaust plume leaves the highway. The effects of major parameters, including fuel sulfur content, ambient conditions (temperature, relative humidity, wind speed), the condensations of condensable organic compounds in the exhaust, and vehicle speeds on the concentrations and sizes of nanoparticles near highways will be discussed.

8PA2

2-DIMENSIONAL PARTICLE TRACKING IN VIRTUAL IMPACTORS. SATYANARAYANAN SESHADRI Dr. John Haglund Dr. Andy McFarland Aerosol Technology Lab, Texas A&M University, TX

For successful operation of a biological detection system, it is necessary to have significant concentration of the biological agent in the detection unit. Virtual impactors are used as a precursor stage to the detection unit to improve the aerosol concentration by 10X times depending on the number of stages and the total to minor airflow ratios used. One prime concern that may offset the advantage gained by using such a system would be loss of aerosol due to collision with the walls of the impactor. Movement of aerosol in a virtual impactor is strongly influenced by the geometry and alignment of the critical nozzle section. Understanding the flow dynamics and particle motion in a virtual impactor is a key step in successful operation of the device.

Flow dynamics of a virtual impactor have been extensively analyzed numerically by various researchers. Lagrangian particle tracking schemes have been used to determine particle trajectories and to evaluate the effect of impactor geometry on particulate collection and separation. Despite the success of various numerical analyses, there is one vital link missing that completes the analyses. That is experimental validation of obtained particle tracks. In this study we propose to use Particle Tracking Velocimetry to analyze the flow fields in the virtual impactor. This experiment can serve as a benchmark for researchers worldwide to validate their numerical schemes and have faith in their predictions.

To simulate numerical studies, a 2D plane was visualized using a plane laser sheet generated from a Continuous Wave (CW) Ar-Ion laser. The desired nozzle geometry was obtained by independent positioning of nozzle blades fitted with a micrometer. Particle tracks were obtained for monodisperse aerosol generated using a vibrating orifice aerosol generator, seeded in to the virtual impactor flow. Variations in the particle tracks were obtained for different geometric considerations such as nozzle width, receiver width, stand off distance etc.

8PA3

A SYSTEMATIC STUDY OF CHANGE OF THE MOBILITY DIAMETER AND SURFACE AREA OF AGGLOMERATES DURING SINTERING.

Kuk Cho, Chris Hogan and Pratim Biswas, Washington University, St. Louis, MO

The surface area of agglomerates is an important parameter that changes as sintering proceeds. However, it is not easy to measure the change in surface area in contrast to the measurement of mobility diameter. There is currently no way to relate these two properties for non-spherical agglomerates. A simple technique to relate the mobility diameter of an agglomerate to its surface area is presented.
Electrohydrodynamic and traditional atomization were used to generate polystyrene latex (PSL) particle agglomerates with known (monodisperse) primary particle size. A tandem DMA setup was used to measure the mobility diameter change by sintering. The first DMA was used to select a certain mobility size of PSL agglomerates with N primary particles. The value of N was found by complete sintering of the agglomerate, and also verified by electron microscopy. Since the ratio of final surface area to initial surface area is known, the ratio of final mobility diameter to initial mobility diameter was related to the ratio of surface areas. After obtaining the relationship, the mobility diameter change with residence time was plotted and compared with the surface area change.
It was found that the mobility diameter of doublets is almost the same as the mobility diameter of fully sintered doublets, which is compatible with the random orientation drag calculation in the free molecular regime. Hence it was not possible to measure mobility change of doublets during sintering. Instead, the initial mobility diameter of triplets was measured and it was verified by SEM images. The ratio of final mobility diameter to initial mobility diameter for triplets was related to the ratio of final surface area to initial surface area. Also, the mobility diameter change of triplets with residence time at a fixed temperature was measured and the mobility diameter was converted to surface area with the relationship obtained. The converted surface area decay was very close to the reduction in surface area proposed by Koch and Friedlander (1990).

8PA4

NANOPARTICLE NUCLEATION AND CONDENSATION IN TURBULENT SHEAR FLOWS.

Sean Garrick, NATHAN MURFIELD, University of Minnesota, Minneapolis, MN

The underlying physics of nanoparticle production and growth are becoming increasingly important as the manufacture and detection of such particles becomes more commonplace. Simulation of nanoparticle formation and growth is especially important when controlling the properties of nanoparticles formed in vapor-phase synthesis type reactors. To better understand the aforementioned processes, more insight is needed as to when each mechanism of production and growth, i.e. nucleation, condensation and coagulation, is important. As most commercial simulation techniques still lack the computational power needed to resolve all of the physics of nanoparticle production and growth, it is important to know under what flow conditions (temperature, Reynolds Number, etc.) each mechanism is important. Here the effect of condensation in conjunction with nucleation is compared to the case in which nucleation occurs with the absence of condensation. Direct numerical simulation of the formation and surface growth of Dibutylphtalate (DBP) nanoparticles in turbulent, two-dimensional jets is performed. DBP vapor is introduced to the system by means of a hot jet containing air and DBP vapor, which mixes with cooler co-flowing air. Particles are formed by homogeneous nucleation from saturated DBP vapor, while surface growth occurs by the condensation of DBP vapor onto the newly formed nuclei. Novel methods for handling the nucleation and condensation are utilized to more accurately model condensation involving nano-sized particles. Vapor is represented here by particles equivalent in size to one molecule of DBP. A classical nucleation model is used to calculate when and where nanoparticles will nucleate, and the subsequent Brownian type collisions between nuclei and the molecular-sized vapor “particles” constitute condensation. The standard approach, by contrast, involves considering the vapor to be a condensable species, thus making collisions between gas molecules and nanoparticles difficult to resolve since the vapor molecules are not explicitly accounted for. A nodal approximation to the aerosol general dynamic equation (GDE) is employed to track the evolution of the particle populations whereby the effect condensation has on the particle size distributions can be observed. Several flow configurations are investigated to elucidate under what conditions nucleation and condensation are significant. The results are presented as a function of space, time and particle size and comparisons to simulations utilizing a standard nucleation approach qualify the methodology employed here.

8PA5

FAST ESTIMATIONS OF THE OPTICAL FIELDS INSIDE OF THE SPHERICAL AEROSOL. Nick BELOV, Nina Belova, ATECH KFT, Moscow

Presented investigations are based on original statements of the similarity criterion, new precise equation for the optical field intensity at the center of droplet. These data was gathered in number of tables and approximation equations. The properties of the optical field distributions in absorbing particles are summarized by the standard curves. The standard curves are calculated for transparent particles according with the similarity criterion. This data are used for the description of the optical fields in the spheres from non-transparent materials. The standard curves for internal fields are represented with the standard tables, graphic data and approximation equations. The characteristics of transparent particles are calculated by own software with the Mie theory algorithms. These standard relations can be tabulated with some step on the refraction indexes and on diffraction parameters. The error of estimations will be than less, than less the step of the standard table (standard curve). The highest rate of heating of the droplet material happens near the main maximum. Therefore, the minimum of necessary energy, needed for evaporation of the droplet material, may be estimate by the value of intensity of the main maximum of optical field. The present paper are established the simple procedure for determination of the optical fields inside the most different absorbing particles with large accuracy and without difficult calculations under the Mie theory. For this purpose the next step of criterions of similarity are entered. The different kinds of presenting of the tabulated data or graphic distributions of internal field intensities in transparent particles are used as standard ones. There are:

- The three-dimensional image of distribution of intensity of the field in the main cross-section of the particle in the direction of light propagation;
- Two-dimensional image of the distribution of intensity of the field in the main cross-section of the particle - isolines;
- Distribution of intensity of the field along the principal axis of the particle in the direction of incident radiation;
- Density of volumetric distribution of intensity of the field provides numerical informat
ion about intensity distribution inside the particle of given size. This value is very helpful for calculation of the nonuniform heating of the large aerosol particles.
- Dependence of the intensity at the main maximum of aerosol particle from the radius and index of refraction of particle.

8PA6

VISCOUS SINTERING OF AEROSOL-WRITTEN NANOSTRUCTURED GLASS FILMS. DAVID STOKER, Desidario Kovar, Michael F. Becker, John W. Keto, The Center for Nano- and Molecular Science and Technology and the Texas Materials Institute at The University of Texas at Austin, Austin, TX

We have developed a technique to create thick, nanostructured glass films with optical quality. The films are grown from collecting nanoparticles formed from Laser Ablation of Microparticles (LAM). Initially high porosity and low optical quality, the films are then subjected to heat treatment at the viscous sintering temperature of the glass to produce a material with high optical transmission.

An aerosol of SiO2 microspheres is ablated to form a SiO2 nanoparticle aerosol, with mean particle diameter of 10 nm. In this process, a Krypton Fluoride Excimer laser is directed at and absorbed by a gas-focused microparticle aerosol. During laser absorption the microparticles are converted into an ionized atomic gas, which compressively heats, and condenses into nanoparticles as a shockwave propagates through the plasma. Si microparticles are added in a 1:10 volume ratio to generate a bidisperse nanoparticle aerosol. It is deposited on a sapphire substrate, under vacuum at room temperature. We model the impaction kinetics in this situation and control the initial porosity of the film by changing the carrier gas. We find Argon is well-suited for this purpose, because it lowers the impact energy of the aerosol on the thick nanoparticle film, compared to other noble gases. This technique produces a high porosity material with a uniform, small average pore size.

The film and sapphire substrate are positioned on a high temperature pyrolytic boron nitride heater (PBN). PBN heaters can generate over 50 W/cm^2 of heat flux. This heater is built into an Alumina assembly, which acts as a sample stage and box furnace. The furnace is designed to sustain the 1400 C viscous sintering temperature of SiO2. At this temperature, Si:SiO2 composite materials do not suffer from inter-diffusion, so we expect the material will maintain phase-separation. The sintering can be carried out in inert atmosphere or under vacuum to create a dense, thick SiO2 film, which is doped with nanostructured Si.

8PA7

NEDOYMIUM DOPED NANO-PARTICLES PRODUCED BY THE LASER ABLATION OF MICRO-PARTICLE AEROSOLS. ROBERT MORGAN, Todd Ditmire, Univ Texas at Austin Physics Dept. Texas Center for High Intensity Laser Science, Austin Texas; John Keto Univ. Texas at Austin Physics Dept. Texas Materials Institute Center for Nano- and Molecular Science and Technology, Texas Center for High Intensity Laser Science, Austin, TX

Nano-particles (NPs) made from solid state gain media suspended in fluid offer an intriguing solution to the longstanding problems of heat transport constraining the development of high average power lasers. Such fluids could possess active ion densities comparable to high energy laser glasses (e.g. Schott LG-760) while remaining transparent. A transparent material with the energy storage capacity of a solid that could be cooled in a heat exchanger like a liquid would enable the development of compact high average power diode pumped lasers. Toward this end, fluorescent Neodymium doped NPs have been successfully collected in transparent dielectric solutions via the laser ablation of micro-particles (LAM).

In the LAM apparatus, a powder is suspended in a laminar gas stream and then ablated with a UV excimer laser producing NPs. Care must be taken when preparing the powder since fine inhomogeneous powders tend to agglomerate resulting in poor powder flow and inefficient NP nucleation. Additionally, for a micro-particle to ablate, it must absorb enough energy from the laser light to launch a shock and explode, in spite of the fact that optical glasses typically have absorption lengths much greater than 10 microns in the UV. Spherical micro-particles have been demonstrated to enhance absorption by focusing the light at the back surface; however, producing high quality micro-spheres from arbitrary glass compositions is also difficult. We will report studies of different micro power preparations to improve the quantity and quality of the NPs produced. After ablation the NPs are sprayed through a super sonic nozzle to accelerate the particles so that they impact into the dielectric fluid. Surface passivation of the particles can be accomplished by collecting the nano-particles in an appropriate surfactant. Studies of different surfactant combinations for stabilization of the NPs in solution will be reported with their optical attenuations. Fluorescence of a nano-particle suspension (LG-760 Nd^{+3}:phosphate glass) peaked at 1053nm was observed in a preliminary experiment. Once the LAM process is adapted to laser glasses, solutions of high enough particle density and optical quality will be manufactured to build a small test laser system.

8PA8

EXPERIMENTAL EVALUATION OF CHARGED NANOPARTICLE AEROSOL PRODUCED BY LASER ABLATION OF A MICROPARTICLE AEROSOL. CHONG HUANG ,Jan Neering, Desiderio Kovar, John W. Keto, Michael F. Becker Texas Materials Institute, The University of Texas at Austin, Austin, TX

The Laser Ablation of Microparticles (LAM) method has been shown to produce large quantities of nanoparticles (NPs) that are suitable for use as the starting materials for direct-write applications. We have previously reported that the metallic NPs are not agglomerated after LAM for a certain period of time because they are positively charged due to photoemmission and thermionization. However, since the LAM process occurs at 1 atm, the NPs are neutralized by collisions with fast moving electrons and charged gas molecules in the aerosol. Neutral NPs tend to agglomerate due to Van Der Waals interaction; agglomeration lowers the productivity of the direct-write process and therefore is undesirable. Thus, a better understanding of the properties of the NP aerosol is desired.

In this study, we developed a series of cylindrical Faraday cups that were inserted at various downstream positions to explore the charge distribution and recombination dynamics of the silver NP aerosol after laser ablation. The diagnostic tools were designed to record 1) the spatial distribution of charges; 2) the recombination rate; 3) the performance of the electrostatic collection of the charged NP aerosols. Experimental results will be presented that describe the electrical properties of the NP aerosol. High resolution TEM images demonstrate the condition of the NP aerosols after ablation. The performance of several types of Faraday cup is evaluated. Preliminary results show that the charge carried by the NPs decays exponentially with respect to the downstream distance from the ablation area at 1 atm, and that the charged NP aerosol is confined near the center of the flowing aerosol. On-going research aimed at evaluating the electrostatic collection of charged metallic NPs will also be presented. We believe the high density of negative charge carriers and the short mean-free-path of the NP aerosol may account for this relatively rapid neutralization.

8PA9

LASER ASSISTED NANOPARTICLE AEROSOL FOCUSING FOR APPLICATION TO SUPERSONIC JET DIRECT WRITING. CHANGYI LAI, Chong Huang, Desiderio Kovar, John W. Keto, Michael F. Becker, Texas Materials Institute, The University of Texas at Austin, Austin, TX

A novel optical technique for focusing nanoparticles in an aerosol jet has been developed for application to surface patterning in direct write processes. Pattern feature size can potentially be decreased to 150 nm based on a model calculation. The technique utilizes the principles of optical trapping and manipulation of microscopic particles by a focused laser beam and supersonic jet deposition of nanoparticles generated by our Laser Ablation Microparticle (LAM) aerosol process. The proposed system combines a modified optical trap with the aerosol jet direct writing process. A sub-millimeter supersonic jet is used to impact nanoparticle aerosols onto a substrate at a nozzle-to-substrate distance of 1-2 mm. The substrate intercepts nanoparticles to separate them from carrying gas stream for deposition by impaction. A laser is focused down the throat of the nozzle of the jet to provide the trapping force. As the exiting nanoparticle aerosol cools by supersonic expansion through the jet, dissipation will relax the nanoparticles into a potential well formed by the inward radial force of the laser field gradient. The temperature of the nanoparticle within the trap should be near the transverse translational temperature observed for clusters formed in supersonic jets, T~5-10K. Using a linear force constant approximation and Generalized Lorenz Mie Theory simulation, the potential well depth provides a stable trap for ~10 nm Silver nanoparticles when a TEM00 Ti: sapphire laser (800 nm) or Nd: YVO4 laser (532 nm) is used.

We have demonstrated the feasibility of this technique in recent experiments. As the focused laser spot was translated along the jet axis through the nozzle, we observed the deposited nanoparticles linewidth pass through a minimum. These experiments do show the line narrowing effect of optical trapping, in addition to the aerodynamic lens effect. We believe that by adjusting the laser focus position with respect to supersonic jet throat and the aerosol flow conditions, a much narrower linewidth can be achieved. It could perhaps approach the model calculation, provided losses of the optical trapping beam could be kept at a minimum. Further work is continuing to emphasize both linewidth reduction and methods to trap the majority of the aerosol nanoparticles flowing through the jet.

8PA10

A MODEL FOR THE FORMATION OF LIQUID FUEL SPRAYS WITH ATOMIZING AIR. DAVID J SCHMIDT, ExxonMobil Upstream Research Company, Houston, TX; Goodarz Ahmadi, Clarkson University, Potsdam, NY; William Kvasnak, Pratt-Whitney

The formation of sprays from a liquid jet in the presence of atomizing air is studied. The instantaneous fluctuating fluid velocity and velocity gradient components are evaluated with the use of a PDF-based Langevin model. Motions of atomized fuel droplets are analyzed, and ensemble and time averaging are used for evaluating the statistical properties of the spray. Effects of droplet deformation, breakup and evaporation are included in the model. The results show that the mean-square fluctuation velocities of the droplets vary significantly with their size and shape. Furthermore, the mean-square fluctuation velocities of the evaporating droplet differ somewhat from those of point and solid particles. Droplet turbulent diffusivities, however, are found to be close to the diffusivity of point particles. The formation of sprays in nonswirling flow conditions is simulated. The model accounts for the evaporation, deformation, and breakup of liquid droplets. The droplet velocity, concentration, and size of the simulated spray are compared with the experimental data and reasonable agreement is observed.

8PA12

DEPOSITION UNIFORMITYOF GENE GUN PARTICLES.

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Starting 1989, gene gun (or particle bombardment-mediated gene delivery technology) has been commercially available for gene transfer into specific target cells of somatic tissues. But gene gun has a major problem of the low transgenic efficacy, probably due to micrometer-sized particles having a tendency to stick together and crush the cell and formed pit damage. Therefore, the ultimate goal of this work is to enhance the efficiency of gene transfer, with the focus on improving the uniformity of particle deposition by micrometer-sized particle bombardment technology.

Helios gene gun was used in this work. The main operation parameters were (1) helium jet pressure to drive the gold particles onto target surface, from 100 to 600 psi, (2) distance between gene gun and target, 20 to 100 mm, (3) the expansion angle of the spacer, from 52 to 85 degree, (4) the size of the awl installed in spacer, diameter from 1.2 to 3.0 mm, and (5) the amount of gold particles. The size of gold particle used was 2 micron. The images of gold particle deposition were taken by using a digital camera connected to an optical microscope. The uniformity and coverage of the particle deposition were then measured and analyzed by using an image process software.

The results showed that uniformity of particle deposition decreased with increasing jet pressure, because the gold particles (high density, and thus high inertial) have shorter time to diverge. The uniformity increased with increasing distance between gene gun and target filter due to the same reason. However, the transition loss increased with decreasing spacer size. The uniformity increased with increasing expansion angle of spacer. The size and location of awl installed in spacer also had significant influence on uniformity of gene gun particles.

8PA13

COMPUTATIONAL MODELING OF LIQUID-GAS-SOLID THREE-PHASE FLOWS IN MICROGRAVITY.

XINYU ZHANG, Goodarz Ahmadi, Clarkson University, Potsdam, NY

An Eulerian-Lagrangian model for simulations of liquid-gas-solid flows in microgravity was developed. In this study, the liquid phase was described by volume-averaged Eulerian governing equations, whereas motions of particles and bubbles were evaluated using Lagrangian trajectory analysis approach. Bubbles were assumed to remain spherical and their shape variations were ignored. The two-way couplings between particle-liquid and bubble-liquid were accounted for in the study. The discrete phase equations included drag, lift, buoyancy, and virtual mass forces. Particle-particle and bubble-bubble interactions were accounted for by the hard sphere model. The bubble coalescence was also included in the model. The simulation results under normal gravity condition were compared with the available experimental data in earlier simulations, and good agreement was obtained. The transient flow characteristics of the three-phase flow were studied and the effects of gravity, inlet bubble size, bubble number density as well as the bubble superficial velocity on the flow characteristics were discussed. The simulations for low gravity showed that most bubbles are aggregated in the inlet region. Due to the longer stay of the bubbles and bubble coalescence, the Sauter mean bubble diameter becomes rather large which can be more than10 mm. The early evolvement of bubble plume under microgravity condition exhibits a plug type flow behavior. Most particles are concentrated outside the bubble plume; very few particles are retained in the plume. Compared to the flow in normal gravity condition, the mixing of three phases under microgravity condition is not good. The velocities of three phases in microgravity are of the same order. The bubble size, number density, and initial velocity significantly affected the characteristics of the three-phase flows under microgravity condition. At the condition of same inlet bubble number density, the flow with larger bubbles evolves faster.

8PA14

ANGSTROM TURBIDITY PARAMETERS: AN EMPIRICAL RELATIONSHIP. Ganesh K E , University of Mysore, Mysore, India Umesh T K , University of Mysore, Mysore, India Narasimhamurthy B , University of Mysore, Mysore, India

Introduction:
Angstrom turbidity coefficient b is an index of amount of aerosols present in the atmosphere where as the wavelength exponent a is related to the ratio of small to large aerosols. This does not indicate any relationship between the two. However some workers have found an anti correlation, that a increase while b decrease and vice versa.

In the present work, the change in a with b is examined to arrive at an empirical relationship between the two parameters, for a low latitude continental station, Mysore (12.30 N) in the peninsular India. On the East, South and West of Mysore, Sea waters lie more than 200km away, while on the North lies a vast mass of Asiatic land.

Experimental:
The experimental data have been collected with the use of a portable Sunphotometer Microtops II, developed by Solar light company. Sun's direct radiation is collected through five optical channels at 440, 500, 675, 936 and 1020nm.The radiation gets processed by a built-in algorithm and the aerosol optical thickness (AOT) t appears on display. For the present study, AOT's are collected on the twelve days of cloud free sky in the month of December 2004. The duration of observation on the day's started from 04:30hr to 11:00hr UT. A database of more than 1000points has become available for further analysis.

Results and discussion:
Angstroms formula t---l = b l-a becomes linear on logarithmic scale. By least squares fitting between lnt---l and lnl, a and b are derived for each scan. This method is the most appropriate one (Cachorro, V.E., deFrutos, A.M., Casanova, J.L. 1987 Determination of the Angstrom turbidity parameters, Appl Opt, 26, 3069.). In the present investigation about one thousand data points are used to retrieve sets of a and b. From the graphical plots of a verses b for each day, it is observed that a decreases linearly with b. Least squares analysis shows that the intercept on the days do not vary significantly, but approach a value of 4 as is expected (Iqbal M, 1983: An Introduction to Solar radiation, Academic Press, Ontario, Canada). However the slopes differ largely. This indicates that the rate of variation of a with b change from day to day. On low b-days the slopes are higher compared to those of high b-days. On a low b-day the coarse particulates get depleted fast resulting in larger value of the ratio of fine to coarse particulates. This ratio is an index of a, and consequently the values of a are high. The b-parameter is determined by the coarse particulate and low b-results when the coarse particles are depleted. This phenomena explains large value of slope on low b-day. To arrive at a plausible relationship between a and b, a mass plot is made with 188 sets of parameters. With least squares fitting it is found that a = (2.65 ± 0.04) – (11.02 ± 0.71) b. Production-depletion processes determines the values of a and b. Consequently the a-b relationship may exhibit temporal and spatial characteristics. Further studies in this direction need to be under taken.

8PA15

MICROSCOPE-VIDEO BASED SMOKE AND DUST MONITORING. THORSTEN SCHULTZE, Ingolf Willms, University Duisburg-Essen, Campus Duisburg, Germany

Fire detection is usually based on the detection of smoke by light scattering. The most common detectors are near infra-red light scattering sensors, where the detection of smoke is carried out by measuring the light scattered by the aerosol inside of the detector. The technique is reliable within certain limits, being able to detect very low smoke densities.

Drawback of this simple technique is the fact that also non-fire aerosols like haze or dust lead to an alarm, as it is hard to distinguish between fire- and nuisance-aerosols using only one pair of IR-light emitter and receiver.

In a new approach a microscope-video system is implemented to scan microscopic characteristics of aerosols. Comparable techniques are being successfully applied in e.g. waste water analyses or the flow dynamics analysis in turbines (so called Particle Image Velocimetry). The aim of this study is a more reliable discrimination between smoke and nuisance aerosols as base for a microscope-video fire detection system.

The prototype hardware of the scanning system consists of a highly-sensitive microscope-camera mapping a thin illuminated air layer under the ceiling of a room. The patterns originated by the scattering particles give, in a narrow range, information about the particle size distribution of the aerosol. But not only the static attributes are analysed. In addition to static attributes flow characteristics are also scanned, providing data for a later automatic detection and discrimination between fire and non-fire aerosols.

This presentation shows recent results from tests performed in the fire detection laboratory of the University Duisburg, discussing the possibilities and limitations of an automatic microscope-video based smoke detection system.

8PA16

SIZE DISTRIBUTION DYNAMICS OF A HYGROSCOPIC AEROSOL FLOWING THROUGH A CONSTANT WALL TEMPERATURE TUBE WITH COUPLED HEAT AND MASS TRANSFER EFFECTS: MODELING AND EXPERIMENTAL INVESTIGATION. ALAN SHIHADEH, Rawad Saleh, Aerosol Research Laboratory, American University of Beirut, Lebanon

We present an experimental and computational study of a volatile continuum regime polydisperse aerosol flowing through a constant wall temperature tube. Following Finlay and Stapleton (1995) a Lagrangian numerical method for simulating 2-way coupled heat and mass transfer between the aerosol, bulk phase, and tube wall was developed to predict hygroscopic growth or shrinkage. The aerosol particle size distribution is discretized using a moving grid in which each bin is characterized by a single particle volume that is allowed to change in accordance with the coupled heat/mass transfer model. Wall heat and mass transfer is approached using a boundary layer formulation. Computations are compared to experimental data generated with a nebulized saline solution flowing through a heated constant wall temperature tube. The initial size distribution of the nebulized saline particles is determined using the residual method with a QCM cascade impactor. The evolution of the bulk temperature of the aerosol as it travels through the tube is measured for a variety of flow conditions and saline concentrations, and is compared to predictions from the 2-way coupled model. By using bulk-phase temperature as the primary diagnostic, a number of practical difficulties – which have thus far hindered presentation of experimental data for this fundamental problem – associated with analyzing a volatile aerosol are avoided. The experimental setup and data are presented which can be used to validate computational models of flowing hygroscopic aerosols, including Finlay and Stapleton's 2-way model which has been widely used to predict hygroscopic aerosol particle growth for lung deposition calculations of inhaled aerosols.

8PA17

DETERMINING THE COLLECTION EFFICIENCY OF IMPINGERS (MODELS #7541 AND #7531). Richard Tuttle, PATIRICIA REUTHER, Gary Sparks Jr.

Impingers are commonly used for the collection of aerosols for determining challenge aerosol concentrations for exposure studies and for environmental air quality monitoring. To improve the accuracy of aerosol concentration results obtained from impinger samples, a system was designed and constructed to assess the collection efficiency of two types of impingers that are utilized for aerosol collection. The collection efficiency assessment of model 7541 and 7531 impingers (ACE Glass, Vineland, NJ) were assessed by challenging the impingers with polystyrene latex microspheres (PSL) at size ranges of 0.993, 1.92, and 2.92 µm. The system for PSL challenge generation and collection efficiency assessment consisted of a nebulizer for PSL aerosol generation, and single aerosol containment plenums located upstream and downstream of the test impinger. Operating the system dynamically, the challenge flow rate supplied to the system was equal to the impinger sample flow rate to maintain a uniform flow rate through both plenums. Impinger sample collection efficiencies were assessed at flow rates of 1 and 2 L/min for the 7531 impinger and at 6 L/min for the 7541 impinger, with collection media volumes (DI water) of 10 and 20 mL for each impinger type respectively. Collection efficiency tests were performed for each impinger by supplying a volume of the selected PSL aerosol challenge to displace the volume of the aerosol containment plenums a minimum of five times prior to upstream and downstream aerosol concentration measurements. Impinger upstream challenge aerosol concentration and downstream impinger penetration aerosol concentration measurements were performed using two count and mass correlated APS's (Model 3321, TSI Inc, Minneapolis, MN) sampling simultaneously from each plenum. Prior to aerosol concentration measurement, the plenums were isolated from the system generation and exhaust components using electrically activated solenoid valves, and the system plenums were equipped with solenoid valves activated to provide HEPA filtered air to each plenum for APS sample volume displacement.

The collection efficiency, and/or destruction effect of the impingers was also assessed for bioaerosol collection. A non – virulent strain (C099-3015) of Y. pestis was aerosolized into a CH technologies nose only exposure system using a Collison 3 jet nebulizer. Multiple tests were performed with both impingers sampling simultaneously for viable bioaerosol collection comparison.

8PA18

MULTIPHASE FLOW THROUGH POROUS MEDIA WITH APPLICATIONS TO CO2 SEQUESTRATION. MELISSA RICHARDS, Josh Cook, Goodarz Ahmadi, Clarkson University, Department of Mechanical and Aeronautical Engineering, Potsdam, NY, Susan Powers, Clarkson University, Department of Civil and Environmental Engineering, Potsdam, NY, Duane H. Smith, National Energy Technology Center, US Department of Energy, Morgantown, WV

Increase of the greenhouse gases in the atmosphere is believed to be one main cause of the global warming, which may have detrimental consequences. CO2 is one of the greenhouse gases which mainly being produced by the combustion of fossil fuel in vehicles and power plants. Research is currently being conducted on how to alleviate or reduce the negatives effects of greenhouses gases in the atmosphere. One proposed methods for CO2 sequestration (sometimes referred to as carbon management) is to pump the carbon dioxide into the geological brine fields. This study is concerned with providing a fundamental understanding of gas flows into liquid saturated porous media.

An experimental setup for visualizing multiphase gas-liquid flows in porous media was developed. The key component of the apparatus used is flow cell that allows the observation of the gas-liquid flow in the porous media. A CCD camera, a syringe pump, a pressure transducer, and a computer are used to capture the images of the flow pattern, analyze images and measure pressure drop data. At the start of the experiment, the flow cell fully saturated with water (the defending fluid). Then air (the invading fluid) is injected at constant rate via the syringe pump. Images are taken of the interface between the defending and invading fluid at different times and further analyzed using image processing software. The pressure at the inlet is measured by the pressure transducer and stored in the computer. The experiment results indicate the potential for formation of viscous and capillary fingerings of the invading fluid into the liquid. The corresponding fractal dimensions of the interface were evaluated and discussed. The performed study provides insight into the volume of CO2 that can be sequestrated in brine saturated underground reservoirs.

8PA19

GAS-LIQUID DYNAMIC BEHAVIOR AND BUBBLE SIZE DISTRIBUTION IN 2D BUBBLE COLUMN. WEI CHEN and Goodarz Ahmadi Department of Mechanical and Aeronautical Engineering Clarkson University, Potsdam NY 13699

Bubble coalescence and breakup-up are important processes that control the bubble size distribution in bubble column reactors. An experimental and computational study of the effect of gas superficial velocity on the bubble size distribution in a (200×10×1000 mm3) rectangular bubble column was performed. Bubble size distributions were measured using a high speed digital CCD camera and analyzed by LabVIEW image process system. Dispersed gas-liquid flow in bubble column was simulated by a population balance model Eulerian multiphase flow approach within the FLUENT code. The mechanisms of bubble breakup by the turbulence eddy and bubble coalescence were included in the analysis. It is seen that a central wave-like bubble plume appears with two staggered rows of vortices which control the roughly chaotic oscillation characteristics of the bubble column. The relations between the bubble size distributions in horizontal and vertical direction were studied. The model predictions were found to agree well with the experimental data.

8PA20

NUMERICAL AND EXPERIMENTAL STUDY ON BUBBLE MOTION AND DEFORMATION IN A SIMPLE SHEAR FLOW.

WEI CHEN and Goodarz Ahmadi Department of Mechanical and Aeronautical Engineering Clarkson University, Potsdam NY 13699

Bubble motion and deformation in a simple shear flows was studied. An experimental simple shear flow device was used to test the bubble motion under shear flow condition. For the passage Reynolds number below 522, the liquid velocity profile shows a linear laminar variation. At larger Reynolds numbers, the liquid velocity profile shows non-linear turbulence variation and also becomes asymmetric. The bubbles drag force comparatively is larger and distorts the shear flow field at the lower shear rate while the shear rate effect is larger and does not change the shear flow field at larger shear rate. The turbulence intensity is quite higher near the wall and decreases toward the centerline. The turbulence intensity and both increase as the shear rate increases. Bubble injection frequency always increases the turbulent intensity. A detailed numerical study on the deformation of gas bubble in viscous Newtonian liquids in a simple shear flow was also performed. The cases that the volume of bubbles are constant, bubbles grow and when bubble dissolution is present are studied. The typical S shape of the deformed bubble was found in the simulation. The simulation results show that as the capillary number (the ratio of the shear force to the surface tension forces) increases, the bubble becomes thinner and longer. The shear rate affects the boiling point in the bubble growth and dissolution rate in the bubble dissolution. Further studies found that the dissolution or growth rate is roughly proportional to the shear rate to the 3/8 power for high capillary number as suggested by Hinch and Acrivos. The simulation results were found to agree well with available and performed experimental data.

8PA21

THEORETICAL AND EXPERIMENTAL STUDIES OF NANOPARTICLE CHARGING IN A SOFT-X-RAY ENHANCED CORONA SYSTEM.

JINGKUN JIANG, Myong-Hwa Lee, Pratim Biswas, Washington University in St. Louis, St. Louis, MO

Charging of nanoparticles is an important field of study with applicability in a number of different areas such as aerosol instrumentation, production of materials from aerosols, and ultrafine particle control. Developments in our research group have shown that soft-X-ray enhanced corona system can increase nanoparticle charging efficiency and improve the capture efficiency of ultrafine particles, including virus particles (1, 2). In this presentation, a theoretical model was developed to predict the charging of nanoparticles using a combination of a soft x-ray source and a corona. The model was based on Fuchs diffusion charging theory for nanoparticles and direct charging by photoemission of ultrafine particles through soft-X-ray irradiation. The equations included a balance expression for the positive and negative ions, and one for each charge level of the particles. The governing equations were solved by a numerical algorithm that was used to solve population balance equations and get the particle charge distribution. The model results demonstrated the role of soft-X-ray irradiation at enhancing particle charging efficiency, especially for the smaller nanometer sized particles. A statistical approach, which assigned discrete charge levels to particles with the same size, in conjunction with the transport equation was used to compare this charging model to experiment results.

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8PA22

CHARACTERIZATION OF SEMICONDUCTOR CORE-SHELL NANOPARTICLES GENERATED BY LASER ABLATION OF MICROPARTICLES.

IGNACIO GALLARDO, Kay Hoffmann, Desiderio Kovar, John Keto, University of Texas at Austin, Austin, TX

A new two step LAM (Laser Ablation of Microparticles) process for ZnS/CdSe core-shell nanoparticle production has been implemented.

In a LAM process micropaticle powder passes through an aerosol generator and is then inserted into a laser ablation cell. There a laser pulse (high energy excimer laser) hits the microparticles and generates a plasma. A subsequent shockwave front produces the particle breakdown (vaporization) which is followed by a condensation of nanoparticles behind the shockwave. The hot and charged nanoparticles are cooled down by travelling through a supersonic nozzle and expanding after it. The size distribution of these particles was successfully investigated in the past by surface impaction and analyzed by SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy), [1, 2].

To make a core/shell nanostructure, first, spherical ZnS nanoparticles are generated by a standard LAM process described above. In a second cell, they are mixed with CdSe microparticles and ablated again. Due to a subsequent condensation of the CdSe around the seed ZnS nanoparticles, core-shell structures are formed. Micrographs show high contrast TEM images of such structures. EDS technique is used to analyse the 20nm ZnS-CdSe core shell materials. Furthermore thermodynamic numerical calculations of the LAM process were made to describe the behaviour of nanoparticles at the second ablation cell. Such calculations show that the diameter of the nanoparticles decreases 20% when exposed to the laser beam in the second cell.

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8PA23

AERODYNAMIC FORCES ON A SPHERE ATTACHED TO A WALL IN A LAMINAR BOUNDARY LAYER.

Lyle Sweeney, WARREN FINLAY, University of Alberta, Edmonton, Alberta, Canada

Lift and drag forces on a particle attached to a wall is examined numerically. Specifically, the variations in the coefficients of lift and drag with particle Reynolds number in laminar flow over a sphere attached to a flat plate is examined.

The coefficients of lift and drag are functionally dependent on the Reynolds number of the particle in the boundary layer, as shown by dimensional analysis. A commercially available computational fluid dynamics package (CFX) was utilized to study the problem. To ensure model accuracy, computational solutions were tested for grid size and boundary placement independence. As well, the results were verified against an exact solution of the problem in the limiting case of Stokes flow and against existing experimental results.

Grid independence occurred at a level of ~400 000 nodes for drag calculations, and ~800 000 for lift calculations. The free-slip boundary placed parallel to the wall had the greatest influence on flow solution, and its ideal placement was dependent on the Reynolds number of the flow. Results indicate that both coefficients of lift and drag decrease exponentially with increasing Reynolds number to asymptotic values. The model has been validated against the experimental data in the high Reynolds number range.

Future work involves examining the problem with unsteady effects included at higher Reynolds number. Additionally, grid and boundary placement studies at the bounding Reynolds numbers of the problem are underway. The data generated by the computational model will be fitted into a functional form, and should aid impending motion and entrainment studies of spherical objects attached to a flat wall in a laminar boundary layer.

8PB1

CONCENTRATIONS OF PARTICULATE ORGANIC SPECIES MEASURED IN INDOOR AND OUTDOOR ENVIRONMENTS DURING THE TAMPA ASTHMATIC CHILDREN'S STUDY (TACS). DAVID A. OLSON, Stephen R. McDow, Ron Williams, Carvin Stevens, National Exposure Research Laboratory, United States Environmental Protection Agency, Research Triangle Park, NC; John Turlington, Alion Science and Technology, Research Triangle Park, NC

The Tampa Asthmatic Children's Study (TACS) was completed to assess environmental exposures for a group of asthmatic children (n = 9) under the age of six and living in Tampa, Florida. Concentrations of particulate organic species are reported from residential indoor, residential outdoor, and ambient microenvironments from the TACS. Concentrations of particulate organic species are reported from three different compound classes: alkanes (C27 to C35), polycyclic aromatic hydrocarbons (PAHs), and hopanes. All samples were collected on Teflon filter media using Harvard Impactors (PM2.5 size selection) which operated for 24 hours at 10 L/min (four consecutive days per subject). To increase analytical sensitivity for quantitation of these low volume samples, all samples were analyzed using a programmable temperature vaporization (PTV) injection gas chromatograph mass spectrometer (GC-MS). Preliminary data indicate that outdoor concentrations from all three chemical classes were typically at least a factor of two higher than indoor concentrations, suggesting the possible influence of mobile sources. As an example, average hopane concentrations from one study participant were 40.4 pg/m3 outdoors and 3.8 pg/m3 indoors. Results from all study participants and all compound classes will be presented.

Disclaimer – Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

8PB2

IN-SITU CHARACTERISTICS OF FINE AND ULTRAFINE PARTICLES FROM THREE COMBUSTION SOURCES.. JOAKIM PAGELS and Andreas Dahl Div. Aerosol Technology (EAT), Lund University, Lund, Sweden Erik Swietlicki, Div. Nuclear Physics, Lund University, Lund, Sweden

Indoor particle sources constitutes a substantial fraction of the total PM exposure in the population. The aim of this work was to characterise particles from three indoor sources of fine and ultrafine particles.

The methods include instrumental techniques such as Scanning Mobility Particle Sizer (SMPS), Electrical Low-Pressure Impactor (ELPI) and Tandem Differential Mobility Analysers (TDMA) based on volatility and hygroscopic growth. Filter samplers and impactors were used for collecting particles on substrates for subsequent chemical analysis.

Particles from the indoor sources of cigarettes, incense and candles were examined in the laboratory by using an airtight 22 m3 stainless steel chamber.

Sidestream cigarette smoke and incense particles are well internally mixed aerosols dominated by organic compounds. Each particle consists of components with a relatively wide range in vapour pressure. The volatile fraction decreases at lower particle concentrations in the chamber and upon ageing, which is attributed to different degrees of evaporation from the particle to the gas phase during ageing. The hygroscopic growth is low for cigarette smoke and incense (1.05-1.10 at RH=90%), it is not clear whether the hygroscopic growth can be attributed to polar organic compounds, ash components as KCl or additives.

Smoke particles from candles can be divided into 4 different groups in terms of volatility. High number concentrations of ultrafine particles (10-50 nm), which are volatile at either 150 C or 450 C and have high hygroscopic growth factors 1.6-1.9 at 90% RH are emitted during continuous burning. At high air velocities non-volatile soot-particles (200-300 nm) are emitted. During smouldering, particles volatile at below 100 C are emitted.

8PB3

AN ASSESSMENT OF INDOOR AIR QUALITY IN HISPANIC IMMIGRANT HOUSING IN COMMERCE CITY, CO.. Peter Scaramella, SHELLY L. MILLER, University of Colorado, Boulder, CO; Jill Litt, Carolyn DiGuiseppi, Sandra Diaz-Castillo, University of Colorado Health Sciences Center, Denver, CO; Fernando Pineda-Reyes, Diana Pineda-Ford, Harry A. Ford, Groundwork Denver, Denver, CO; Edward Hendrikson, Salud Family Health Clinic, Commerce City, CO.

An indoor air quality assessment is being conducted on 100 homes of Hispanic immigrants in Commerce City, Colorado, an industrial suburb of Denver. Home-owners are interviewed to determine risk factors associated with allergic asthma and exposure to particulate matter, carbon monoxide, and carbon dioxide. Their homes were also inspected for possible sources of indoor air pollutants, such as combustion appliances, tobacco smoke, pets, molds, and water damage. Carbon monoxide and carbon dioxide are measured for 24 hours inside the main living area and outside of the homes (AQ-501, Metrosonics, Inc., Rochester, NY). Harvard Impactors (Air Diagnostics and Engineering, Inc., Naples, ME) are used to collect 24-hour samples of particulate matter for particles with diameters smaller than 2.5 microns at the same locations for gravimetric analysis. Dust samples are collected by vacuuming carpeting and flooring in 45 by 45 cm grids placed randomly at four locations in the entry way, living room, kitchen, and bedrooms. The dust collected is analyzed by enzyme-linked immunosorbent assays (ELISA) for dust mite (Der p 1), cockroach (Bla g 1), Fungi (Asp f 1 and Alt a 1), Rat (Rat n 1), Mouse (Mus m 1), and Cat (Fel d 1) allergens. This study will provide information needed to understand risk factors for asthma and other respiratory illnesses among Spanish-speaking immigrant families in a fast-growing urban industrial community in Colorado.

8PB4

INDOOR/OUTDOOR RELATIONSHIP OF PM2.5 DURING ACUTE WINTER INVERSIONS IN LOGAN, UTAH. PHILIP J. SILVA, Eric Vawdrey, Mark Erupe, Department of Chemistry and Biochemistry, Utah State University, Logan, UT

Logan (Cache County), Utah frequently experiences very high PM2.5 mass loadings during wintertime inversions. During 2004, this resulted in 17 exceedances of the 24-hour PM2.5 standard and 10 days with mass concentrations above 100 ug m -3. These high values of fine particles raised public health concern over the indoor concentrations of fine particles because local schools have frequently canceled recess and outdoor activities during “yellow” and “red” air quality days. A total of 40 days had outdoor activities cancelled between January and February 2004.

This past winter, we conducted an indoor/outdoor comparison study of fine particle concentrations and composition in Logan throughout the winter season using an aerosol mass spectrometer. Indoor concentrations of fine particles are 60-80% lower than outside mass loadings. The concentrations of all chemical species detected (ammonium, nitrate, sulfate, organic carbon) are significantly lower indoors than outdoors. The organic fraction of fine particles drops by less relative to other components, showing a greater fraction indoors than outdoors. However, the composition of indoor aerosols is nominally the same as that observed outside with no significant indoor sources apparent.

8PC1

CHARACTERIZATION OF NEW BUTANOL-BASED CONDENSATION PARTICLE COUNTERS (TSI MODELS 3771 AND 3772). MELISSA FINK, Rob Caldow, Hee-Siew Han, Ed Johnson, Steve Olson, Mike Woessner, TSI Incorporated, Shoreview, MN

Two new butonal-based condensation particle counters (CPC) have been developed and characterized. CPCs have been widely used in aerosol technology to gather information on aerosol number concentrations. The TSI Model 3772 CPC operates with a flowrate of 1.0 L/min and detects an upper concentration limit of 10,000 particles/cm3. The TSI Model 3771 CPC operates with a flowrate of 2.8 L/min and detects an upper concentration limit over 3,000 particles/cm3. Both include a removable saturator wick and an automated micropump to remove condensate from the saturator. The 3772 is compatible with TSI Scanning Mobility Particle Sizer TM spectrometer. The 3772 and 3771 succeed previous TSI Models 3010 and 3762, respectively.

Measurements were made on three units of each model. Results include detection efficiency, concentration linearity, response time and false count detection. Efficiencies were determined by comparing the performance of the CPC units against an aerosol electrometer (TSI Model 3068A) using NaCl and sucrose aerosols. The aerosols were generated using electrospray, furnace, and atomizer techniques. The 3772 instruments detected 50% of 10 nm particles. The 3771 instruments detected 50% of 5 nm particles. For concentration linearity measurements, the concentration of 40 nm sucrose particles was varied from under 1,000 particles/cm3 up to the upper concentration limit of the model. The electrometer and the CPCs were found to have well correlated counting performance. Instrument response to a step change in aerosol concentration was under 3 seconds for both models. False count detection fell well under 0.01 particles/cm3.

8PC2

LABORATORY CHARACTERIZATION OF A MULTI-ANGLE LIGHT-SCATTERING SPECTROMETER. WILLIAM DICK, Keung Woo, Mihai Chiruta, Francisco Romay, MSP Corporation, Shoreview, MN

This paper summarizes the characterization of the optical portion of an aircraft-based multi-angle light scattering (MLS) spectrometer. The optical assembly was designed for measurement of the phase function, sphericity, and size of individual aerosol particles ranging from 0.5 to 15 µm in diameter.

The MLS measures particle phase functions at 32 polar angles ranging from 10 to 170°. Laser light (532 nm) scattered by a particle is reflected by a custom ellipsoidal mirror, collimated with an aspheric lens and projected onto a 32-channel multi-anode photomultiplier tube (PMT) for measurement of the angular intensity distribution.

One of the challenges posed by this design is the determination of the precise mapping of scattering (polar) angle to the linear detector array. Factors such as the exact contour of the ellipsoid mirror surface, alignment of the mirror, and the paraxial performance of the aspheric lens can significantly alter the range of scattering angle projected onto a given element of the detector. To address this problem, an apparatus was designed to directly measure the angular mapping. For the nominal case of a particle illuminated at the center of a laser beam in a well-aligned optical assembly, the mapping is critical for theoretical light-scattering calculations used for data inversion purposes. The mapping apparatus is also useful for alignment and for investigation of the effects of misalignment and variation of particle position within the laser beam. Results from these investigations will be presented.

The performance of the MLS spectrometer will be characterized in terms of its response to aerosols of known size, shape, and composition. Calibration of the phase function detector will be carried out with PSL spheres of varying size. Sensitivity of the phase function to composition will be demonstrated with monodispersions of transparent droplets. Characterization of the sensor’s response to particle shape, consisting of measurement of the variation in azimuthal scattering, will be accomplished with nonspherical particles composed of crystalline materials.

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8PC3

COMPUTATIONAL FLUID DYNAMIC MODELING OF TWO PASSIVE SAMPLERS.

Suresh Dhaniyala, Thomas M. Holsen, JUSTIN THOMAS, Clarkson University, Potsdam, NY

To effectively use a passive sampler for contaminant monitoring, knowledge about its interaction with the external flow and ambient contaminants is needed so that sorbed concentrations can be converted to equivalent ambient concentrations. In this study, two commonly used passive samplers (Jaward et al., 2004) that consist of a polyurethane foam disk (PUF) as the sampling medium enclosed in bowl-shaped chambers are evaluated using computational fluid dynamics (CFD).

Preliminary experimental studies with these samplers have shown that they sample at rates, which are largely independent of the ambient wind conditions for external wind speeds of 1 to 4 m/s (Tuduri et al., 2005). The objective of this study was to characterize the external-internal flow linkages for the samplers and to quantify the uptake rate of contaminant species on the PUF in the samplers. The dampening factors that relate internal flow speeds to external speeds were calculated from CFD simulations and compared favorably with the values obtained experimentally. The simulations, however, show that the flow fields in the samplers have strong velocity gradients and single-point measurements do not capture the flow interactions accurately.

Contaminant uptake by the PUF in the samplers was modeled using a species transport model. Sampling rates calculated assuming the PUFs are perfect sinks are greater than those obtained experimentally at similar internal velocities, although this comparison is complicated by the strong position-dependent velocities in the samplers. A shift in location used to determine internal velocities could change their values by a factor of 5. Numerical calculations of sampling rates for a PUF sampling in freestream (i.e., without an enclosure) are in general agreement with those calculated for PUFs in the samplers. The variable sampling rate slopes found experimentally for PCBs can be attributed to differences in boundary layer characteristics over the PUF. Laminar boundary layers result in relatively constant uptake rates, while turbulent flows results in much larger uptake rates. Further detailed species transport modeling is underway and the results will be used to develop a new optimized passive sampler.

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8PC4

A NEW INSTRUMENT FOR NEAR REAL-TIME SIZE-RESOLVED SUB-MICRON PARTICLE COMPOSITION.

Manish Ranjan, Graduate Student, Clarkson University Suresh Dhaniyala, Assistant Professor, Clarkson University

Real-time instruments for particle sizing and composition analysis are required to effective characterization of ambient aerosol. The currently available instruments are large in size, expensive, and often complicated in operation. Towards development of a compact instrument for size-resolved sub-micron particle composition studies, a new instrument design is presented. This instrument builds on the design of the Miniature Electrical Aerosol Spectrometer (MEAS) (Ranjan and Dhaniyala, 2005). The MEAS design is composed of three sections: a charging section; ESP section; and classification section. The particles are charged in the classification region using a radioactive source (Po210) and sent to the ESP section where charged particles are sent through a parallel channels, spaced ~1mm apart. A potential difference is applied to capture charged particles in all channels except one, through which charged particles are sent to the classification region. In the classification region, charged particles migrate due to an applied electric field and are collected on plates. The position of the collection plate and the magnitude of the applied voltage determine the particle size collected on the plates. The transfer function of the EAS has been calculated theoretically (Knutson and Whitby, 1974) as a function of operating conditions and instrument dimensions. Preliminary experimental results with electrometers connected to the plates suggest that the particle size distributions measured by MEAS compare well with that obtained by SMPS for high concentration input aerosol.

Current research has focused on extension of MEAS for composition monitoring. For these measurements, the collection plates are heated to desired temperatures to volatilize the collected particles and the resultant sample is analyzed by gas-analyzers at the MEAS exit. The collection plates are heated in succession to get size-resolved near-realtime composition characteristics of aerosol particulate matter collected on the plates. The temperature distribution in the detection region and the flow behavior of the volatilized species are modeled to ensure effective transport to analysis section. Results of the instrument design, flow modeling, and preliminary experiments will be presented.

References:
Knutson and Whitby (1974)
Ranjan and Dhaniyala (2005), to be sent to (Aerosol Science and Technology, July 2005).

8PC5

INSIGHTS INTO PARTICLE MOTION, AIR FLOW, AND THERMODYNAMIC FIELDS IN AN ICE NUCLEATION CHAMBER. DEREK J. STRAUB, Susquehanna University, Department of Earth and Environmental Science, Selinsgrove, PA; David C. Rogers, National Center for Atmospheric Research, Boulder, CO; Anthony J. Prenni, Paul J. Demott, Colorado State University, Department of Atmospheric Science, Fort Collins, CO.

Thermal gradient diffusion chambers have been used for decades to study the abundance and characteristics of aerosol particles that act as cloud condensation nuclei (CCN) and ice nuclei (IN). These chambers typically consist of two parallel, wetted plates separated by a short distance. By holding the two plates at different temperatures, linear gradients in temperature and water vapor develop between the plates and produce supersaturated conditions within the chamber. One such instrument is the Colorado State University (CSU) continuous flow ice nucleation chamber, which has been developed to investigate IN in the lab and from aircraft. The airborne version of the CSU ice nucleation chamber consists of two 90 cm long concentric cylindrical plates. Both walls are ice coated and held at controlled temperatures to create a region of supersaturation in the annular space between the walls. Sample aerosols, which are continuously injected at the top of the chamber between two sheath air flows, transit the chamber in approximately 10 s.

Computational fluid dynamics (CFD) analysis has been used to investigate flow dynamics, thermodynamic properties, and particle trajectories in the CSU ice nucleation chamber. Previous CFD modeling efforts have provided useful profiles of velocity, temperature, turbulence, supersaturation, and particle motion within the chamber, but have focused on a single set of chamber conditions. The current CFD modeling attempts to expand upon the previous results by providing insight into chamber operation for a range of conditions encountered during airborne use. Of particular interest are model simulations representative of cirrus clouds (300 mb, -50 degrees C, 95% RH). The current work also evaluates the effects of slowly changing boundary conditions as warm wall evaporation and cold wall deposition occurs. Additional modeling efforts have focused on the effects of unintentional gradients in boundary conditions along the length of the chamber and an updated inlet geometry.

Modeling of the CSU ice nucleation chamber was performed with the CFD package FLUENT (Fluent Inc., Lebanon, NH). The model domain consists of an unstructured 3D mesh that encompasses a 5 degree wedge of the chamber, with periodic boundary conditions simulating the full annular space. The domain extends from the inlet to the outlet of the chamber in order to provide complete particle histories for the initialization of nucleation and growth models. The CFD simulations included water vapor transport, Reynolds Stress Model turbulence parameterization, and wall functions for near-wall flow. Trajectories of spherical particles were simulated using FLUENT’s lagrangian particle model.

8PC6

DEVELOPMENT AND PERFORMANCE OF CHARGED NANO PARTICLE COLLECTOR. YONGJING ZHAO and Anthony S. Wexler, University of California-Davis

Nucleation events have been observed at many sites worldwide, but the mechanism of the nucleation process is not clear – several hypotheses have been posed to explain these events. To obtain further insight into the chemical composition of these nano particles, a Nano Particle Collector (Nano PC) has been developed based the size dependence of particle mobility. We constructed a narrow slot mobility spectrometer with the air flow perpendicular to the electric field. In conventional particle mobility spectrometers, the Reynolds number of the sheath flow is governed by the electrode spacing whereas in a narrow slot mobility spectrometer, the Reynolds number is governed by the slot width allowing much higher mobility particles to be analyzed. Sheath and sample gases pass through the spectrometer and the field causes particle migration towards a collection surface. By adjusting the flow speed and electric field strength, charged particles less than 10 nm can be collected on a 3” long substrate or on TEM (Transmission Electron Microscope) grids.

To test the Nano PC, a TSI atomizer was used to generate nano particles, particle sizes were confirmed with a TEM, and composition was analyzed using XRF and EELS. Nano PC theory, design and test results will be shown in this presentation.

8PC7

DESIGN, CONSTRUCTION AND EVALUATION OF A TWO-DIMENSIONAL AERODYNAMIC FOCUSING INLET FOR PARTICLE CHARACTERIZATION BY LASER METHODS.

XIHONG WU, Nicolo Omenetto, Jonathan Merten, Benjamin W. Smith, James D. Winefordner, University of Florida, Gainesville, FL

Aerodynamic lenses which are analogous to the band pass filters, allow particles within a particular size range to be transmitted efficiently. Such a device is primarily used as an aerosol concentrator for subsequent mass spectrometric analysis. With their unique structure and high focusing performance, aerodynamic lenses have been widely used in aerosol science. In most applications, the geometry of the aerodynamic lenses is fixed, and pressure is varied to focus particles within a certain size range. Our research group has recently focused on the characterization of a wide range of atmospheric aerosols, from ultra-fine particles to bio-aerosols (20nm-10um). When one needs to focus a wider particle size range, a limitation arises from the fact that only one variable (pressure) is adjustable to achieve different focusing ranges. It is well known that the focusing dynamics of aerodynamic inlets is a complicated function of lens geometry and working pressure. Therefore, on this basis, a new inlet system was proposed, developed, and characterized in our work. Both variables (lens diameter and pressure) can be simultaneously optimized to extend the focusing range or select a particular size range in the new inlet system. In order to provide a fundamental view of focusing dynamics and a guide in instrument design, theoretical simulation using FLUENT protocol was previously carried out to model the dependence of focusing characteristics on lens geometry and working pressure for both single and multiple-lense systems. The particle beam profile, transmission efficiency and detection efficiency as a function of particle sizes under different working conditions are currently being monitored using optical and electrical techniques. The versatility and advantages of this particle collimator will be discussed and compared with existing systems. Eventually, this system will be capable of sampling, sizing and detecing fluorescence and lifetime signal from an individual airborne biological particle on a real-time basis.

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8PC8

SAMPLING OF BIOLOGICAL COMPOUNDS FROM AEROSOLS AND THE PROSPECTS FOR INSTRUMENT MINIATURIZATION.

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The detection of high mass ions is important in the identification of biological compounds and this has traditionally been done by matrix-assisted laser desoprtion/ionization time-of flight mass spectrometry (MALDI/TOF). The detection of large molecules directly from aerosols has been less common, and indeed aerosol analysis poses a specific challenge in this case, because unlike conventional MALDI, the individual starting conditions for ions, particularly their spatial distributions, vary significantly, both from particle to particle and from a single particle. Previous work in our laboratory has utilized an approach to small TOF design that has been useful in detecting high mass biomarkers from Bacillus spore simulants. This approach is applied here to aerosol particles.

The effects of initial conditions on the mass spectra were investigated using a TOF mass spectrometer with a drift tube 8 inches in length and an MS source region of 6 mm. Both prompt and delayed extraction can be used to accelerate the ions. Samples spotted on a probe are inserted into the mass spectrometer in a configuration that enables us to vary the initial positions. The sample probe is irradiated with a nitrogen laser (337 nm) where a variable attenuator is inserted in the beam to regulate the laser power. The entire mass spectrometer source and mass analyzer is installed on a heavy-duty xyz micrometer stage to optimize its position with respect to the probe and/or an incoming aerosol beam.

Mass spectra of different proteins were obtained from both the direct insertion probe and from an aerosol phase. The experimental flight times of ions were in good agreement with the theoretical flight times obtained from the modeling studies, but can vary as much as 700 ns (insulin) or 660 ns (ubiquitin), depending upon the initial position.

The effect of delayed extraction on aerosol phase sampling was investigated using insulin as the test compound. Generally, because the effects of initial spatial distribution are greater than those from initial energies, the resolution decreases at longer delay time, though overall signal intensity is not greatly affected (7% at 45 ns; 45% at 800 ns). Prompt extraction has also been used and compare with these results, and in some cases produces better mass resolution and intensities. This contrasts with conventional MALDI instruments in which the spatial distribution is minimal.

8PC9

EVALUATION OF ORGANIC CARBON ARTIFACTS WITH IMPROVE AND STN SAMPLERS.

Max Peterson, James O'Rourke, JAMES FLANAGAN, and R.K.M. Jayanty RTI International, Research Triangle Park, NC

Particulate matter with aerodynamic diameters of 2.5 µm and smaller (PM2.5) 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 of PM2.5 in ambient air, but whether the correlation is actually to total mass concentration or to specific chemical species comprising PM2.5 is a key question.

The deployment of PM2.5 monitoring networks in the U.S. is a critical component in the implementation of the PM2.5 National Ambient Air Quality Standards (NAAQS). Data from the FRM compliance network are used to determine attainment with the NAAQS. In addition, two nationwide networks currently monitor chemical species in PM2.5. The Speciation Trends Network (STN) provides PM2.5 monitoring in urban areas for the purposes of identifying sources, developing implementation plans, and supporting ongoing health effects research. The IMPROVE network (originally established for visibililty research) provides monitoring in remote areas. Because there is much current interest in merging and intercomparing data from these two networks, RTI International has undertaken a series of experiments to compare results obtained from the IMPROVE sampler and the URG, Inc. MASS 450 STN sampler. This presentation will show the results of an investigation into several different methods for determining the background organic carbon often present on quartz filters used in sampling for PM2.5 organic carbon.

It is thought that quartz filters used for sampling Organic Carbon and Elemental Carbon (OC and EC) may acquire a very high OC background by adsorption of vapor-phase organic compounds during handing and use. The IMPROVE and STN programs have different ways of attempting to correct or compensate for this background. IMPROVE uses subtraction of dynamic blank levels obtained from analysis of a backup quartz filter mounted behind the sampling quartz filter. Levels obtained from periodically deployed backup filters are averaged and used to correct the OC measurement. The STN program does not perform an explicit subtraction of background in its dataset; however, data from analysis of trip blank and field blank filters are available and may be used to estimate the OC background. Even though the STN field and trip blanks are not dynamic blanks, previous studies using collocated samplers from the networks have shown that correcting the STN data for background tends to improve OC data agreement.

This presentation will compare OC and OC background results obtained by RTI during a side-by-side sampling study comparison of background OC estimated by the IMPROVE and STN methods. These results may be helpful in intercomparing OC data obtained by the two national speciation networks.

8PC10

ANALYTICAL ADVANCEMENT OF THE PHOTOIONIZATION AEROSOL MASS SPECTROMETER (PIAMS) FOR ORGANIC AEROSOL CHARACTERIZATION.

MATTHEW DREYFUS, Michael Tolocka, Murray Johnston, University of Delaware, Newark, DE

The Photoionization Aerosol Mass Spectrometer (PIAMS) permits real-time characterization of organic compounds in aerosols. Particles are sampled through an aerodynamic inlet and deposit on a probe inside the mass spectrometer. After a sufficient mass is collected (typical detection limits are in the low picogram range), an infrared laser beam irradiates the probe to desorb the collected material and a vacuum ultraviolet beam crosses the vaporized plume to softly ionize organic molecules. Several changes have been incorporated to the original PIAMS instrumental design to enhance laboratory and field measurements. First, various collection probe materials, including copper, stainless steel, and tungsten were compared to the original aluminum probe. The stainless steel probe requires the lowest desorption laser energy and gives the highest signal intensities with the least amount of molecular fragmentation. Second, a cooling system was coupled to the probe. The “cold” probe assists PIAMS by retaining semivolatile compounds on the probe during sampling, particularly during long collection periods. Third, the manual aerosol inlet valve was replaced with a computer-operated valve. This allows for full automated control of the instrument.

Using the aforementioned changes, the detection efficiencies and detection limits of various individual and mixed organic aerosols have been obtained. The detection efficiencies permit quantification of organic components in the sampled aerosol. Laboratory experiments of SOA formation are performed by direct sampling into the PIAMS. Ambient aerosol measurements are performed in conjunction with an aerosol concentrator so that ambient concentrations on the order of 1 ng/m3 can be measured with a time resolution of a few minutes. Examples of these types of measurements will be presented.

8PC11

PARTICLE FOCUSING AT ATMOSPHERIC PRESSURES.

RAVI S CHAVALI, Goodarz Ahmadi - Clarkson university, Potsdam, NY 13699

Conventionally, particle beams are produced by passing a particle laden gas through a series of orifices at near vacuum pressure conditions. In this present work, a variety of designs for aerodynamics lens are considered and their performance at near atmospheric pressures for focusing of nano and micro-particles is studied. For comparison, geometries with orifices, converging nozzles, and converging-diverging nozzles are considered. For a range of inlet pressure conditions, the axisymmetric compressible airflow conditions in the device for near atmospheric outlet condition are evaluated. The gas-particle flow computations are done using the Reynolds averaged compressible Navier-Stokes equation along with the continuity and the energy equations using the CFD software FLUENT® 6.1.1.22. Lagrangian trajectory analysis is used to evaluate the particle motions. The governing equation of particle motion includes the effects of drag, lift and Brownian forces. One-way coupling is used, and the effect of dilute particle concentrations on the flow field is ignored in determining the particle trajectories.

8PC12

ULTRASENSITVE MEASUREMENT OF AEROSOL LIGHT ABSORPTION BY THE PHOTOACOUSTIC METHOD.

W. PATRICK ARNOTT, Hans Moosmüller, Desert Research Institute, Reno NV; Jeffrey Brook, Environment Canada Air Quality Processes Research Division, Toronto CANADA

Measurements of light absorption by black carbon aerosol are needed to quantify their effects on the atmospheric radiation budget. These measurements are also useful for quantifying the mass concentration of black carbon aerosol since light absorption typically takes place throughout the entire particle volume. Measurements are needed for very clean environments such as remote areas distant from combustion sources and aloft, for highly polluted environments such as mega-cities, and for source-samples from vehicles. Photoacoustic measurements of aerosol light absorption make use of the heat transferred from particles periodically heated by a laser beam, and the associated acoustic pressure disturbance, to determine aerosol light absorption in situ. Photoacoustic measurements have been shown to be highly effective for heavily polluted environments, where the wide measurement range of the microphone provides superior dynamic range, while being adequately sensitive for the lower range. In this paper we report on a recent instrument that achieves 0.07 inverse megameter sensitivity with a 15 second time constant, corresponding to an aerosol black carbon mass loading of around 12 ng per cubic meter. A compact laser diode at 870 nm with modulated output power of around 1 W is used for this instrument. Measurement examples from ambient air and from use on a mobile sampling laboratory will be presented along with a description of the instrument.

8PC13

DEVELOPMENT OF A UNIFORM GROWTH PARTICLE COUNTER (UGPC) USING CONDENSATIONAL GROWTH AND ELECTRICAL MEASUREMENT TECHNIQUES.

SEUNG-BOK LEE, Gwi-Nam Bae, Kil-Choo Moon, Korea Institute of Science and Technology, Jun-Ho Ji, Samsung Electronics

The condensation particle counters (CPCs) are widely used for measuring ultrafine particles. The ultrafine particles are grown with the condensation of alcohol vapor, and they are detected optically. The optics has possibility to be contaminated with the overflow of alcohol vapor. Recently, the electrical technique is also widely utilized in real-time measurement of particles. The aim of this study is to replace the optics with electrical unit in a CPC. A prototype uniform growth particle counter (UGPC) was developed using the condensational growth and electrical measurement techniques.

The UGPC consists of a diluter, screens, an impactor, a saturator, a condenser, an aerosol charger and a Faraday cage, an electrometer, and flow control unit. The particles below or above the measuring range of particle size are removed using a screen or an impactor, respectively. The polydisperse ultrafine particles passing through the preseparators are grown uniformly by the condensation of n-butanol vapor in a saturator and a condenser, and then all particles have almost same charges with ions generated by a corona discharger. The flow rate passing through the saturator is set to about 1.0 L min-1. The ion flow containing n-butanol vapor is mixed with sampled flow containing uniform growth particles downstream the condenser to prevent the evaporation of n-butanol vapor condensed on particles. The thin glass fiber filter media of HEPA grade is used to detect charged particles in the Faraday cage. The current response of a UGPC was compared with that of a cartridge type HEPA filter using coarse oleic acid and ultrafine NaCl particles.

The performance of condensational growth unit was tested changing the temperatures of a saturator and a condenser. The mean diameter and geometric standard deviation of particles at the exit of condenser was about 5 mm and 1.2, respectively, when the temperatures of a saturator and a condenser was 38°C and 18°C, respectively.

8PC14

PORTABLE AEROSOL SPECTROMETER FOR QUICK DIFFERENTIATION OF ABIOTIC AND BIOTIC MATERIAL.

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INTRODUCTION

As novel prototype, a portable instrument for quasi real time differentiation of abiotic and biotic mate-rial is presented. Particles are analyzed concerning their size distribution and collected for further bio-logical evaluation. This is a particle counter from 0,3 to 30 µm measurement range in combination with a integral impactor and collector for immedi-ate biological UV spectrometry analysis.

MATERIAL AND METHODS

The detection of the aerosol takes place in two steps. In the first step the aerosol passes through an “optical particle counter” (OPC) and in the second step particles of possibly biotic/abiotic size are separated with an impactor and collected on a mi-croscope slide.

One of our high resolution aerosol spectrometer with on-line qualification determinates the particle size and number concentration.

The sampled air passes a special collection device where all particles counted are collected. An addi-tional analyser of the microscope slide makes the conventional analysis of the particles (e.g. using a fluorescence microscope or a CCD camera can be carried out). By staining of the collected sample and following measurement with UV light, the bi-otic particles can be differentiated from the abiotics.

This new instrument is a battery driven stand-alone unit and allows to collect and store data measure-ment data from many different particle sizes for many hours as well as the collect sample. Connect-ing the unit to a computer permits instantaneous size and concentration analysis using our comfort-able software package.

8PC15

CALIBRATION OF PHOTOACOUSTIC MEASUREMENTS OF AEROSOL LIGHT ABSORPTION USING THE OXYGEN A-BAND AND A TUNABLE DIODE LASER. ALI ABU-RAHMAH, Hans Moosmüller, and W. Patrick Arnott, Desert Research Institute, University of Nevada System, Reno, NV

Atmospheric aerosols play a key role in radiative transfer and thereby influence the climate of the Earth. In particular, aerosol light absorption reduces the amount of sunlight at the surface and heats the atmosphere, resulting in dynamical changes of air motions and reduction in cloudiness. These aerosols also reduce visibility in cities and scenic areas, influence satellite remote sensing, and affect human health.

Measurements of aerosol light absorption by filter techniques are difficult to interpret from lack of a primary calibration standard as well as from the variable influence of aerosol chemical composition and hydration state. On the other hand photoacoustic techniques can provide a first principle measurement of aerosol light absorption that is commonly calibrated with strongly light absorbing gases. In the visible and near-ultraviolet spectral region, nitrogen dioxide has been used exclusively for this purpose. Disadvantages of this procedure are directly related to the use of nitrogen dioxide, a noxious gas with related safety concerns. Introduction and complete removal of nitrogen dioxide from the photoacoustic system can also be cumbersome and time consuming.

Currently, we are exploring to replace nitrogen dioxide as calibration gas with molecular oxygen. Oxygen is ubiquitous in the earth atmosphere at a relatively constant concentration of 21%. It has strong isolated absorption lines in the oxygen A-band between 759.5 and 775.25 nm. No other atmospheric gases absorb significantly in this wavelength range. We are using a commercial external cavity diode laser for this work. Calibration of the photoacoustic instrument with a narrowband diode laser using absorption lines in the oxygen A-band is expected to be much superior to the previously utilized nitrogen dioxide calibration. The calibration can be performed at any time during atmospheric measurements, as oxygen is always an integral part of any ambient sample. Aerosol light absorption and extinction do not interfere with the calibration process either, because the narrow oxygen lines (FWHM?0.1 cm-1/atm) allow differential online - off-line measurements without interference from the broadband aerosol optical properties. In addition, the spectral region just below the A-band in wavelength has remarkably low absorption, ideal for the measurement of aerosol absorption. Oxygen A-band spectra taken with the DRI photoacoustic instrument will be shown and implications for the use of oxygen as calibration medium will be discussed.

8PC16

ION MOBILITY ANALYSIS OF PARTICULATE MATTER AND GAS PHASE PRECURSORS. Mang Zhang, Anthony S. Wexler, University of California, Davis, CA

Based on a novel (patent pending) 2D ion mobility spectrometer, a suite of new instruments enable a wide range of chemical aerosol measurements to be performed with light (a few kg), power stingy (<10w), and cheap (<$3K parts cost) that will provide high frequency, quantitative concentrations of the gas and particulate semivolatile compound concentrations.

The heart of these instruments is a 2D ion mobility spectrometer able to perform continuous gas-phase chemical analysis. The mobility cell separates ions in space, as does a DMA. The resulting spatial current distribution is recorded by a linear array of electrometers. Key to the viability of the mobility spectrometer is recent progress in CMOS active pixel sensors and multiplexed electrometer arrays. These instruments will be tested side-by-side against standard instruments. We will present these instruments and field test data if available.

8PC17

IN-LINE SAMPLE PREPARATION OF BIO-AEROSOL PARTICLES FOR AEROSOL MALDI MASS SPECTROMETRY. J.C.M. MARIJNISSEN, M.A. Stowers, W. A. Kleefsman, Delft University of Technology A.L. van Wuijckhuijse, Ch.E. Kientz, O. Kievit, TNO Prins Maurits Laboratory

For the analysis of bio-aerosol particles an aerosol MALDI mass spectrometer has been developed (Wuijckhuijse et al, 2005). This instrument combines aerosol time-of-flight mass spectrometry with matrix assisted laser desorption/ionization (MALDI). In this method the matrix, usually an organic acid with a molecular mass of 200-300 Da, allows high mass molecules to be transported into the gas phase.

For on-line analysis of bio-aerosol particles, such as airborne bacteria, the matrix compound must be applied as a coating on the particle in their flight, when the particles enter the spectrometer. We have developed a device to apply matrix to particles in flight, based on the evaporation-condensation principle.

Different variations of this application technique with their advantages and disadvantages will be discussed and some attention will be given to a complete new approach of matrix coating.

This work was co-funded by the Dutch Ministry of Defence and TNO Prins Maurits Laboratory.

8PC18

PERFORMANCE CHARACTERISTICS OF THE AEROSOL PARTICLE MASS ANALYZER. NOBUHIKO FUKUSHIMA, Naoko Tajima, Kanomax Japan Inc., Suita, Japan; Kensei Ehara, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; Keven J. Coakley, National Institute of Standards and Technology, Boulder, CO

The APM, which can classify the particles having the same mass to charge ratio, has been developed for years by authors, and has already confirmed the basic operation as a classifier based on particle mass, and was applied to the measurement of some atmospheric aerosol research. Meanwhile, it has been known there was unknown problem of the delay of the response, for example, it was necessary to wait almost ten times longer than the calculated response time. This problem was clarified under the assumption to prevent the adhesion and repulsion of the charged particles on the insulation material inside the classifier, and has already reported. To keep the accuracy of classification of the particle on mass basis, it is necessary to certify the important dimensions, for example, the diameters of inner and outer electrode, and the gap of these electrodes. Therefore, the distance of the electrodes was determined precisely with the accuracy of 10um level, and to keep the gap under high totating spped, we have designed to reduce the dimensions of the electrodes, in other words, to reduce the mass of electrodes. Moreover, since the transfer function of the APM has been eveluated using the PSL particles larger than 100nm so far, the characterstics of the transfer function for several scores of the nanometer sized particles were examined in this study. New design concept and the performance of this instrument, particularly the classifying characteristics of smaller particles will be shown experimentally.

8PC19

CHARACTERIZATION OF AN AEROSOL FLOW TUBE-FTIR (AFT-FT) TECHNIQUE TO STUDY THE HETEROGENEOUS CHEMISTRY OF AEROSOLS. CINDY DEFOREST HAUSER, Jamie Ferguson, Steve Tolson, Davidson College, Davidson, NC

Validation studies are presented for a method in which an aerosol flow tube is combined with Fourier Transform Infrared Spectroscopy (FTIR) to study the heterogeneous chemistry of aerosols. In this method, the reaction time between the aerosol particle and the gas-phase reactant, ozone, is varied by introducing ozone at different positions along the length of the flow tube. Following reaction, the aerosol particles are evaporated using thermoconductive heating elements. The vapor is then analyzed in a heated long-path White cell. Interpretation of the infrared spectrum provides information regarding the products and rate of the reaction between the aerosol particle and the gas-phase species of interest. Method parameters to be presented include detection limits, limits of linearity, calibration curves for aerosol and ozone concentration, flow tube characteristics, exploration of degradation and reaction in the heating stages and application to the system of unsaturated organic aerosols reacting with ozone.

8PC20

UNDERSTANDING VIRTUAL IMPACTION BY CFD. Marwan L. Charrouf, Richard V. Calabrese, and JAMES W. GENTRY, Department of Chemical Engineering, University of Maryland, College Park, MD, USA

In this work Computational Fluid Dynamics Simulations were conducted to model the fluid and aerosol transport inside a widely used particle collector-separator known as the virtual impactor. Our objective is to use computer modelling to design and optimize innovative designs to efficiently sample biological aerosols of the one micron range. The device geometry and flow conditions were taken from the experiment of Sioutas et al. (1994) who reported a 50% cutpoint diameter of 0.12 micro-meter. For this high-speed impactor, the steady state, three dimensional RANS equations were solved for both incompressible and compressible flow to predict the turbulent velocity field. Particle trajectories were then calculated using a one way coupling technique with two different Lagrangian tracking schemes. The first uses only the mean velocity field (tracking relative to streamlines). The second uses a Random Walk model (stochastic approach) to account for the effect of turbulent velocity fluctuations. Since fluctuations can significantly affect particle trajectories and wall loss, it is important to realistically predict turbulence levels. As a result, two closure schemes were considered. These are the standard k-epsilon model, which requires an assumption about how the turbulent kinetic energy yields the individual components of root mean square (rms) turbulent velocity, and the more computationally intensive Reynolds stress model (RSM), which directly yields the rms velocities by solving their respective transport equation. The results show that it is necessary to account for the compressible nature of the flow in order to achieve the desired flow cutpoint. In addition, it was found that the choice of the turbulence closure model that is used in conjunction with the stochastic scheme significantly influences the predicted collection efficiency and wall loss. This was tracked down to be an outcome of the isotropic handling of k-epsilon model in contrast to the inherently non-isotropic Reynolds stress model which yielded more realistic results. The efficiency and wall losses curve exhibit reasonable agreement with classical experimental behavior.

8PC21

COUNT AND MASS CORRELATION OF TWO APS 3321 INSTRUMENTS.. Richard S. Tuttle, GARY L. SPARKS, JR., Patricia A. Reuther

This study was designed to determine count and mass measurement correlation between two independent Aerodynamic Particle Sizer (APS) (TSI, Inc., St. Paul MN) instruments. The purpose of count correlating the APS units was to assess the validity and accuracy between the units for impinger collection efficiency testing. This APS count correlation method could also be used for aerosol system homogeneity testing and aerosol system transport loss measurement. Polystyrene Latex Microspheres (PSL) (Duke Scientific, Palo Alto CA) standards at sizes of 0.993µm, 1.992µm, and 1.92µm were utilized in the experiments. Independent PSL standards at each PSL size were prepared suspended in a solution of 50% sterile H2O and 50% ethanol. Each standard was aerosolized into a 1 liter plexiglas plenum using a new disposable VixOne TM nebulizer (WestMed, Tucson, AZ). The system was operated dynamically while maintaining a differential pressure in the range of 0 to -0.05 inches of water for all tests.

The APS units were connected to the plenum using Tygon® sample tubes of identical length. Both units were synchronized to sample simultaneously for thirty seconds in triplicate following a 1 minute period from the initiation of nebulizer aerosol dissemination. Post test count and mass concentration results were compared for each PSL size. To correct for non – count and mass correlation results, APD (avalanche photo detector) voltages were adjusted for each unit, and tests repeated, until count and mass correlation results were within 5 % for each PSL size. Decreasing the APD voltage results in a reduction of laser intensity and sensitivity for particle measurement and detection. Count and mass results for each unit was plotted using Sigma Plot version 8.02A graphing software. Percent deviation of count and mass results for each instrument was calculated for aerosol measurement correlation. The results showed a count and mass correlation result to be less than 3.5% for all PSL sizes tested.

8PC22

CHARGED REDUCED ELECTROSPRAY SIZE SPECTROMETRY: THE APPLICATION OF AEROSOL SIZING INSTRUMENTATION TO THE ANALYSIS OF VIRUSES AND MEGADALTON MACROMOLECULES. CHRISTOPHER J. HOGAN JR., Eric M. Kettleson, Bala Ramaswami, Da-Ren Chen, Pratim Biswas, Environmental Engineering Science, Washington University, St. Louis, MO.

In recent years, the use of electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) to produce gas phase ions from biomolecules has allowed for the mass analysis and identification of macromolecules via mass spectrometry. However, multiple charging effects make identification via mass spectrometric methods difficult for molecules with masses in the Megadalton (MDa) range. Macromolecules in this mass range typically have characteristic sizes in the 10 to 100 nanometer range, thus making it possible to utilize differential mobility analysis with condensation particle counting in order to identify large biomolecules. Recent work by Kaufman and co-workers (1-3) has shown that globular proteins and nucleic acid molecules with molecular weights in the 5000Da to 2MDa range can be identified via differential mobility analysis and that the mobility diameter of such molecules can be correlated with their molecular weight. This correlation is dependent on the fact that globular proteins and nucleic acid take on a similar shape and bulk density when in the aerosol phase.

Here, traditional aerosol sizing instrumentation is used to analyze whole viruses and virus DNA, whose molecular masses extend beyond the Megadalton range. Bacteriophages from the leviviridae, myoviridae, and siphoviridae families were aerosolized via nanoelectrospray with subsequent charge reduction. Scanning mobility size spectrometry was then used to identify and quantify each virus. It was found that each virus had a unique mobility diameter, with characteristic lengths for the viruses in this study ranging from 24 to 92nm. This shows that size spectrometry can be used to determine the number concentration and type of viruses present in a solution. Electrosprayed viruses were also collected for viability testing to determine if electrospray atomization can be used to produce viable, single virus particles. The data shown here demonstrate how aerosol mobility sizing instrumentation can be used for rapid analysis of macromolecules whose mass is greater than what is measurable by current mass spectrometric methods.

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8PC23

3-D MODELING ON THE PERFORMANCE OF AN AIRBORNE COUNTERFLOW VIRTUAL IMPACTOR.

JUNHONG CHEN, Pengxiang, Wang, University of Wisconsin-Milwaukee, Milwaukee, WI; William C. Conant, Tracey A. Rissman, Richard C. Flagan, John H. Seinfeld, California Institute of Technology, Pasadena, CA

A three-dimensional model has been developed within the framework of the commercial computational fluid dynamics program, FLUENT, to investigate the collection efficiency of an airborne counterflow virtual impactor (CVI). The model assumes steady-state, isothermal, compressible, and turbulent flow. Particle trajectories are computed based on the Lagrangian discrete phase model (DPM). In addition to predicting the effects of flight velocity and counterflow rate on the particle collection efficiency as do prior models, the model quantifies the effect of flight attack angle on the particle collection efficiency. The critical size (the minimum particle size that is collected by the CVI) increases with decreasing flight velocity and increasing counterflow rate, which is explained by the increase of the distance between the two stagnation surfaces created inside the CVI. The flight attack angle has a negligible effect on the critical size and cut sharpness of the collection efficiency curve of the CVI. With an angle of attack as small as 5°, the CVI collection efficiency drastically degrades at large particle sizes and only particles with intermediate sizes are collected. Smaller particles do not have sufficient inertia to fight the counterflow, and larger particles tend to impact the CVI inner walls and are lost to the CVI walls. The modeling results show that the alignment between the free stream flow and the CVI inlet is critical to the performance of the CVI. A shroud based on the design of Twohy (1998) is used to straighten the flow entering the CVI tip. The performance of the CVI with the shroud is also evaluated with the model.

8PD1

NANOPARTICLES GENERATED IN THE RESULT OF THE POLITETRAFLUOROETHILEN THERMAL DECOMPOSITION.

M.P. Anisimov, A.M. BAKLANOV, I.A. Zayko, and A.A. Onischuk

Politetrafluoroethilen (Teflon-4)-polymer $(C2F2)n$, $n = 50-200$. Nanoparticles of Teflon-4 have a wide distribution in chemical and atomic industry, mechanical engineering, transport etc. as a chemically inert material. The good adhesive behavior and low friction coefficient of Teflon - 4 make it a profitable as the machine oil additive. Study of kinetics and mechanism of nanoparticle formation in a result of thermal decomposition of a polymer, for example politetrafluoroethilen, is an important problem of nucleation. The aim of the present research is an investigation of nanoparticle generation from the residue of politetrafluoroethilen thermal destruction. For generation of politetrafluoroethilen nanoaerosol the thermal decomposition is used. Flow reactor was composed of heated quartz tubing with inside diameter 12mm. A sample was placed inside of the tubing. Nitrogen gas with flow rate 1 l/s was used. The temperature of reactor was controlled by chromel-alumel thermocouple. Efficient length of hot zone was 350mm. A thermoprecipitator was applied for nanoparticles collection on formvar film. Concentration and particle size distributions are measured by screen diffusion battery. Resulting mean diameter was 20-100 nm for particles which are generated from the politetrafluoroethilen thermal decomposition residue. Morphology and size of nanoparticles was determined using TEM. In many cases one can see dark and relatively transparent areas for the same particle. We think that the different transparency within one particle is associated with the polymerized and nonpolymerized parts of single particle. The overview of the total results gives us the ability to conclude that possible initial monomers can produce particles of polymerized and nonpolymerized tetrafluoroethilen and their mixtures with nanosize dimensions. The reasonable wide interval of temperatures of decomposition and nucleation as well as the gas variety gives the ability to produce the nanosize particles in the result of the politetrafluoroethilen thermal decomposition. Variation of the nucleation conditions have chance to allow generation of particles with different ratio of polymerized and nonpolymerized tetrafluoroethilen in each single particle, which can be important for some particular problem solution.

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8PD2

REACTIVE UPTAKE OF NO3 RADICALS BY PROXIES FOR ORGANIC-COATED AEROSOL PARTICLES.

JACKSON MAK, Daniel A. Knopf, Simone Gross, Lori M. Anthony, Allan K. Bertram, University of British Columbia, Vancouver, BC

The reactions of NO3 radicals with organic surfaces may play an important role in atmospheric chemistry. Field studies have shown the presence of organic films on aerosol surfaces, particularly those originated from marine regions. The oxidation of organic films modifies the aerosol’s surface composition and may consequently change their hygroscopic properties. This may lead to an increase in cloud condensation nuclei (CCN) and the altering of the particles' optical properties, which may influence climate. Furthermore, the products released following reactive uptake may potentially be important to the chemistry of the atmosphere.

Using a range of experimental techniques, we are carrying out kinetic and product studies of the uptake of NO3 radicals by various organic surfaces. Self-assembled monolayers were used as proxies for organic-coated aerosols. Uptake coefficients were measured with a coated-wall flow tube reactor coupled to a chemical ionization mass spectrometer (CIMS). Gas-phase products were measured with CIMS, and surface products were analyzed with polarization modulation infrared reflection-absorption spectroscopy (PMIRRAS) and X-ray photoelectron spectroscopy (XPS). Results from these kinetic and product studies will be reported and the atmospheric implications will be discussed.

8PD3

SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS CE-MN-MCM-41 MOLECULAR SIEVES.

Tai Gyu Lee, Byong Hoo Kim, Manickam Selvaraj, Department of Chemical Engineering, Yonsei University

Mesoporous Ce-Mn-MCM-41 molecular sieves with Si/(Ce+Mn) molar ratio = 50, 100, 150 and 200, were synthesized using cetyltrimethylammonium bromide as surfactant, manganese acetate and cerium sulfate as source of manganese and cerium under hydrothermal conditions. The mesoporous materials were characterized using several techniques, e.g. XRD, FTIR, TG/DTA, Nitrogen adsorption, ICP-AES, SEM, TEM, UV-visible and ESR. XRD studies indicated that the materials had the standard MCM-41 structure. FTIR studies showed that cerium and manganese ions were incorporated into the hexagonal mesoporous materials. The thermal stability of the as-synthesized materials was studied using TG/DTA. Nitrogen adsorption was used to determine specific surface area, pore volume, pore diameter and wall thickness in the calcined Ce-Mn-MCM-41. ICP-AES studies indicated that the content of cerium and manganese in the mesoporous materials were determined. The morphology of Ce-Mn-MCM-41 materials was observed by SEM studies. The inference that the Ce-Mn-MCM-41 mesoporous materials had uniform pore size was determined by TEM studies. The incorporated of cerium and manganese ions oxidation state was determined by UV-visible and ESR. The incorporated metal ions as Ce4+, Mn2+, Mn3+ in Ce-Mn-MCM-41 are coordinated to Si(IV) by tetrahedral, disordered octahedral and tetrahedral environments, respectively. The cerium and manganese ions are homogenously dispersed on the inside silica surface of Ce-Mn-MCM-41, under hydrothermal conditions. The materials will be used for some oxidation reactions. Thus, details of the materials characterization results will be presented.

8PD4

DEPENDENCE OF WATER ACTIVITY, COMPOSITION, AND SIZE WITH NITRIC ACID REACTIVE UPTAKE.

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Chloride to nitrate conversion in sea salt aerosols has important consequences for the marine environment including production/destruction of tropospheric ozone, nitrogen cycling between the atmosphere and coastal ecosystem, and global climate change. Acid-displacement has been proposed to explain the depletion of chloride in marine boundary layer aerosols: HNO_3 (g) + NaCl (aq) -> $NaNO_3$ (aq) + HCl (g). Freshly created marine aerosols are expected to have a similar chemical composition to that of seawater, which is ~84% by weight NaCl. The relative humidity of the surrounding environment equilibrates the water activity, and thus solute concentration, in these marine aerosols. In this work, the kinetics of chloride to nitrate conversion in size-selected aerosols is monitored above and below the efflorescent relative humidity for pure sodium chloride, sodium chloride doped with magnesium chloride ($X_{Mg/Na}$=0.114), and a representative marine sea-salt. The water content of the mono-disperse aerosol is established by the relative humidity of the carrier gas stream. Particle diameters, and thus water activity, are monitored with the assistance of a SMPS. These size-selected aerosols are then mixed in a laminar flow tube reaction chamber with a steady state of nitric acid vapor (~60 ppb) at several contact times. Particle composition measurements are performed in real time with a single particle mass spectrometer (negative-ion mode). At room temperature and pressure, the pseudo first order rate constants and uptake coefficients for the nano-droplets (D_d ~100 nm) are determined at all relative humidities. HNO_3 uptake onto larger nano-droplets (D_d ~200 nm), under the same experimental conditions, was then explored to examine the reaction mechanism for all compositions of aerosol. Results indicate that the greatest magnitude of uptake occurs at the efflorescence relative humidity. Due to the alterations in particle hydroscopicity, the initial aerosol composition is a major factor in reactivity below the efflorescence relative humidity. Above the efflorescence relative humidity, uptake decreases with increasing relative humidity because the initial chloride concentration in the aerosol decreases.

8PD5

INVESTIGATION OF HIGH MOLECULAR WEIGHT (>282 U) PRODUCTS FROM THE HETEROGENEOUS REACTION OF OZONE WITH OLEIC ACID PARTICLES.

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The reaction of ozone gas and oleic acid particles has been used as a model system for investigating heterogeneous chemistry of more complex multi-component aerosols found in the atmosphere. In this work, we present a detailed discussion of both direct and indirect ozonolysis products of oleic acid, specifically focusing on higher order oxygenates observed in the aerosol mass spectrum at m/z values greater than the molecular weight of oleic acid.

Photoelectron resonance capture ionization (PERCI) is a soft method of molecular ionization developed for the analysis of organic analytes in atmospheric particles and resulting from aerosol-gas phase heterogeneous reactions in the atmosphere. Identification of organic compounds is facilitated by the reduced molecular fragmentation afforded by PERCI, which relies on the attachment of low-energy photoelectrons ($E < 10$ eV) to vaporized molecules. Tuning of the photoelectron energy can produce either associative or dissociative attachment, making the ionization method widely applicable or selective respectively.

Results are presented from application of the PERCI method, in combination with aerosol mass spectrometry (AMS) to the model heterogeneous reaction system oleic acid + ozone. In these studies, we measure all four major anticipated products, in addition to the unprecedented measurement of higher mass (>282 u) products, which suggests that Criegee intermediates generated in ozonolysis have sufficiently long condensed-phase lifetimes to undergo 1,3-dipolar additions. These additions typically occur between the carbonyl oxide zwitterions of the Criegee intermediate and a carbonyl group that is usually generated in situ. Mechanisms for the generation of 1, 2, 4-trioxolanes (300, 330, and 360 u) as well as geminal diperoxides (316 and 346 u) are proposed.

Current focus in our lab is on the measurement of higher molecular weight products (400 – 1000 u) generated during ozonolysis of oleic acid and other fatty acids by addition of the Criegee intermediates to intact oleic acid molecules, including polymers, from the ozonolysis of oleic acid and other fatty acids. These products are proposed to form as a result of successive 1,3-dipolar additions of Criegee intermediates to carbonyls as well as other Criegee biradicals.

8PD6

UNCERTAINTIES IN THE THERMOCHEMICAL DATA FOR BINARY SULFURIC ACID-WATER CLUSTER IONS.

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Uncertainties in the recently published thermochemical data for the binary sulfuric acid-water $H^+(H_2SO_4)_m(H_2O)_n$ and $HSO_4^-(H_2SO_4)_m(H_2O)_n$ cluster ions [1,2] obtained using experimental reaction constants and Ab Initio RHF/6-31+G(d) calculations are discussed. Two major sources of uncertainties not discussed in the original papers have been identified. First source relates to the van't Hoff analysis of the experimental reaction constants and the second relates to input parameters, which were not measured directly. The linearization of the van't Hoff equation performed in [1,2] has been found to be erroneous in a number of cases that lead to significant uncertainties in the reaction entropies and enthalpies derived from the van't Hoff plot. The thermochemical data derived in [1,2] are denoted as "experimental thermochemical values"; however, they are not strictly experimental. The evaluation of the experimental data includes, in addition to the derivation of the standard enthalpies and entropies from the linear fit of the van't Hoff plot, estimation of the cluster decomposition effect and the construction of the thermocheical cycle, with experimental enthalpies derived in [3] and theoretical Ab Initio RHF/6-31+G(d) entropies as input parameters. It has found that the employment of the Ab Initio method, which was not tested comprehensively, may largely affect the derived thermochemical properties. Our reanalysis of the same experimental dataset performed using non-linear fits to the van't Hoff plot leads to quite different values of derived entropies and enthalpies.

Deviation in enthalpy (kcal/mole)	>2	> 3	>5
Positive ions (%)	44.12	23.53	17.65
Negative ions (%)	35.42	27.08	16.67
Deviation in entropy (cal/mole/K)		>10	>20
Positive ions (%)		29.41	17.65
Negative ions (%)		27.08	12.50

Table 1. Percentage of the data points for standard conditions reaction enthalpies and entropies obtained [1,2] vs. difference in values between data of [1,2] from those obtained in [4].

This study suggests that thermochemical data presented in [1,2] feature considerable uncertainties and care should be taken when these data and thermodynamic models [5,6] derived using these data are used.

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8PD7

QUANTITATIVE LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR AEROSOLS VIA INTERNAL CALIBRATION: APPLICATION TO THE OXIDATIVE COATING OF ALUMINUM NANOPARTICLES.

DIBYENDU MUKHERJEE, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN; Ashish Rai and Michael R. Zachariah, Department of Chemistry and Mechanical Engineering, University of Maryland, College Park, MD

We present a methodology for the quantitative use of Laser Induced Breakdown Spectroscopy (LIBS) for the compositional characterization of nanoaerosols, using an internal standard. The approach involves finding the optimal laser delay time to collect spectra for each of the elemental species of interest, and measuring the plasma temperature, and background gas density under the same conditions. This enabled us to eliminate effects due to different experimental conditions, species excitation from different energy states, temporal evolution of the plasma volume itself and instrumental collection efficiencies and biases.

We apply the method to the problem of determining the extent of oxidation or coating thickness of aluminum nanoparticles. The specific choice of system is based on a need to understand the nature of energetic properties of nano-materials and in particular the reactivity and stability of passivation coatings, such as metal oxides.

The present work establishes LIBS as an effective analytical tool for quantitative estimation of the extent of oxidation in Al nanoparticles from time resolved atomic emission spectra. More generically this approach of using the background gas as the internal standard mitigates the need for the use of materials standards and should be extendable to the characterization of other multi-component aerosol systems.

8PD8

HETEROGENEOUS REACTIONS BETWEEN DIESEL PARTICULATE MATTER AND OZONE. Zhong Chen, ritt Holmén, Civil & Environmental Engineering, University of Connecticut, Storrs, CT

Diesel particulate matter (DPM) is suspended in the urban atmosphere and exposed to relatively high levels of ozone and other well-known urban pollutants. Little is known about the products of heterogeneous reaction between DPM and ozone. The polar organic products of these reactions are likely to be associated with adverse health effects, including premature mortality and higher instances of respiratory illness. In this study, “aging” experiments on the surface of DPM in the presence of ozone (O3) are investigated in order to determine the products of the oxidation reactions. After exposure to ozone at a constant concentration of 0.001-0.005 wt% for periods of 1 – 72 hours, products of both gas and particle phases are identified by TD/GC/MS. Because polar organic chemicals are more mutagenic, quantification of products is focused on carbonyls and carboxylic acids after derivatization with PFBHA and BSTFA. The results of these studies are used to further our understanding of atmospheric diesel particle chemistry and the impact of human activities on the atmospheric environment.

8PD9

A NEW ANALYTICAL MODEL FOR PARTICLE DEPOSITION TO FORESTS. F. Birsan, S.C. PRYOR, Indiana University, IN

The best known and most widely used analytical model for particle deposition to vegetation is that published by Slinn in 1982 (Atmospheric Environment 16 1785-1794). The theoretical framework used in the derivation of this model considers a steady state process with no horizontal advective flux, therefore the transport mechanism is in the vertical direction through turbulent mixing. In addition, it is assumed that both diffusivity coefficient, and the product of the drag coefficient, wind speed and the drag element distribution are constant within the canopy. Here we propose a modified form of this model which retains the theoretical framework mentioned above but removes these restrictive assumptions. We present the derivation of the model and some examples of the results including comparisons with the formulation of Slinn.

8PD10

TOPOLOGY OF THE NUCLEATION RATE SURFACES FOR LASER ABLATION OF CRYSTALS. M.P. Anisimov, A.M. Baklanov, V.S. Akimov, and P.K. HOPKE

There are a lot of investigations of the boiling kinetics for melted materials which are generating aerosol then. As examples can be mentioned the conducted wires which can blow up under electrical current (Martynyuk, 1977), the laser ablation of crystals (Q.Lu et al., 2002) etc. Crystal sublimation, liquid boiling and superheating up-to the spinodal conditions then aerosol production are considered in the mentioned articles. One might say that nucleation rate surface topologies for the gas and liquid embryos formation from crystal are not discussed up-to now in the scientific literature.

The nucleation rate surface topology for vapor embryo-forming from droplets under the laser ablation is considered qualitatively. The nucleation rate surfaces for droplets and vapor embryos are drown schematically. Surfaces overlap each other between critical points. Assumptions used for design are such as: nucleation rate along the phase equilibrium lines has zero values and the maximum nucleation rates are achieved at the spinodal conditions. It is assumed that nucleation rate surface is represented by continuous and monotonous function for one given phase state. Nucleation rate at the critical points has zero value because these points are representing the second order phase transitions where two different phase coexistence is impossible.

When the laser impulse radiation become over then vapor gets supercooled and generates mikrocrystals and mikro glasses in the same fashion as Buckle at al. (1986) get the amosphous and crystal particles from Mg vapors. Non-evaporated droplets should grow under the vapor cooling then freeze to the crystal or glass. First example of the nucleation rate surface topologies for the gas and liquid embryos formation from crystal under laser ablation is discussed. The topology of the vapor nucleation rate gives the reasonable basis for interpretation of aerosol generation under laser ablation.

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8PD11

IMPACT OF RELATIVE HUMIDITY ON GAS-PARTICLE PARTITIONING FOR THE CYCLOHEXENE/OZONE SYSTEM: COMPARISON OF EXPERIMENTAL VS. THEORETICAL PREDICTIONS.. QUENTIN MALLOY, Bethany Warren, Chen Song, David R. Cocker III, University of California, Riverside

Recently, theoretical studies on secondary organic aerosol (SOA) formation have predicted the impact of water on gas-particle partitioning for cyclohexene ozonolysis and selected biogenic compounds (e.g. Seinfeld et al., 2001). The cyclohexene predictions were based on the detailed chemical composition presented by Kalberer et al., (2000) performed for dry cyclohexene ozonolysis. However, little to no experimental work has been done concerning this system at elevated relative humidity (RH). In light of this, a series of cyclohexene/ozone experiments in the presence and absence of inorganic seeds were conducted in the UCR EPA environmental chamber at relative humidities between 25-75%. We utilize the derivatization techniques described by Yu et al. (1999), coupled with a denuder/filter/PUF-XAD system, to identify the species and measure the gas-particle partitioning for the dry and humid systems. Experimental results are compared with previous cyclohexene/ozone experiments performed by Kalberer et al. (2000) under dry (RH <5%) conditions, as well as with theoretical predictions from Seinfeld et al. (2001).

8PD12

THE EFFECT OF DISSOLVED INORGANIC SALTS ON THE FORMATION OF SECONDARY ORGANIC AEROSOLS FOR THE CYCLOHEXENE/OZONE SYSTEM.

BETHANY WARREN, Chen Song, David R. Cocker III, University of California, Riverside, CA

Several researchers have studied secondary organic aerosol formation from a number of different hydrocarbons; however, many of these studies have been performed in the presence of little to no water vapor. Therefore, the role of water in SOA formation remains poorly understood for many atmospherically relevant aerosol precursors.

One such aerosol precursor is the m-xylene/NOx system. This system has been extensively studied, and the impacts of varying NOx concentrations were reported at last year's AAAR conference. We now extend this work to investigate the role of gas-phase water on the SOA formation potential for the m-xylene/NOx system at both high and low hydrocarbon:NOx ratios.

We will also discuss the impact of water in the cyclohexene-ozone system. This system (dry) has been described extensively by Kalberer et al. (2000) and theoretical predictions of the SOA formation as a function of RH have been reported by Seinfeld et al. (2001). The present work carefully investigates the impact of gas- and aerosol-phase water on the total SOA formation potential for the cyclohexene-ozone system by first performing SOA experiments in the absence of inorganic seed aerosol, and then investigating the role of different seed aerosols (both dry and aqueous) on the SOA formation potential. These results will then be directly compared against theoretical predictions presented by Chang et al. (2004) at the previous AAAR conference.

8PE1

REGIONAL IMPACT OF THE OHIO RIVER VALLEY ON BOUNDARY-LAYER SO4 CONCENTRATIONS: RESULTS FROM INTEX-NA.

CHRIS HENNIGAN, Scott Sandholm, Rodney J. Weber, Rick Peltier, Greg Huey, Robert Stickel, Saewung Kim, Georgia Institute of Technology, Atlanta, GA

In the summer of 2004, measurements of fine inorganic aerosol composition were made aboard the NASA DC-8 as part of the INTEX-NA study. PM1 was measured with a PILS-IC system over the continental United States and parts of Canada, focusing on the eastern US and Canada. Sulfate was the dominant species measured, with the highest concentrations observed at low altitudes (below 2 km). Accounting for approximately 20 – 25 percent of continental US point-source sulfur dioxide emissions according to the 1999 EPA National Emissions Inventory, the Ohio River Valley (ORV) can impact the air quality of downwind regions significantly. An analysis has been performed to assess the influence of the ORV on fine particulate sulfate measured over the eastern US and Canada from the NASA DC-8 during INTEX-NA. The analysis was conducted using back trajectory models and produced several significant findings. Our analysis suggests that there was long-range transport of pollutants from the ORV over distances greater than 1000 km and transport events were observed over much of the sampling domain. Also, air masses with the highest sulfate concentrations observed in the study were apparently influenced by the ORV. Additionally, the sulfate concentration in air masses that were influenced by the ORV was, on average, a factor of three higher than in air masses that had no ORV influence. Multiple back trajectory models were employed to increase the confidence and utility of the analysis performed.

8PE2

AN INVESTIGATION INTO AQUEOUS OXALATE PRODUCTION USING A PARTICLE-INTO-LIQUID SAMPLER (PILS) DURING ICARTT 2004. ARMIN SOROOSHIAN, Fred J. Brechtel, Rick C. Flagan, John H. Seinfeld, California Institute of Technology, Pasadena, CA

Currently, the role of in-cloud processes toward the formation of organic particulate matter is not well understood. Previous filter-based studies have shown that oxalate and sulfate loadings are correlated in the atmosphere suggesting an in-cloud formation pathway for oxalate. Oxalate often comprises a significant mass fraction of the ambient organic aerosol. During the 2004 ICARTT field campaign, oxalate and nine inorganic ions (Na+, NH4+, K+, Mg2+, Ca2+, Cl-, NO2-, NO3-, and SO42-) were measured on board the CIRPAS Twin Otter research aircraft. The sampling area included Ohio, its neighboring states, and Lake Erie. A particle-into-liquid sampler (PILS) collected five minute liquid samples into individual vials held on a rotating carousel. The vials' contents were analyzed off-line by ion-chromatography (IC) with a limit of detection range of 0.01 to 0.14 micrograms/m3 for all of the measured species (excluding Na+ and Ca+). Measurement results show a correlation (R2=0.77 for the entire mission) between oxalate and sulfate during each of the 12 flights, most of which were marked by the presence of clouds, reinforcing the idea that the formation of oxalate is associated with in-cloud aqueous phase chemistry. The maximum observed oxalate mass loading was 0.43 micrograms/m3, found in the sample with the maximum observed sulfate loading. During a power plant plume study, as the plane transected the plume further downwind of the plant the total mass loading was observed to increase and sulfate and oxalate loadings were well-correlated. Oxalate field measurement results will be compared to results from a cloud parcel model that calculates the aqueous phase production of dicarboxylic acids. Results from the various research flights will be summarized with special attention to flights downwind of power plants. The intercomparison between the model and field data will help advance knowledge of the formation of oxalate in the atmosphere.

8PE3

AIRCRAFT MEASUREMENTS USING AN AEROSOL MASS SPECTROMETER DURING ICARTT. KATHERINE HAYDEN, Desiree Toom-Sauntry, Richard Leaitch, Anne Marie Macdonald, Kurt Anlauf, Wanmin Gong, Amy Leithead, Shao-Meng Li, Sangeeta Sharma, Walter Strapp, Environment Canada, Toronto, ON

An airborne in-situ sampling study was conducted out of Cleveland, Ohio from 21 July – 18 August, 2004 to investigate the role of clouds in the transport and transformation of pollutants. This study was part of the ICARTT (International Consortium for Atmospheric Research on Transport and Transformation) 2004 field intensive. Measurements of particle size distribution and chemistry and cloud microphysics were made from the National Research Council of Canada Convair 580 aircraft. During cloud passes, cloud droplet residuals from a counterflow virtual impactor (CVI) were sampled with an Aerodyne aerosol mass spectrometer (AMS), a TSI condensation particle counter, and a TSI differential mobility analyzer.

Total mass concentrations as determined from the AMS (sulfate + nitrate + ammonium + organics) were lower by a factor of 3-4 compared with mass estimates from physical size distribution measurements. In clear air, AMS sulfate concentrations compared with those from a PILS-IC (Particle-In-Liquid-Sampler) indicated that the AMS collection efficiency (CE= [PILS_SO4=]/[AMS_SO4=]) was variable within a flight and ranged between 1-8. The CE of the AMS appeared to be even lower when sampling cloud droplet residuals; likely due, in large part, to the low relative humidity (< 5%) downstream of the CVI. AMS data from several flights are presented and discussed with respect to factors contributing to the observed low CE. These results are contrasted with AMS measurements made in other field studies.

8PE4

INVESTIGATION OF CARBONYLS IN BULK CLOUDWATER SAMPLES COLLECTED DURING ICARTT. AMY LEITHEAD, Shao-Meng Li, Anne Marie Macdonald, W. Richard Leaitch, Desiree Toom-Sauntry , Kurt G. Anlauf, Katherine L. Hayden, Dave Halpin, J. Walter Strapp, Meteorological Service of Canada, ON, Canada

An aircraft based study was carried out from July 20 to August 18, 2004 as part of ICARTT to investigate in-cloud processes and transport of chemical species.
Bulk cloud water samples were collected by a slotted rod collector and analyzed for carbonyls, inorganics, pH, and hydrogen peroxide.
Cloudwater samples were collected at multiple altitudes within convective clouds. Multiple aldehydes were measured in the cloud samples. In-cloud formaldehyde results will be discussed focusing on the partitioning between the gas and liquid phases at each level in the cloud. Henry's Law constants will be used to calculate the expected aqueous partitioning to show whether simple gas-liquid equilibrium was established in the convective cloud situations observed during the study.
Specific cloud events will be investigated in detail including observations over Toledo, Ohio on August 13, 2004. Samples during this event were collected at 4 levels in-cloud, liquid water content ranged between 0.25-0.70 gm-3, HCHO levels were 66.0 -341 ppt, and pH was from 3.62-6.60. The possible net production of formaldehyde within the cloud during this event will be investigated.

8PE5

REAL-TIME FORECASTS OF PM2.5 AND ITS CHEMICAL COMPONENTS BY THE ETA-CMAQ MODEL DURING THE 2004 ICARTT STUDY. SHAOCAI YU*, Rohit Mathur**, Daiwen Kang*, Kenneth Schere**, Brian Eder**, Jonathan Pleim**, Atmospheric Sciences Modeling Division, NERL, U.S. EPA, RTP, NC,**On assignment from Air Resources Laboratory, NOAA, RTP, NC, *On assignment from Science and Technology Corporation, Hampton, VA; Stuart A. McKeen, Aeronomy Laboratory, NOAA, Boulder, Colorado

Atmospheric distributions and loadings of fine particulate matter (PM2.5; particles with diameters less than 2.5 micrometer) can adversely affect human and ecosystem health, and are thus of major concern. It is desirable for local air quality agencies to accurately forecast PM2.5 concentrations to warn the public of unhealthy air and to encourage people to voluntarily reduce emissions-producing activities. This work examined spatial and temporal performance of the Eta-CMAQ forecast model for PM2.5 mass over the eastern U.S during the 2004 International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) by comparison with observations from the U.S. EPA Air Quality System (AQS) network. The model spatial performance for PM2.5 chemical constituents (SO42-, NO3-, NH4+, OC and EC) is evaluated with the observational data from the IMPROVE, CASTNet, and STN networks. The ability of the model to represent the vertical profiles of the chemical and physical properties (SO42-, NO3-, NH4+, number and surface area concentrations) of PM2.5 is assessed with the observational data from the aircraft (NOAA P -3 and NASA DC-8) flights during the 2004 ICARTT field experiments.

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. This work constitutes a contribution to the NOAA Air Quality Program. Although it has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

8PE6

SPECIATED ORGANIC AEROSOL COMPOSITION AT CHEBOGUE POINT, NOVA SCOTIA DURING ICARTT 2004 USING THERMAL DESORPTION AEROSOL GC/MS-FID (TAG).

BRENT J. WILLIAMS, Allen H. Goldstein, University of California, Berkeley, CA; Nathan M. Kreisberg, Susanne V. Hering, Aerosol Dynamics Inc., Berkeley, CA

We report ambient aerosol measurements made at Chebogue Point, Nova Scotia, Canada from July-August 2004 during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT 2004). Measurements were made using a new, in-situ instrument, the Thermal desorption Aerosol GC/MS-FID (TAG). This is an automated instrument for the time-resolved identification and quantitation of selected organic marker compounds in airborne particles over the size range from 0.1 to 2.5 µm. Atmospheric aerosol samples are collected into a small thermal desorption cell by means of humidification and impaction. The sample is transferred onto a GC column by thermal desorption, with subsequent GC/MS-FID analysis. The collection and analysis steps are automated, yielding around the clock speciation. Field blanks are fully automated and instrument calibrations are performed manually by direct syringe injection of standards into the thermal desorption cell. An advantage of our approach is that it builds on the extensive body of knowledge on the quantification of organic material, and on the identification of the origins of organic aerosols available from past research using filter-based GC/MS analyses.

This presentation will focus on both analysis of instrument performance and the use of observations for particle source identification using factor analysis. Factor analysis is a statistical technique which can be used to track temporal covariance between selected individual organic marker compounds, and is applicable for organic aerosol source apportionment using the fast time resolution data measured by TAG. Organic aerosol chemical composition varies greatly as a function of distance from primary sources, as a function of time for secondary formation, and as a function of temperature. We will compare the typical summertime remote Nova Scotia organic aerosol composition and the typical wintertime urban Berkeley, CA organic aerosol composition to show how the organic fraction of aged particles differs from freshly emitted particles. Also, it will be shown how individual organic marker compounds detected by TAG during ICARTT 2004 are used to differentiate between aerosols arriving from the U.S., aerosols arriving from Canada, and local aerosol production in Nova Scotia.

8PF1

STUDY OF THE EVOLUTION OF SOOT EMITTED BY AIRCRAFTS - EXPERIMENTAL DEVELOPMENT.

ANNE-LISE BRASSEUR, David Delhaye, ONERA, CHATILLON, FRANCE; Olivier Penanhoat, Sébatien Guedon, SNECMA MOTEUR VILLAROCHE, REAU, FRANCE

The study of air quality and of its impact on health has recently become a priority subject. In particular, the fine particles are recognized to have a considerable impact on human health (respiratory problems).
Among those, soot resulting from transport represent a significant, but poorly defined, fraction. The two main sources are road and air transports. Many studies have been undertaken on the soot emitted by the road transport. For the soot emitted by aircraft engines, very few studies have been performed. Several reasons can explain this: difficulties on the methodology of the sampling (representative of reality), scant knowledge of the physicochemical composition of particles…
The French national project PRIMEQUAL 2 (\aerosols and particles\) relates to the physicochemical characterization of the soot emitted by aircrafts at airports, the physicochemical study of their evolution in the atmosphere and the development of a numerical model describing soot emitted by aircraft plane and their evolution in the atmosphere.
Two large research orientations are proposed:
1- The development of a methodology in order to characterize physically and chemically soot emitted by aircraft engines, in order to study their chemical reactivity and to evaluate their ageing in the atmosphere. Soot will be sampled behind an engine on a civil test rig of Snecma Moteurs. The study of the soot ageing will be carried out in controlled atmospheres. Soot at various stages of ageing will be useful for compared studies of reactivity and of physical and chemical properties.
2- Based on the obtained experimental data, a model describing the aircraft soot emitted in the atmosphere will be developed, validated by previous experimental results. This model will be coupled with a reactive dispersion model, in order to describe the evolution of soot in airport areas.

To conclude, the PRIMEQUAL study will allow a better knowledge of the soot emitted by aircrafts thanks to a rather complete physico-chemical characterization and a detailed study of their atmospheric reactivity. This knowledge will allow understanding their evolution in airport areas, to develop a model describing the emitted aircraft soot in order to study their evolution in the atmosphere boundary layer. This will provide the opportunity to better quantify the medical and environmental impact of fine particles, which remains (with the noise) the first concern of the residents near airports.

The present paper will focus on the experimental campaign of the project, with description of the measurements and the particles characterisation, which will be performed.
PRIMEQUAL PARTICIPANTS: ONERA, SNECMA, ENPC, LCE, INERIS, LPM, CRCM, LISA, LCSR.

8PF2

CHEMICAL CHARACTERIZATION OF THE GAS PHASE EMISSIONS FROM A COMMERCIAL AIRCRAFT JET ENGINE DURING PROJECT APEX. JOHN KINSEY, Lee Beck, and Michael Hays, U. S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC Craig Williams, Russell Logan, Tom Balicki, and Yuanji Dong, ARCADIS-Geraghty & Miller, Durham, NC

The toxic air emissions from aircraft operations are a major health concern for individuals living near major airports. This is especially true in those areas having regulations limiting such emissions. To address the lack of substantive emissions data for modern engine designs, the U. S. Environmental Protection Agency's National Risk Management Research Laboratory (NRMRL) has initiated a major research program to chemically characterize the gas phase emissions from commercial aircraft engines. This paper provides results from a ground test conducted in April 2004 of a National Aeronautics and Space Administration-owned DC-8 aircraft equipped with CFM56-2-C1 turbofan engines located at their Dryden Flight Research Center during Project APEX (Aircraft Particle Emissions eXperiment). Sampling was conducted both at approximately 1 m behind the engine using NRMRL's dilution stack sampler and at approximately 30 m behind the engine using our Diesel Emissions Aerosol Laboratory configured for plume sampling. Available data on the chemical characteristics of the gaseous emissions determined during APEX will be presented which incorporated both an engine test cycle indicative of airport landing and take-off operations as well as a series of steady-state engine operating conditions.

8PG1

USE OF AEROSOLS TO INCREASE RECOVERY OF EXHALED BREATH PROTEIN FROM UNANESTHETIZED PIGS. OWEN MOSS, Earl Tewksbury, CIIT Centers for Health Research, Research Triangle Park, NC; Nathan Boggs, Joany Jackman, Johns Hopkins University Applied Physics Laboratory, Laurel, MD.

Detection of the inflammatory response of the lung is useful not only for the identification of environmental, industrial, or bio-terrorism exposure agents, but for expediting treatment of the exposed individual. By examining the levels of recoverable volatile compounds, exhaled breath has been used to assess the physiological state of humans. More recently, non-volatile compounds, including proteins such as IL-4 and tumor necrosis factor, have been successfully recovered from human exhaled breath. In order to apply this method to rapid and specific identification of exposed individuals there is a need to enhance analytical capability as well as develop animal models. As part of the development of a porcine model of exhaled breath, the work described here focuses on the evaluation of the impact of inhaled particles on scavenging protein from breath. In order to obtain base-line samples of exhaled breath, breath collections of 32 piglets were initiated at a local farm. Each piglet (5 to 11 kg) was individually held during a half hour collection period. Breath was collected into a two-stage cold trap through the use of a face mask system based on a modified anesthesia cone with one way valve. During collection of exhaled air, half of the piglets received filtered air while the other half received unfiltered air. In addition to measurements of room temperature and relative humidity, particle count and size were measured with a passive cavity aerosol spectrometer (PCASP-X, Particle Metrics, Inc., Boulder, Co). Breath condensate was analyzed for total protein using the Coomassie Blue Assay. Particle count in the room remained around 3000/cc. The particle size distribution was bimodal (35% and 65% by count) with count median diameters of 150 nm and 300 nm and geometric standard deviations of 1.2 and 1.3 respectively. We found that the presence of particles in the air increased the recovery of protein in breath condensate. In both groups only some of the samples contained protein above the limit of detection of the assay: 13% of the samples from piglets breathing filtered air; 44% of samples from piglets breathing particles. After correcting for protein content in condensate from room air, inhalation of particles increased protein recovery in breath by approximately two fold. (This work was performed at CIIT under investigator-designated exploratory research funds; and at APL as part of a DARPA funded project MDA972-01-D-005)

8PG2

EFFECTS OF AMBIENT PARTICULATE SUSPENSION (APS) ON BARRIER PROPERTIES OF RAT ALVEOLAR EPITHELIAL CELL MONOLAYERS (RAECM).

HARISH C. PHULERIA, Constantinos Sioutas, Departments of Civil & Environmental Engineering, University of Southern California, Los Angeles, CA, USA; Nazanin Yaghoobian, Kwang J. Kim, Zea Borok, Edward D. Crandall, Departments of Medicine, University of Southern California, Los Angeles, CA, USA

Particulates in ambient air are believed to contribute to the deleterious effects of exposure to air pollution. In this study, we investigated the effects of APS collected from six different locations in greater Los Angeles on barrier properties of alveolar epithelium. Transmonolayer resistance (Rt) and equivalent short-circuit current (Ieq) of rat alveolar epithelium cell monolayer (RAECM) on days 4-6 in culture were estimated in the presence and absence of varying concentrations of APS added to apical fluid as a function of exposure time. In some monolayers, apical-to-basolateral fluxes of radio-labeled mannitol or inulin were estimated with or without apical APS exposure. APS in general did not cause appreciable changes in Rt or Ieq when measured for up to 24 hrs with up to 60µg/ml added to apical fluid, except for APS collected near a major freeway (UAPS). Apical exposure to UAPS led to dose-dependent decreases in Rt, with an effective half-maximal concentration (EC50) of ~4 µg/ml. At the maximal concentration of UAPS (36 µg/ml) tested, Rt declined by ~60%, with a half time of ~30 min. From 30 min to ~24 hr, Rt did not appreciably change, despite continued presence of UAPS in apical fluid. Ieq decreased up to ~25% in a dose-dependent fashion after apical exposure to UAPS, with effective half-maximal concentration of ~4 µg/mL and time course similar to that for Rt. Neither mannitol nor inulin fluxes were altered after exposure to UAPS (36 µg/ml). These data suggest that apical exposure of primary RAECM to UAPS (but not other APS) causes disruption of barrier properties. Lack of effects of UAPS on paracellular fluxes of hydrophilic solutes suggest that the observed decrease in Rt may reflect primarily changes in cellular transport properties.

8PG3

MODELING OF POWDER DEPOSITION IN ORO-PHARYNGEAL CAST DURING INSPIRATORY FLOWS.

ARKADIUSZ MOSKAL, Tomasz R. Sosnowski, Leon Gradon

Information about temporary and spatial distribution of deposited aerosol particles in oro-pharyngeal region during inspiration is very important for aerosol therapy. This allows to optimize drug formulation, design of inhaler and the technique of its use in order to minimize the undesirable deposition of the drug in the mouth, throat and pharyngeal region. This paper presents the result of mathematical modeling of aerosol behavior in the oro-pharyngeal region during realistic inspiration conditions. Based on the CT-image obtained for an adult male, the numerical 3D model of oro-pharyngeal region was implemented into CFD package FLUENT. The CFD was used for calculation of the airflow pattern in oro-pharynx during inspiration and expiration, as well as the corresponding aerosol particle deposition in this region. Two types of respiratory curve were studied, A nad B, corresponding to quick and deep inspiration and weak inhalation, respectively. Curves can be approximated by equation: $V(t)=a[1-\cos(t/b)]$ where a = 1.368 or 1.383 and b = 1.141 or 0.921, respectively. The calculations were carried out for monodispersed aerosol particles with diameters: 0.3, 1 and 10 micrometers and for two material densities: 1,1 and 2,3 kg/m3. The temporary and spatial distributions of aerosol deposition in oro-pharynx were obtained. For smallest particles the highest deposition was observed in the beginning and in the end of the inspiration. The spatial distribution shows the rather equal coverage with intensification in the anterior region. For the largest particles the temporal distribution during inspiration is almost uniform. The spatial distribution of deposited matter concentrates in the palate region. The results show that the aerodynamic conditions during inspiration strongly influence the deposition process, and should be taken into account instead of time – averaged flows.

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8PG4

THERMAL DESORPTION GC/MS ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS, N-ALKANES, HOPANES, AND STERANES IN ATMOSPHERIC AEROSOLS. XINGHUA FAN, Jeffrey R. Brook, Environment, Toronto, ON, Canada

Many epidemiological studies indicate that both short-term and long-term exposure to particulate matter (PM) has an impact on human health. However, PM composition is extremely complex due to multiple and variable sources. This leads to complex chemical characteristics and current evidence suggests that PM's health effect is dependant upon its composition, particularly the carbonaceous components (OC and EC) related to traffic. However, little ambient data exist on OC and EC and organic species that are suitable for health studies. One goal of this research is to examine organic compounds on PM2.5. The traditional approach for analysis of individual organic compounds involves extraction of aerosol materials by solvent, fractionation by solid phase extraction (SPE) based on the polarity of organics of interest, and separation and detection by chromatographic methods (e.g., GC or HPLC). These approaches are time consuming, labor intensive, and expensive. They are also prone to low recoveries due to solvent evaporation and multiple steps of sample preparation. Solvent impurities may introduce contamination to samples. In addition, large quantities of solvents are often required and thus these approaches are not environment-friendly. An alternative to the solvent extraction approach is to use thermal desorption (TD) to extract organic aerosol species from filter substrates, followed by GC/MS analysis without further sample treatment. This TD/GC/MS method is fast and sensitive and requires small sample mass. Therefore it is potentially able to offer better resolution of PM organic components for short and episodic air pollution events and is also sufficient for several multi-site measurement efforts.

This research focuses on the method development of TD/GC/MS towards organic speciation of urban PM2.5. A list of more than 100 target compounds, which includes polycyclic aromatic hydrocarbons (PAHs), methylated PAHs, oxygenated PAHs, n-alkanes, hopanes and steranes, has been proposed. NIST SRM 1649a, 1648, and 8785 (urban particulate matter) will be analyzed for the target compounds to evaluate the performance of the method. Figures of merits of the method (e.g., detection limits, accuracy, and precision) will be shown. An intensive sampling study was launched in Windsor, ON, Canada in February 2005. Fifty PM2.5 samples were collected concurrently at different locations. Preliminary organic speciation results of this intensive study will also be presented.

8PG5

CONTAINING AIRBORNE RESPIRATORY INFECTIOUS DISEASE SPREAD. WESLEY DEHAAN, Jeff Kastra, Karim Kokash, Matthew Brande, Robert Clarke and Wiwik Watanabe Pulmatrix Inc., Cambridge, MA

Decreasing exhalation of pathogen laden aerosols may decrease transmission of airborne respiratory infectious diseases (ARID) such as influenza and tuberculosis. Exhaled bioaerosols (EB) are known to be produced during coughing and sneezing; the role of tidal mouth breathing, nose breathing and talking is less understood. To identify the contribution of the most prevalent exhalation maneuvers in EB production, we evaluated tidal mouth breathing, nose breathing, and talking on six human subjects. After flushing the lungs with particle free air, the number and size distribution of particles produced in the range of 0.3-25 micrometers were measured along with the flow rate curves for the exhalation maneuvers over 2 minute intervals. Tidal mouth breathing was found to produce the highest number of particles greater than 300nm in diameter. Nose breathing produced 20% less particles in the 300-500 nm range and 80% less particles greater than 500nm while talking produced the lowest number of particles across the size ranges studied. The nasopharynx proved to be a more effective filter of larger aerosols but not a significant source of exhaled bioaerosols.

An initial pilot clinical study involving 11 human subjects (Edwards, et al. (2004) PNAS, 50, 1783-1788) showed large interpersonal variability, with 5 of the subjects producing 97% of the total particles measured. In the event of a natural pandemic, identification of the highest EB producers would augment clinical outcomes in prevention of ARID. The diagnostic used in the evaluation of patients in this study would assist medical professionals in identifying the highest EB producers. Development of a countermeasure to suppress EB production would provide a first-line defense beyond quarantine.

Pulmatrix is developing a pathogen-independent anti-infectivity aerosol (AIA) that will safely limit the production of exhaled bioaerosols. The study of Edwards et al. showed that aerosol treatment with respirable isotonic saline as an AIA can suppressed bioaerosol exhalation up to 72.9 + 8.0% of untreated baseline for six hours. A second study in cattle indicated ACA suppression is dose dependent. With 1mL administration, similar suppression was seen as that in the human study while at 0.3 and 2mL administrations, bioaerosol suppression was not evident. The combination of exhaled bioaerosol assessment and intervention in exhaled bioaerosol production by anti-infectivity aerosol provides a novel approach to the concept of limiting airborne respiratory infectious disease transmission.

8PG6

IN VITRO EXPERIMENTS ON INHALER ADAPTOR DESIGN.

Jinbo Wang, Ahmed Fadl, Pao Yang, Zongqin Zhang, University of Rhode Island, Kingston, Rhode Island; Yung Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque, NM

The delivery of aerosolized medicine to the human lungs has become an increasingly important aspect of medical therapeutics. Portable Aerosol Inhalers are very popular devices among patients with lung diseases. However, the current efficiency of the aerosol inhaler is very low. In general, only between 5 to 20% of the aerosol medicine will reach the lung while most of the drug particles will deposit in mouth and back of throat. Targeted aerosol delivery is an important issue to be addressed.

We conducted in vitro experiments using various innovative inhaler adaptor/mouthpiece designs to enhance aerosol lung delivery. The head airway model includes oral cavity, pharynx, larynx, and ending at the trachea. Two-phased R134a and mono-dispersed solid fluorescent aerosols are charged into the canister of the commercial MDI inhalers. Each canister can be used to produce more than 100 high quality consistent sprays before the R134a run out. As distinct from the other methods, flow rate and aerosol collection are both controlled by a balloon attached at the downstream of the head airways and placed in the vacuum chamber. Transient and steady flow rates are obtained by controlling the degree of vacuum pressure. Aerosols penetrated through the oral airway model are all collected by the balloon and washed out by distill water. Concentration of the aerosol-water solution was then measured by spectrophotometer. Our experiments showed that by manipulating some adaptor/ mouthpiece configuration designs, a significant enhancement of aerosol delivery efficiency can be achieved.

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8PG7

COMPUTER SIMULATION OF AEROSOL ORAL AIRWAY DELIVERY.

Jinbo Wang, Ahmed Fadl, Zongqin Zhang, University of Rhode Island, Kingston, Rhode Island; Yung Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque, NM

Knowledge regarding particle deposition processes in the human oral airway compartment is important in aerosol therapy applications. Portable Aerosol Inhalers are very popular devices among patients with lung diseases. However, the current efficiencies of these portable inhalers are excessively low. On the average, about 50% of total inhaled medicine will deposit on the back of the throat and 10% (with or without spacers) will reach to the targeted lung region. Considering the large populations of patients using inhalers, the total added cost by patients as well as resource waste due to low efficiency delivery are enormous.

In this presentation, the ideas of improving aerosol medicine delivery through optimizing the mouthpiece or spacer channel configuration design are discussed based on numerical investigations. Benchmark simulations were carried out and showed good agreement with the experiment data in the literature. Computer simulations reveal that, in addition to the well-known parameters such as particle diameter, particle density, and respiratory flow rate, there exist strong correlations between the aerosol delivery efficiency and the particle entrancing angle, velocity and initial locations. The concept of the optimum inhaler adaptor design, to guide particles away from the paths where they will likely hit the back of the throat, is demonstrated by the computer simulations.

--Research described in this article was supported by Philip Morris USA Inc.

8PG8

INVESTIGATE THE EFFECT OF DILUTION PROCESS ON THE DISTRIBUTION OF OC, EC AND SULFATE IN DIESEL PARTICULATE MATTER (DPM).

Zifei Liu, MINGMING LU, Tim. Keener, Fuyan Liang, University of Cincinnati

Diesel emission is a complex mixture of noxious gases and diesel particulate matter (DPM). DPM is causing increasing health concerns due to their suspected carcinogenicity, especially the carbonaceous fractions. DPM mainly consists of elemental carbon (EC), organic carbon (OC), sulfate, and other trace materials. EC is a byproduct of incomplete combustion and it forms the cores of diesel soot particles. Particulate OC contains adsorbed or condensed hydrocarbons. It may be generated directly from unburned fuel and lube oil, and it may be also from nucleation and condensation of organic vapor during secondary processes such as dilution. Sulfate is supposed to play an important role in the nucleation and condensation of OC. This study investigates the effects of dilution process on the distribution of OC, EC and sulfate in DPM. A Generac diesel generator rated at 80 kW and 1800 rpm serves as a stationary DPM emission source in the study. Samples are taken from the same source using three different sampling systems: (1) EPA Method 5 is used to sample undiluted DPM directly from the stack; (2) A hi-vol sampler with artificial dilution system is used to take samples from the stack at certain dilution ratios; (3) A hi-vol sampler is used to take DPM influenced ambient samples in vicinity of the emission outlet under nature dilution conditions. OC, EC and sulfate in the DPM samples from the three sampling systems are analyzed and compared. Samples are taken at various loads and various diesel fuels are used. The results will be useful to obtain better understanding of the effect of the dilution process on DPM compositional variations. The influences of loads and fuel sulfur content will also be studied.

8PG9

USE OF STOKES NUMBER TO SCALE PARTICLE DEPOSITION EFFICIENCY CURVES FOR RAT, MONKEY AND HUMAN NASAL AIRWAYS.

Brian A. Wong and Julia S. Kimbell, CIIT Centers for Health Research

The efficiency of particle deposition in the nasal airways is used in risk assessments of exposure to airborne particulate pollutants and for optimizing the delivery of therapeutic aerosols. Rats are commonly used to assess the toxicity of inhaled pollutants, while monkeys are used to assess the therapeutic potential of inhaled substances and to a lesser extent the toxicity of inhaled xenobiotics. Interspecies comparison of particle deposition efficiency curves may be feasible with the use of a simple scaling factor. We have used nasal replicas and molds of a human, monkey and rat to determine particle deposition efficiency. We have also used computational fluid dynamics (CFD) models of these species to calculate deposition efficiency. Predictions of the CFD model calculations were compared to the experimental deposition measurements in the molds and replicas. In the comparison studies, we found that the deposition efficiency curves showed similarities when plotted against the impaction parameter (da^2Q). The impaction parameter is a property of the particle aerodynamic diameter (da) and flow conditions (Q) being studied. In this work, we explore the use of the Stokes number, which like the impaction parameter, incorporates particle size and flow rate, and additionally incorporates a parameter of the nasal airways, the minimum cross sectional area (Amin). Coincidence of deposition vs Stokes number curves would demonstrate that the airways could be scaled in size from one species to the other. When compared according to equivalent Stokes numbers based on minimum cross-sectional area, the deposition efficiencies of the monkey and rat nasal mold tended to overlap the extremes of the human nasal replicas. This study indicates that it may be possible to scale particle deposition efficiency in the nasal airways of the rat, monkey and human using Amin in the Stokes number.

8PG10

BIOAEROSOL MASS SPECTROMETRY (BAMS) FOR THE RAPID DETECTION OF INDIVIDUAL AIRBORNE HEALTH RELATED VEGETATIVE BACTERIA. HERBERT J. TOBIAS, Lawrence Livermore National Laboratory, Livermore, California; Millie P. Schafer, National Institute for Occupational Safety and Health, Cincinnati, Ohio; Maurice Pitesky, David P. Fergenson, Joanne Horn, Matthias Frank, and Eric E. Gard, Lawrence Livermore National Laboratory, Livermore, California.

Single-particle laser desorption/ionization time-of-flight mass spectrometry, in the form of Bioaerosol Mass Spectrometry (BAMS), is being developed as a biological particle detector that could detect and identify various airborne bacterial spores, vegetative cells, viruses, and biological toxins present as or in micron sized particles. In this work, BAMS mass spectral signatures for aerosolized Mycobacterium tuberculosis H37Ra particles were found to be distinct from other gram positive bacteria such as M. smegmatis, Bacillus atrophaeus, and B. cereus, when using a unique biomarker. This is the first time a potentially unique biomarker was measured in M. tuberculosis H37Ra on a single-cell level. In addition, M. tuberculosis H37Ra and M. smegmatis were aerosolized into a bioaerosol chamber and were sampled and analyzed using BAMS, an Aerodynamic Particle Sizer, a viable Anderson six-stage sampler and filter cassette samplers which permitted direct counts of cells. In a background free environment, BAMS was able to sample and detect relative clean M. tuberculosis H37Ra particles at airborne concentrations of > 40 M. tuberculosis H37Ra CFU/L air in 1 min, as determined by viable Andersen six-stage samplers. These results present a promising approach to airborne health related aerosols detection in applications where real-time, unmanned, and/or continuous operation is required. More work needs to be done to evaluate the robustness of potentially unique biomarkers in bacteria of interest and to develop BAMS as a system useful in realistic environmental and respiratory particle backgrounds expected in health related diagnostic scenarios.

8PG11

QUANTIFICATION OF AIRBORNE MYCOBACTERIUM TUBERCULOSIS IN HEALTH CARE SETTING USING REAL-TIME QPCR COUPLED TO AN AIR-SAMPLING FILTER METHOD. Chih-Shan Li, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University Pei-Shih Chen, Graduate Institute of Environmental Health, College of Public Health, National Taiwan University

Mycobacterium tuberculosis infection remains one of the major public health issues worldwide. Current qualitative assays (only positive or negative results) do not provide comprehensive information regarding health risk of M. tuberculosis. This study attempted to develop a quantitative assay to measure air concentration of M. tuberculosis in a health care setting.
A total of 22 air samples were taken from the negative pressure isolation rooms of tuberculosis patients. The air was filtered through a Nuclepore filter with sampling time of 8 h. The DNA of M. tuberculosis in these airborne samples was then analyzed by the ABI 7700 real-time quantitative polymerase chain reaction (real-time qPCR) system.

The real-time qPCR method could perform measurements of counts in a dynamic range of over 6 orders with a high sensitivity. The measured M. tuberculosis concentrations varied widely, from 1.43 × 10 copies/m3 to 2.06 × 105 copies/m3. Comparisons among airborne M. tuberculosis levels, sputum smear, results, and sputum culture results showed moderate correlations.

The filter/real-time qPCR method proved extremely sensitive and rapid for quantifying airborne M. tuberculosis. In addition, it is a powerful sampling tool that has potential applications as an investigational device, which might be valuable in conducting studies that validate the efficacy of engineering controls and work practices.

8PG12

INTRANASAL IMMUNIZATION PROTECTS MICE AGAINST INTRAPERITONEAL CHALLENGE WITH TICK-BORNE ENCEPHALITIS VIRUS.

Elena Goncharova, Evgeny Ryzhikov, Vasiliy Poryvaev, Leonid Bulychev, Amir Maksyutov, ALEXANDR RYZHIKOV, State Research Center of Virology and Biotechnology “Vector”, Koltsovo, Novosibirsk region, Russia

Neurotropic viruses belonging to various virus families may invade the brain via the olfactory tract after parenteral infection. Intranasal (i.n.) immunization inducing mucosal and systemic immunity blocks neurotropic virus propagation into the brain via olfactory pathway and neutralize virus multiplication in visceral organs. I.n. immunization against representatives from Flavivurus family, such as Dengue, Japanese encephalitis, yellow fever, West Nile and Tick-Borne encephalitis (TBE) viruses, would allow for using all the advantages of mucosal vaccines for inducing an effective immunity.
Recombinant vaccinia strains carrying TBE virus genes C, prM, E, NS1, NS2a/b, NS3 were efficient after i.n. vaccination inducing a double barrier of mucosal and systemic immunities against penetration of the neurotropic virus into the brain via the olfactory tract, indicating 100% protection against intraperitoneal (i.p.) challenge with TBE virus.

Our further studies were focused on the safe non-replicating vaccines. Effectiveness of i.n. immunization with killed TBE virus or antigenic peptide 89-119 from the envelope protein E of TBE virus in nanoemulsion formulation was studied in Balb/c mice. I.n. immunization with nanoemulsion containing inactivated TBE viral particles induced specific virus neutralizing serum antibodies, specific mucosal IgA antibodies in lung and nasal lavages. All i.n. immunized mice were protected against i.p. challenge with 100 LD50 of TBE virus. The ratio of virus specific IgG2a to IgG1 indicated a prevalence of the Th2 type immune response as was upon subcutaneous immunization of mice with the commercial FSME-Immun inject vaccine against TBE virus. Thus, the experimental data obtained for the first time demonstrate the feasibility of nanoparticles containing inactivated TBE virus for effective protection of i.n. immunized mice against the lethal viral infection caused by TBE virus.

The profile of occurrence of the fragments locally similarity to human proteins was constructed using a computer analysis of the antigenic structure of TBE virus proteins and human proteins. This approach allows for identification of potentially immunologically safe antigenic peptides. One of the candidates to TBE peptide vaccine, peptide 89-119 of E protein of TBE virus, was synthesized. Applied i.n. in nanoparticulate formulation the peptide induced TBE virus specific antibodies and displayed a particular protection in the case of i.p. challenge with TBE virus.

Further development of non-invasive vaccines against neurotropic insect-borne viral infections is promising. We proposed principles of candidate vaccine constructs for effective i.n. immunization, which should be applied for commercially available vaccines for the representatives of Flavivirus family.

8PG13

GENERATION OF VERY LOW DENSITY FIBROUS CARBON POWDERS (SINGLE-WALLED CARBON NANOTUBES AND PYROGRAF III).

PAUL BARON, Gregory Deye, National Institute for Occupational Safety and Health, Cincinnati OH; Anna Shvedova, Vincent Castranova, National Institute for Occupational Safety and Health, Morgantown WV

Concerns have been expressed regarding potential health effects of new materials being produced in the ultrafine particle size range. Two such materials include single-walled carbon nanotubes (SWCNT, Carbon Nanotechnologies, Inc.) and carbon nanofibers (Pyrograf III, Applied Sciences). Both these materials may be produced as a powder and then processed in various ways to obtain a final product, such as conductive plastic. In the as-produced state, these materials can consist of an extremely low density powder (0.1- 0.01 g/cm3); difficulties were encountered aerosolizing these materials using conventional feeding and generation systems. The present study was initiated to develop an efficient means of producing a respirable aerosol from dry powder to simulate potential exposure in the workplace, so that a relevant test of the material toxicity could be obtained through an animal inhalation study. The target generation rate was 25 mg/m3 at a flow rate of 10 L/min for a nose-only mouse exposure.

As-produced material was obtained from the manufacturer of the single walled carbon nanotubes and carbon nanofibers. Both carbon powders were initially processed to reduce the powder grain size by sieving or chopping in a high speed blender. The powder was then placed in a hopper and a portion fluidized in a controlled fashion using timed acoustic pulses to allow powder particles to be fed by gravity and controlled air flow into the generator. The generator consisted of a high-speed knife mill modified extensively, both to increase the shear force on the powder particles and to operate in a continuous manner for long periods. The resulting aerosol was then classified both gravitationally and inertially (in a cyclone) to reduce the remaining large powder clumps. Tests with the generation system indicated relatively high efficiency for the nanofibers, with 10-12% of the fed material occurring in an aerosol with a number mode at 150 nm diameter (measured with a Wide Range Particle Spectrometer, MSP, Inc.). The nanotubes gave a higher mode at about 1 micrometer with a higher efficiency of generation. The nanofibers dispersed into smaller particles more easily than the nanotubes because they were less likely to self assemble into ropes and extended and tightly bound structures. The described generation technique may have wider application to generation of low density powders.

8PG14

INTERACTIONS BETWEEN ORGANIC AEROSOLS, OZONE AND EPITHELIAL CELLS. CINDY DEFOREST HAUSER, Karen Bernd, Shari Barnett, Sandy Ockers, Davidson College, Davidson, NC

With advances in online aerosol monitoring methods, information regarding the chemical composition of aerosols is increasing. Continuing studies of heterogeneous chemical reactions between atmospheric aerosols and gas-phase oxidants are furthermore revealing changes in the chemical and physical characteristics of organic aerosols from primary and secondary sources. Although strides are being made in unraveling the effects of aerosols on human health, many questions still remain. In these studies, epithelial cell mimics are exposed to aerosols, which have undergone heterogeneous reactions with ozone. In addition to looking at the membrane composition, the aerosol and resulting gas-phase products are also monitored using Fourier Transform Infrared Spectroscopy. Using a combination of information about the heterogeneous chemistry of organic aerosols and cell response after exposure we will explore the impact of aerosols on the biological systems in which epithelial mimics are relevant such as the breathing passage.

8PG15

TOWARD DETERMINATION OF DROPLET COMPOSITION FOR AEROSOL DRUG DELIVERY DEVICES. CARY PRESSER, Bradley S. Johnson, National Institute of Standards and Technology, Gaithersburg, MD

Modern inhalers (e.g., metered dose inhalers, dry powder injectors, and jet nebulizers), and other microelectromechanical (MEMS) injection devices, often based on inkjet technology, are being developed to distribute aerosol droplets of well-defined size at a higher efficiency and with more consistent nebulization than achievable with previous generation devices. State-of-the-art characterization of these injectors at most includes droplet size and velocity distributions, number density for respiratory applications, and perhaps some global collection of particles for chemical analysis. However, no quantitative information is provided on spatially or temporally resolved composition of therapeutic agent throughout the aerosol, which of course is critical to evaluating the transport efficiency of that substance to reach the site of action. To address this issue, a reference aerosol generator is used that is well characterized and provides repeatable characterization, especially with respect to droplet size and composition. Such a generator is being used to evaluate current measurement techniques used by the industry (e.g., laser diffraction techniques are used to determine droplet size, and extractive sampling and analysis are used to monitor globally dosage concentration) so that these techniques can then be applied confidently to commercially available inhalers to ensure consistency of dosage. We are using an ultrasonically driven droplet array generator (that generates well-controlled droplet size and spatial distributions) with fluorescence spectroscopy to measure aerosol composition. We will discuss the technical issues related to carrying out such droplet measurements in real time.

8PG16

USE OF RADIOLABELED AEROSOL INHALATION DELIVERY AND INDUCED SPUTUM TECHNIQUES TO ASSESS IN-VIVO PARTICLE CLEARANCE AND UPTAKE BY AIRWAY MACROPHAGES.

WILLIAM D. BENNETT, Neil Alexis, John C Lay, Kirby L Zeman, Center for Environmental Medicine, Asthma and Lung Biology, UNC Chapel Hill, Chapel Hill, NC; Marianne Geiser and Nadine Kapp, Institute for Anatomy, University of Bern, Switzerland.

Introduction: Both particle uptake by airway macrophages and rapid mucociliary clearance may reduce drug targeting/availability to the bronchial epithelium, especially for drugs designed for controlled, sustained release. To quantify mucociliary clearance kinetics and macrophage phagocytosis in vivo, we combined the techniques of radiolabeled aerosol inhalation delivery and induced sputum to measure particle clearance and uptake by airway macrophages in human volunteers.

Methods: In a group of mild asthmatics (N=7) and healthy adults (N=8), we determined the percent of deposited particles associated with the cellular component of their induced sputum (IS) sample 2h following inhalation of radiolabeled sulfur colloid aerosol (Tc99m-SC, 0.2um colloid size delivered in 5um droplets by jet nebulization (Devilbiss 646)). The aerosol was inhaled with a breathing pattern designed to target the bronchial airways of the lung, 500 ml tidal volume at 25 breaths/min. After monitoring particle clearance by gamma scintigraphy for 2 hours, IS was obtained by having subjects inhale 5% hypertonic saline for 22 min and selecting the mucus plugs from the expectorated sample. After reduction (mucolytic reagent, DTT) and centrifugation of the plug sample, particle uptake was expressed as the ratio (%) of radioactivity in the cell pellet vs. that in the cell-free supernatant plus cell pellet fraction.

Results: Central-to-peripheral (C/P) ratio of deposited activity, an index of bronchial vs. alveolar deposition, was not different between asthmatics and healthy subjects, C/P = 2.00+/-0.43 vs. 1.69+/-0.58 respectively. % Clearance through 2 hours (i.e. pre sputum induction) was considerable but not different between the two groups, 35+/-13 (asthmatic) and 30+/-24 (healthy). The % cleared by sputum induction (as % of initial lung deposition) was also not different between the two groups, 23+/-10 (asthmatic) vs. 20+/-10 (healthy). However, analysis of particle uptake in cells retrieved from sputum induction showed asthmatics with significantly enhanced uptake compared to healthy volunteers (58% +/- 14 vs. 27% +/- 21, p<0.01). Using energy filtering transmission electron microscopy, we also verified that sulfur particles could be found within macrophages obtained from the cell pellet.

Conclusions: Enhanced particle uptake by airway macrophages in asthmatics may be the result of a “primed airway” due to the presence of low level chronic inflammation. Both rapid mucociliary clearance and high macrophage uptake of pharmaceutical macromolecules or nanoparticles in the airways may diminish the durability of their therapeutic effect. Strategies for transiently slowing mucociliary clearance and avoiding macrophage uptake might be considered for drug delivery to the bronchial airways.

8PH1

PM EMISSIONS FROM BACKUP GENERATORS: METHOD 5 VS. ISO 8178.

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Backup generators (BUGs) are an important source of emergency power at medical facilities, military bases, and other critical installations throughout the United States. Currently, there exist two procedures to certify emissions from BUGs. New BUGs are certified by the manufacturer using the ISO 8178 test procedure, while in-use BUGs are certified using the California Air Resources Board (CARB) Method 5. There are significant differences between the two test procedures, and these translate into widely varying emission factors for the same BUG operating under the same load conditions depending upon the choice of test procedure. First, the Method 5 filter is sampled at 120(± 14) ºC while the ISO 8178 filter is sampled at about 47(± 5) ºC. Second, the Method 5 requires sampling of raw exhaust, while the ISO requires sampling through a secondary dilution system. Third, Method 5 requires the use of an impinger catch, which is absent in the ISO 8178 method.

The objective of this work is to directly compare the two methods with a view towards reconciling the emission factors obtained from these methods. Towards this end, we concurrently tested PM emissions from 6 in-use BUGs on the ISO 8178 and Method 5 tests using the UCR/CE-CERT Mobile Emissions Laboratory (MEL) for the former, and a conventional method 5 for the latter. The BUGs were tested at three different load points: 50 %, 75 % and 100 %.

Our results show significant differences between data collected using the two procedures. First, grams per hour PM emissions reported using the Method 5 procedure were about 3 times higher than the corresponding emissions using the ISO procedure. Also, we observed that the upfront filter catch (PM in g/hr) from the Method 5 testing roughly equaled the entire PM (g/hr) from the ISO 8178 procedure—an indication of the role of the condensable fraction in determining the PM emission factor. These results enable the effective translation of emission factors obtained using one procedure into those using the other, and are a step in the direction of a unified test method for stationary source certification.

8PH2

EMISSIONS FROM THE LABORATORY COMBUSTION OF WILDLAND FUELS: CHARACTERIZATION OF PARTICLE MORPHOLOGY. Rajan K. Chakrabarty, Hans Moosmüller, W. Patrick Arnott, John Walker, Desert Research Institute, University of Nevada System, Reno, NV ; Vladimir A.Kovalev, Ronald A. Sussot,Wei Min Hao,USFS Fire Sciences Laboratory, Missoula, MT

The morphology of particles emitted by wildland fires contributes to their physical and chemical properties but is rarely measured and reported. A study was performed in the Combustion Laboratory of the USFS Fire Science Laboratory to determine the shape, primary particle size, and fractal dimension of particles emitted from combustion of eight different wildland fuels (i.e., sagebrush, poplar wood (excelsior), ponderosa pine wood, ponderosa pine needles, white pine needles, tundra cores, and two grasses). Six of these fuels had been dried before combustion, while two fuels, namely the tundra cores and one of the grasses had high fuel moisture content.

Combustion particles were sampled on nucleopore filters and imaged with Scanning Electron Microscopy (SEM). The particle images were analyzed for fractal dimensions, diameter of primary particles, and three different shape descriptors. Both agglomerate and non-agglomerate particles were also probed with energy dispersive X-ray spectroscopy confirming their carbonaceous nature. The morphology of particles was analyzed using two fractal analysis techniques to derive a density fractal dimension and a textural fractal dimension. These measures quantitatively describe the space filling quality and the roughness of the boundary of the two dimensional projection of the particle. Three shape descriptors, that is Aspect Ratio, Root Form Factor, and Circularity were used to describe different attributes of shape: elongation, ruggedness, and roundness, respectively.

The results indicate that the particles emitted from the combustion of the dry fuels formed agglomerates of small spherules with primary spherule diameters of 30-50 nm, whereas particles from the combustion of the wet fuels (i.e., Tundra cores and wet grass) were amorphous spherules (tar balls) with diameters of 100-150 nm. The average density fractal dimension of the agglomerates ranged from 1.68 to 1.74, while their textural fractal dimension ranged from 1.10 to 1.19 for the different fuels. The larger spherule particles emitted from the combustion of wet fuels exhibited a mean Circularity of 0.96 (scaled to a maximum of 1), whereas the mean Aspect Ratio and Root Form Factor of the various agglomerate particles was between 0.85-0.91 and 0.49-0.63, respectively. Good correlation between the three shape descriptors was observed.

8PH3

EMISSIONS OF NON-REGULATED POLLUTANTS FROM IN-USE DIESEL BACKUP GENERATORS. Ajay K. Chaudhary, ANIKET A. SAWANT, Sandip D. Shah, J. Wayne Miller, David R. Cocker III, University of California, Riverside, CA

Diesel back-up generators (BUGs) are frequently used to meet power requirements in power outage situations. In most cases BUGs are operated in close proximities to populations; there is therefore a need to develop emission factors for such BUGs. Information on current BUGs emissions factors is very limited in terms of population size and test methodology. In contrast, adequate data are available for heavy-duty diesel (HDD) engines used for on-road applications. Though both engines are very similar, the primary modes of operations are quite different. BUGs operate under steady-state load conditions while HDD vehicles operate under transient conditions. Due to the differences in operating modes, the emissions of these engines vary significantly. This work represents the first available emission data set on non-regulated BUGs of varying model year, engine technology and manufacturer in the 60 to 2000 kW size range and has important implications for estimating the impact of these stationary sources on surrounding local communities.

Specifically, engine emissions were measured using CE-CERT's Mobile Emissions Laboratory (MEL) using the ISO 8178 method. The MEL is designed to measure emissions at the quality level specified in the U.S. Congress Code of Federal Regulations for HDD engines. Total exhaust from each BUG up to 600 kW was captured by the MEL while partial exhaust was collected for BUGs exceeding 600 kW. Gaseous emissions were collected through heated lines from the primary dilution tunnel system. PM samples were withdrawn from a temperature controlled Secondary Dilution System operating at 47ºC. NO_x, carbonyls, PAHs and EC/OC data are presented and compared for BUGs and HDD vehicles.

8PH4

ON-BOARD PARTICLE NUMBER DISTRIBUTIONS FROM HYBRID-ELECTRIC AND CONVENTIONAL DIESEL BUSES AS A FUNCTION OF ROAD TYPE.

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Diesel particle emissions, especially in the size range of ultrafine and nanoparticles, have been correlated with health problems. The use of hybrid-electric diesel buses, ultra-low sulfur diesel and diesel particle filters (DPF) have been proposed as possible methods to reduce these heavy-duty vehicle emissions. In an effort to effectively evaluate the effect of these techniques, emissions from two types of heavy-duty transit buses, a parallel-drive hybrid diesel electric 2003 Allison Ep40 Electric Drive bus with Cummins ISL 270 engine and a conventional 2002 diesel bus with a Navistar Series 40 engine, were sampled under real-world driving conditions.

Particulate emissions were collected and measured from a diluted exhaust tailpipe by an electrical low pressure impactor (ELPI) and a scanning mobility particle sizer (SMPS). A 30 lpm ELPI was operated at 1-sec resolution in order to measure number size distributions. The SMPS was operated to obtain size-selected particle number concentrations (10 to 130 nm). Two buses of each type were driven on different real-world driving routes: a steady-state freeway cruise, an inner city \stop-and-go\ route, and arterial travel with a steep grade.

Total route-averaged particle number emissions (ELPI) were highest during steady-state freeway cruise. Differences in particle size distributions for different driving routes were also observed with the SMPS. Freeway cruise showed a peak in the size range of 40 and 80 nm but during travel up the steep (9%) grade the highest number concentration was measured and the distribution mode shifted to the 10-20 nm range. The number distribution during stop-and-go travel was similar to that obtained while traveling the steep grade route. Particle number emissions were examined as a function of bus and operating characteristics such as RPM, vehicle speed and load. Particle number distributions correlated well with percent load during travel on steep grade for the hybrid buses only. Particulate emissions were reduced by more than 90% when using ultra-low sulfur diesel with DPF after-treatment and approached the detection limit of the SMPS instrument when exhaust was diluted ~25:1.

8PH5

STUDY OF FINE PARTICULATE MATTER EMISSIONS FROM LIGHT-DUTY GASOLINE VEHICLES.

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The fine particulate matter (PM2.5) emissions of motor vehicles are seriously concerned in motorized cities in the world. In the last decades diesel engines were thought to be the major source of exhaust PM2.5 emissions, but some recent studies suggested that spark-ignition engines also discharge numerous fine particles, even approaching the emission level of diesel engines according to fine PM number emissions. In this study four gasoline fueled taxies with close-loop electronic fuel injection and three-way catalysts (they were actually gasoline and liquefied petroleum gas bi-fuel taxies but in the experiment only gasoline fuel were used) were tested for exhaust emissions before and after regular maintenance. The experiment was carried out in a chassis dynamometer lab and NEDC1992 test procedure was followed. Electrical low pressure impactor (ELPI, Dekati Ltd., Finland) with double dilution system were employed to measure the real-time number concentration of exhaust fine PM, while traditional methods were used to measure the distance-based emission factors of gaseous pollutants. The average number concentrations of PM2.5 emissions of three taxis ranged from 1.56 million to 4.26 million per cubic centimeters and it was 14.7 million to 15.6 million per cubic centimeters for the other taxi. Concerning the maximum number concentration of PM2.5 emissions, it ranged from 22.0 million to 74.3 million per cubic centimeters for three taxies and was 239 million to 274 million per cubic centimeters for the other one. Generally the highest PM2.5 number concentration occurred as cold start or high speed operation. There was no significant correlation between the PM2.5 number emissions and the vehicle distance traveled, also the regular maintenance had little impact on the emissions. Looking into the number weighted size distribution of PM2.5 emissions, highly skewed curves with highest number concentrations of smallest particles were given for the average for all taxies before and after maintenance. For the maximum PM2.5 number concentrations, the size distribution appeared to be uni-modal with the peak at aerodynamic diameter = 73 nm for the taxi with highest PM2.5 emissions but still be skewed curves for the other three taxis. The number concentrations of PM2.5 emissions of these gasoline taxies are close to that of diesel trucks and ultrafine particles (<100 nm) account for overwhelming significance in the total number emissions. It suggests that gasoline fuel vehicles should be paid more attention to when fine particulate matter emissions are concerned, especially number emissions.

8PH6

THE EMISSION OF PARTICLES FROM COAL-FIRED POWER PLANTS IN CHINA. XINGMING GUO, Jiming Hao, Lei Duan, Honghong Yi, Xinghua Li, Department of Environmental Science & Engineering, Tsinghua University, Beijing, P.R.China

Four coal-fired power plants in China were selected in order to study the particle emission. The four coal-fired power plants are different in fuel and particulate emission control devices (PECDs). At the inlet and outlet of PECDs of the four power plants, particulate matter concentrations and size distribution were determined experimentally by electrical low pressure impactor (ELPI) with a sampling system, which consisted of an isokinetic sampler probe, pre-cut cyclone, two stages dilution system and sample line to the instrument. Size distribution is measured on the range from 0.03μmto 10μm in aerodynamic diameter.
The data obtained from the measurement show that the average PM10 fraction of total particulate matter varied from 24.95% to 72.95% before and after PECDs of the four coal-fired power plants. The mass concentration of PM10 at outlet PECDs of coal-fired power plants is mainly dominated by the particles which are larger than 1um and the number concentration of PM10 is dominated by particles which are smaller than 0.1μm. The maximum penetration rates of electrostatic precipitator (ESP) and bag precipitator both appear in the particle size range of 0.1 ~ 1μm. A phenomenon is seen that the mass and number concentration of PM10 at precipitator outlet will increase obviously because of the rapping the last electrical field or cleaning the last bag house.

8PH7

SYNTHESIS OF PHOTOCATALYTIC ACTIVE ANATASE PHASE TITANIA NANOPOWDER. Ulrika Backman Unto Tapper Olli Jauhiainen JORMA JOKINIEMI

A novel route to prepare supported metal catalytic materials by a one-step aerosol process is presented. The system setup was made as simple as possible in order to ease scale-up. It consisted of a bubbler and a tubular flow reactor. The metal oxide support was prepared by thermal decomposition of a metalorganic precursor and the metal was added by evaporation/condensation. The performance of the system was tested with Ag on TiO2 support. The powders were characterised using transmission electron microscopy, x-ray diffraction, nitrogen adsorption, ICP/AES and elemental analysis. The silver was well dispersed in 1 - 2 nm sized particles on the surface of the agglomerated titania support particles. The primary particle size of the anatase phased titania was 13 - 22 nm. The prepared powder had a high specific surface area, between 40 and 90 m2/g. The photocatalytic activity of the produced powder was tested in UV and visible wave lengths.

The titania particles were agglomerated and had a primary particle size between 25 and 40 nm as analysed by TEM. The silver was dispersed in small (2-3 nm) particles on the surface of the TiO2. The SAED patterns of the TiO2-particles showed that the particles were anatase phased. Also the XRD analyses showed that the collected titania powder consisted mainly of anatase phased material. The anatase phase is the most used phase, both in catalytic and in photocatalytic applications. The specific surface area for the powder produced at 600°C-1100°C was 92 m2/g and at 1100°C-1100°C it was 40 m2/g. The average particle diameter was calculated from the specific surface area assuming nonporous spherical particles. The average particle diameter at 600°C-1100°C was 16 nm and at 1100°C-1100°C 38 nm. The presence of silver in the observed small particles was verified using EDS.

Testing and optimising the photocatylitic activity of the product has also been carried out. The produced powder was compared with Degussa P25 on Asetaldehyde (CH3CHO) decomposition in UV light. Results give similar activity for as produced TiO2. After calcinating 3 hours in N2 clearly better than DgP25 photocatalytic activity was observed. Further optimisation of the produced powder photocatalytic response is under way.

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8PH8

NANOPARTICLE FORMATION DURING METAL COMBUSTION. Igor S. ALTMAN, National CRI Center for Nano Particle Control, Seoul National University, Seoul, Korea; School of Environmental Engineering, Griffith University, Brisbane, QLD, Australia; Igor E. Agranovski, School of Environmental Engineering, Griffith University, Brisbane, QLD, Australia; Mansoo Choi, National CRI Center for Nano Particle Control, Seoul National University, Seoul, Korea

The interest towards investigation of the nanoparticle formation during metal combustion is caused by the recently reported unique properties of such nanoparticles, which were assigned to peculiarities of the particle formation. In this work we summarize results of our theoretical and experimental studies devoted to this process. We demonstrated that the surface condensation is a main process responsible for nanooxides growth during metal combustion. It is shown that the rate of this condensation growth is consistent with the exponential law, which could lead to the formation of the lognormal particle size distribution in the system, where the Brownian coagulation is suppressed. The post-nucleation stagnation of the nanoparticle growth is found. The particle overheating is suggested as a cause of the growth stagnation. The found stagnation leads to the accumulation of the supercritical clusters in the system generating nanoparticles. The role of these supercritical clusters in the nanoparticle agglomeration is considered.

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8PH9

SYNTHESIS OF LITHIUM-COBALT-NICKEL OXIDE NANOPARTICLES FROM SPRAYED DROPLETS OF THEIR AQUEOUS PRECURSOR IN A DIFFUSION FLAME REACTOR. HEE-DONG JANG, Hankwon Chang, Yong-Jae Suh Nano-Materials Group, Korea Institute of Geoscience and Mineral Resources, Daejeon, KOREA

Lithium-cobalt-nickel oxide is of interest as one of the most promising cathode materials in Li-ion secondary batteries. The performance of the cathodes material is affected by a number of factors such as particle size, composition and crystalline phase of the material. Smaller diameter of crystalline particles has been expected to result in a better cycle stability. Li-Co-Ni oxide nanoparticles were produced from an aerosol precursor, sprayed aqueous droplets of nitrate compounds of lithium, cobalt and nickel in a diffusion flame. Effects of process variables such as total molar concentrations of the precursors, molar ratios among the precursors, and flow rates of combustible gases on the particle size and crystal structure of the nanoparticles were investigated. Particle properties of the composite nanoparticles were characterized by TEM, XRD, and BET method. The average particle diameter increased with an increase in the molar concentration of the precursor. Raising the maximum flame temperature by controlling the gas flow rates also led to an increase in the average diameter of the particles. As the average diameter of the precursor droplets decreased, average particle diameter of the product particles also decreased. The crystalline LiCoNi oxide nanoparticles were produced as the flame temperature maintained above 1773 K and residence time of the precursor in the diffusion flame increased. The composite nanoparticles of crystalline phase ranging from 11 to 50 nm in the average diameter were produced in the present experiments.

8PH10

FINE PARTICLE AND TRACE ELEMENT EMISSIONS FROM COMBUSTION OF ANTHRACITE COAL IN POWER PLANT.

HONGHONG YI, Jiming Hao, Lei Duan, Xinghua Li, Xingming Guo, Tsinghua University, Beijing, China

Fine particle and trace element emissions from energy production have continuously been subject to tightening regulations. Much attention has been paid to study its characterization and emission control. In this investigation, size distribution, morphological character and trace element emissions of the fine particles emitted from the combustion of pulverized anthracite coal were determined experimentally at a 220MW power plant on the size range from 0.03µm to 10µm in aerodynamic diameter. Electrical Low Pressure Impactor (ELPI) with a sampling system, which consisted of an isokinetic sampler probe, pre-cut cyclone, two-stage dilution system and sample line to the instruments, were used to measure in situ. Samples were collected before and after the bag-house (BH) at the flue gas temperature is 125° to 135°.
The number size distribution peak values of the fine and coarse mode were about 0.1µm and 1µm, respectively. The BH collection efficiency of PM is 99.94% and 99.57% to PM10. The minimum collection efficiency of BH (99.4%) is appeared in the particle size range of 0.1-1µm. The spherical particles which are smaller than 2.5µm were mainly solid. However, hollow spheres are increase in coarse fraction. The irregular particles appeared in coarse PM more frequently than in fine fraction.
Elemental size distributions of As, Hg, Se, Cd, Cr, Cu, Al, V, Zn, Mn, Fe were obtained. The volatile elements are enriched in fine particles relative to the coarse fraction. The concentration of the trace elements within the submicron and supermicron particles fraction increases with particle size decreasing. The collection efficiencies of trace elements differ from the overall PM collection. The capture efficiencies of relatively non-volatile elements such as Cr approach the overall particle collection efficiency, whereas more volatile elements such as Hg, As and Se are captured less efficiently than the total particulate. The elemental controlled and un-controlled emission inventories of PM1, PM2.5 and PM10 are also obtained.

8PH11

COMPARISON OF SOOT VOLUME FRACTION DETERMINED BY A TEOM, A SMPS AND AN EXTINCTION-SCATTERING DEVICE IN THE INFRARED.

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The study of soot particle physical properties generated during a fire is a complex problem, but a prior interest in the field of fire safety. It is especially useful to predict the behaviour of air cleaning barriers in fire situation (clogging, pressure drop) and to estimate the radiative effect of soot aggregates. The objective of this study is to compare two methods for the determination of the volume fraction based on mass and optical measurements.
The fire zone is located in a furnace of 1 m3, which is surmounted by a hood connected to a ventilation duct. The aerosol is sampled with the help of a dilution system and the size distribution is measured by a Scanning Mobility Particle Sizer (SMPS). The \reference\ volume fraction is determined using a Tapered Element Oscillating Microbalance (TEOM) for mass measurement and by assuming a particle density of 1,74 g/cm3. The volume fraction is also determined by a specific extinction measurement device combined with a value of refractive index from the literature.

We present the results obtained for soot from the combustion of acetylene. The \optical\ soot fraction is close to the \reference\ volume fraction and, depending on ventilation condition, ranges from 10-9 to 10-8. Soot volume fraction is also determined by the SMPS and is generally 2 to 3 times greater than the \reference\ volume fraction. The relative consistency between \optical\ and \reference\ volume fractions underlines the validity of the assumed soot refractive index value and particle density. Further investigation on different methods used to determine the soot volume fraction with the SMPS will be carried out, especially by assuming the fractal morphology of soot aggregates. Moreover we will measure the extinction and scattering coefficients of soot particles and retrieve the refractive index in the infrared by an inversion method based on the Rayleigh-Debye-Gans theory for Fractal-Aggregates. The experimental value of refractive index will be compared to bibliographical data.

8PH12

DEVELOPMENT OF A COMPACT DILUTION SAMPLING SYSTEM FOR STATIONARY COMBUSTION SOURCES.

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Dilution sampling system simulates the cooling and dilution processes after hot flue gas left the stack and recently it has been widely used for characterizing emissions from stationary combustion sources, especially for source apportionment. In order to make this method more convenient and advantageous in field investigation, a compact dilution sampling system was developed and it includes: (1) sampling inlet part, (2) dilution part, (3) residence chamber, (4) sampling part.

In sampling inlet part, a sample flue gas of 30 Lpm is withdrawn from the stack and then divided into two parts, flue gas of about 6 Lpm is drawn to dilution part and the rest is conducted to collect TSP according to U.S. EPA Method 5. Before the flue gas enters into the dilution part, a cyclone is used to remove over 10 um particles.

Dilution part consists of two-stage diluters. The operation principle of the first diluter is based on ejection type dilution (Dekati Ltd, Finland). Ejector type diluter is used to keep the dilution ratio at 10 constantly. 0~50 Lpm can be drawn from the outlet of the diluter to the second diluter according to research requirement. The second diluter is a cylindric enclosure with a perforated cone inside. The sample flow from the first diluter is introduced into the inside of the cone and the dilution air is forced through the apertures of the cone into the inside and mixes with the sample flow. A flowmeter is equipped to record dilution air flowrate in the second diluter. The second diluter can supply dilution ratio from 1 to 10. The total dilution ratio of the dilution part ranges from 10 to 100. The length of the dilution part is less than 800mm. An oil-free air compressor supplies the dilution air that is to be purified before entering into the dilution part.

Residence chamber is 450mm in diameter and 700mm high. It allows aging time of 80-90 seconds for diluted sample gas with flow rate at 80 Lpm. The sampling part is attached to the end of the residence chamber and have 5 sampling port and each sampler is equipped with flow controller.

The sampler is made entirely from stainless steel and Teflon. Preliminary studies indicate the new dilution sampling system is compact and light, good for characterizing emissions from stationary combustion sources in situ.

8PH13

AEROSOL GELS: A CARBON SOOT WITH NOVEL PROPERTIES FORMED INSIDE A CLOSED COMBUSTION CHAMBER.

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A mixture of a hydrocarbon gas and oxygen is exploded inside a closed chamber to rapidly produce nanometer sized (~ 50 nm) carbon particles which quickly aggregate to form ramified fractal structures with fractal dimensions of 1.8 in the monomer to submicron length scale and 2.5 in the supermicron length scale. The fractal dimension 1.8 is the well known morphology for flame soots due to diffusion limited cluster aggregation while the fractal dimension 2.5 results from the percolation of the 1.8 small clusters during the cluster dense stage of the growth process. This soot deposits on the bottom of the chamber to form a gel like substance which we call an aerosol gel. Our carbon aerosol gels are very similar to carbon aerogels produced by well known sol gel processes, but are easier and more economic to produce since there is no need for the supercritical drying step. Carbon aerosol gels have ultra low density of 2 – 6 mg/cc, high specific surface area of 100 – 500 m2/gm, electrical conductivity comparable to that of a typical semiconductor, and a hydrophobic behavior. Electron microscopic pictures show graphitic layers on the surface of the soot monomers. We measured 3 nm Scherrer broadening from X-ray diffraction pattern of the soot. Recently we have built a small combustion chamber which is appropriate to do light scattering studies to investigate the kinetics and morphology of the quickly aggregating carbon soot particles rapidly produced during the explosion. Results from these experiments will also be reported.

8PH14

RADIOCARBON IN PARTICULATE EMISSIONS FROM GASOHOL COMBUSTION IN SMALL ENGINES. CHARLES LEWIS, James Braddock, William Lonneman, U.S. EPA, Research Triangle Park, NC; William Crews, BKI, Inc.; John Volckens, Colorado State University, Fort Collins, CO

Measurements of the radiocarbon (C-14) content of carbon-containing ambient aerosol are increasingly being used to estimate the relative amounts of carbon originating from non-fossil-fuel vs. fossil-fuel sources. Because carbon is generally a large constituent of ambient aerosol such estimates are important in the planning of control strategies for ambient aerosol. When applying this methodology to estimate the contribution of mobile source emissions to ambient aerosol it is generally assumed that there will be no C-14 emitted from these fossil-fueled (gasoline or diesel) vehicles. However this assumption is invalid for those situations in which the fuel is either gasohol (gasoline with approximately 10% ethanol -- generally biogenic) or biodiesel (diesel with approximately 20% vegetable oils). For both petroleum conservation and political reasons such biogenic additives are expected to become increasingly utilized. As a first step in exploring the C-14 implications of biofuel usage PM2.5 emissions samples from a string trimmer and chainsaw, using conventional gasoline and gasohol, were collected at the EPA Small Engine Dynamometer Facility and measured for their C-14 content. Surprisingly, the amount of C-14 found in PM2.5 from gasohol combustion was essentially the same as for gasoline combustion, certainly much less than that suggested by a simple estimate based on the amount of ethanol in the gasohol fuel. Details of the experiment and its results will be reported. Although this work was reviewed by EPA and approved for publication, it may not reflect official Agency policy. We thank Jerry Faircloth, Mike Pleasant, Kevin Hicks, Jason Mills and Richard Snow for their assistance in collecting the small engine samples.

8PH15

REAL TIME DIESEL PARTICULATE FILTER EFFICIENCY MEASUREMENTS FROM SPECTRAL DATA. Tim Hands, CHRIS NICKOLAUS, Jonathan Symonds, Cambustion Ltd, Cambridge, UK

A DMS500 Fast Particulate Spectrometer and High Ratio Dilution system were used to sample diesel engine exhaust both upstream and downstream of a Diesel Particulate Filter. (Fitted to a production passenger car on a chassis dynamometer.) The dataset allows calculation of real time DPF efficiency and includes a regeneration event. Changes in performance of the DPF following regeneration were observed, while measurements of the input to the DPF provide a valuable engine calibration tool.

8PI1

THE ERRORS OF MEASUREMENTS OF TROPOSPHERIC BIOAEROSOL.

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Research Institute of Aerobiology, SRC VB “Vector”, and the Institute of Atmospheric Optics, SB RAS have been performing out systematic monitoring of tropospheric bioaerosols in South-western Siberia since December 1998. Atmospheric air samples are collected from an “Optic-E” airplane laboratory on one of the last 10 days of each month at the altitudes of 0.5; 1; 1.5; 2; 3; 4; 5.5 and 7 km, and the concentrations of total protein and live microorganisms in them are determined. The coordinates are as following: longitude 54°30’ North; latitude 82°20’ West. The obtained data allow us to study seasonal variations of the concentration of the biogenic component of tropospheric aerosols; to determine the microorganism groups present in them; to evaluate the location of sources forming the bioaerosol background of the atmosphere of Southwestern Siberia.

The analysis of the obtained data at the qualitative level showed that the values of the total protein concentration and the decimal logarithm of live microorganisms concentration had a considerable dispersion; and no dependence of bioaerosol concentration on the altitude of observations was revealed. In the general case, the observed great dispersion of the concentration values is caused by the statistical nature of the process of atmospheric pollutants diffusion i.e. the turbulence of atmosphere as well as the errors of measurements causing additional dispersion of the observed concentration values.

The evaluation of the contribution of instrumental errors to the observed dispersion of the concentration of tropospheric bioaerosols in Southwestern Siberia was performed in the work based on the array of experimental data on the concentrations of total protein and live microorganisms obtained in 1999–2003, and the obtained values of dispersion of tropospheric bioaerosol concentration were corrected.

The probability density function of the concentration of total protein aerosols was approximated by the normal law. Normal approximation of Poisson distribution for the concentration of live microorganisms was used.

The relations of dispersions of total protein concentration corrected taking into account the errors to the measured values depending on the month of observations. It was shown that the corrections made are rather significant as they can reach 100%.

The work shows that the evaluation of the contribution of measurement errors to the obtained values of the concentration of tropospheric bioaerosols is a necessary stage of the summarizing and analysis of experimental data, and our previously reported evaluations of the errors of measurement methods should be probably corrected towards reduction.

8PI2

AN INTERCOMPARISON OF MEASUREMENT METHODS FOR CARBONACEOUS AEROSOL IN THE AMBIENT AIR IN NEW YORK CITY.

PRASANNA VENKATACHARI, Liming Zhou, Philip K. Hopke, Clarkson University, Potsdam, NY; James J. Schwab, Kenneth L. Demerjian, Olga Hogrefe, State University of New York, Albany, NY; Dirk Felton, Oliver V. Rattigan, NYS Department of Environmental Consrvation, NY.

Measurement methods for fine carbonaceous aerosol were compared under field sampling conditions in Flushing, NY during the period of January and early February 2004. In-situ 5- to 60-minute average PM2.5 organic carbon (OC), elemental carbon (EC) and black carbon (BC) concentrations were obtained by the following methods: Sunset Laboratory field OC/EC analyzer, Rupprecht and Patashnick (R&P) series 5400 ambient carbon particulate monitor, Aerodyne aerosol mass spectrometer (AMS) for total organic matter (OM), and a two-wavelength AE -20 Aethalometer. Twenty-four hour averaged PM2.5 filter measurements for OC and EC were also made with a Speciation Trends Network (STN) sampler. The diurnal variations in OC/EC/BC concentrations peaked during the morning and afternoon rush-hours indicating the dominant influence of vehicle emissions. Effects of transported aerosol and mixing heights were observed to be minimal. BC/EC slopes are found to range between 0.86 and 1.23 with reasonably high correlations ($r > 0.75$). Strong correlations were observed between BC and thermal EC as measured by the Sunset instrument and between Sunset BC and Aethalometer BC. Reasonable correlations are observed among collocated OC/EC measurements by the various instruments.

8PI3

SOURCE IDENTIFICATION OF AEROSOLS IN THE WESTERN UNITED STATES USING POSITIVE MATRIX FACTORIZATION.

JIN XU, Dave DuBois, Mark Green, Vic Etyemezian, Desert Research Institute, Las Vegas, NV; Marc Pitchford, NOAA Air Resource Laboratory, Las Vegas, NV

In order to identify the sources of aerosols in the western United States, Positive Matrix Factorization (PMF) receptor model is applied to the 24-hr integrated aerosol chemical composition data obtained at the Class I areas of the Western Regional Air Partnership (WRAP) region through the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. Normalized source factors and the quantitative source contributions for each resolved factor are calculated. The major sources that contribute to the aerosol loadings in the western United States, including smoke, dusts, sulfate-rich secondary aerosol, nitrate-rich secondary aerosols, diesel emission and sea salt are identified. The similarities and differences of chemical source profiles, and the major aerosol source contributors in different regions of the western United States are discussed. Based on the profile and the daily contribution to aerosol concentration of each source factor, the contributions of source factors to the aerosol light extinction coefficients are estimated using the IMPROVE method. The importance of the major aerosol sources to regional haze and visibility in the Class I areas of the western United States is discussed.

8PI4

AEROSOL CLIMATOLOGY OVER THE CONTINENTAL AND COASTAL STATIONS IN INDIA.

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Study of atmospheric aerosols is assuming greater importance in view of their role in (i) the formation of fog, mist and clouds in the lower troposphere, (ii) chemical and electrical effects in the upper atmosphere and (iii) radiation budget of the earth atmospheric system and hence climate. Aerosol Climatology and Effects (ACE) project is pursued under the ISRO/DOS-Geosphere Biosphere Programme (ISRO-GBP), India with the long term objective of evolving empirical models of the optical and physical properties of atmospheric aerosols over distinct geographical environments (such as coastal, continental, arid, urban, rural and industrial) of India.

A ten filter solar radiometer referred to as Multiwavelength Radiometer (MWR) is in operation on clear and cloud free days since 1985 in Trivandrum, 1988 in Mysore and Visakhapatnam. Trivandrum is a rural coastal station on the west coast of India, while Visakhapatnam represents an industrialized urban coastal environment, on the east coast. Mysore is a continental station with no significant industrial activity.

Subjecting the output radiation to Langley technique yields the total optical depth at each wavelength. Subtracting the components due to Rayleigh scattering and absorption by ozone and water vapour, the spectral aerosol optical depth (AOD) are obtained. The available AOD data is used to study the aerosol characteristics at the continental station Mysore and coastal stations Trivandrum and Visakhapatnam. However perturbation produced due to Pinatubo (June 1991 to November 1993) is not considered for the study.

To examine the annual variations, the daily values of AOD at each wavelength are grouped in terms of identical months irrespective of the year and monthly mean have been estimated for each month.

In Trivandrum, the optical depths remain at low levels , at all wavelengths in January followed by a gradual build up to reach peak values in May-June. This peak is sharper and occurs earlier (in May) at shorter wavelengths (less than 700 nm) while at the longer wavelengths it is quite broad extending up to July. There is a sharp depletion in AOD from June at the shorter wavelengths, while the effect is gradual and delayed at the longer wavelengths. After the withdrawal of south-west monsoon (in September), there is a faster decrease in AOD in near IR and a slow build up in visible leading to a change in the spectral dependence. With the end of monsoon season (in November), the AODs attain the annual low values in the entire spectral range, which may be considered as the near background level for Trivandrum. For Mysore, it is seen that from an annual low value in December/January months, AOD builds up fast to reach an annual high by April. This peak is rather broad and extends from March to May. Consequent to the depletion in aerosol loading caused by the monsoon activity (June to September/ October), AOD decreases continuously from September/October to reach the annual low by December. In Visakhapatnam, the AOD values are higher in summer with maximum in the month of May and lower extinctions are observed during monsoon season. The reasons for these variations in the aerosol characteristics over the continental and coastal stations in India will be discussed.

8PI5

PREDICTED RESPONSES OF INORGANIC PM2.5 IN THE EASTERN UNITED STATES TO EMISSION CHANGES USING A THREE DIMENSIONAL CHEMICAL TRANSPORT MODEL (PMCAMX+). ALEXANDRA P. TSIBIDI, Vlassis A. Karydis, Spyros N. Pandis, Dept. of Chemical Engineering, University of Patras, Patras, Greece

In the eastern United States, inorganic species account for approximately half of the PM2.5 mass [U.S Environmental Protection Agency, 1996]. In this study we focus on the changes of the inorganic PM2.5 during changes of the emissions of their precursors (SO2, NOx, NH3) and other pollutants (VOCS). Future reductions of SO2 emissions are expected to reduce sulfate, but this can be partially offset by increases in the nitrate concentrations. The effect of NOx, NH3 and VOC emission controls on the PM2.5 concentrations remains uncertain. (McMurry et al., 2004).

A three dimensional chemical transport model is well suited for this purpose as it links emissions to PM2.5 concentrations describing the physics and chemistry of the atmosphere. PMCAMx (Gaydos et al., 2005) is used to simulate the PM size composition distribution in the eastern United States. Four months (January, March, July, October) during the four different seasons are simulated to investigate the seasonal dependence of the PM2.5 responses to emissions changes. The spatial and temporal characteristics of the effectiveness of the different emission control strategies (reductions of SO2, NOx, NH3, VOCS, primary organic PM) are discussed. The results of this model are compared with predictions of an observation based model (TMR, Vayenas et al., 2005). TMR relies on ambient measurements of the NH3 and sulfate concentrations simulating the thermodynamics and removal processes in the sulfate/nitrate/ammonia system.

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8PI6

IMPACTS OF SHIP DIESEL EMISSIONS TO AIRBORNE PM2.5 IN THE SAN DIEGO AREA. JONG HOON LEE, Philip K. Hopke, Clarkson University, Potsdam, NY

There is relatively little reported on the nature of the emissions from compression-ignition ship engines. Ship diesel engines can use a wide range of quality fuels and will typically utilize the lowest cost fuels available. Thus, they often burn low volatility residual oil, often referred to No. 6 or bunker-C oil, in which Ni and V are enriched. There have been efforts to estimate the impacts of ship emissions on NOx and SO2 in which emissions modeling was used. However, there is no direct information on the elemental composition of typical ship emissions.

The ships burn fuel as they enter and leave the ports. There are also emissions from support vehicles, trucks and railroad engines. The objective of this study is to identify the sources of PM2.5 with a particular emphasis on the impacts of ship emissions on the mass concentrations observed along the west coast in the U.S. with an emphasis on the STN sites in the area of San Diego, CA.

For this study, daily PM2.5 composition samples measured at a PM2.5 Speciation Trends Network site in San Diego, CA were analyzed using positive matrix factorization and non-parametric regression models. The impacts of ships, spark- and compression-ignition vehicle emissions as well as the formation of secondary carbon will be separately apportioned so that contributions of each source to airborne PM2.5 are quantitatively assessed.

8PI7

SECONDARY ORGANIC AEROSOL FORMATION FROM THE OXIDATION OF MONOTERPENES BY THE CHLORINE ATOM.

XUYI CAI, Robert Griffin, University of New Hampshire, Durham, NH

Secondary organic aerosol (SOA) in the troposphere exerts significant effects on regional and global air quality. The formation mechanisms of SOA via the oxidation of volatile organic compounds (VOCs) by hydroxyl radicals, ozone, and nitrate radicals have been studied intensively in the last decade. The chlorine atom (Cl) is also an effective oxidant in the coastal/ marine boundary layer and in regions heavily influenced by industrial emissions. It is hypothesized that certain VOC-Cl reactions lead to the formation of SOA. The goal of this work is to verify and quantify this hypothesis for monoterpenes through laboratory experiments.

The model biogenic hydrocarbons chosen for this study are alpha-pinene, beta-pinene, and d-limonene. Before each experiment, the chamber is irradiated for 24 hours and flushed for 48 hours using zero air. During experiments, no other species besides the monoterpene, an internal standard, and molecular chlorine is injected into the chamber. Gas chromatography is used to measure the initial hydrocarbon concentration in the chamber. Approximately 100ppb molecular chlorine is injected into the chamber from a certified cylinder. Ultraviolet lamps are illuminated to photolyze the molecular chlorine to form Cl and to initiate the oxidation reactions. A SMPS is used to measure the size distribution of the newly formed aerosol particles. The experiment is terminated when the aerosol mass does not increase and the amount of reacted hydrocarbons no longer changes. Aerosol yields are estimated based on the measured aerosol size distribution, the mass concentration of consumed hydrocarbons, and the estimation of the wall loss of the newly formed aerosol.

Experiments indicate that significant amounts of aerosol are generated by the oxidation of the three monoterpenes by Cl. For initial concentrations of 10 to 25 ppb alpha-pinene, beta-pinene, and d-limonene, the mobility diameter of the newly formed aerosols is generally around 130 nm, and the generated aerosol mass is in the range of 10 to 35 micrograms per cubic meter. The corresponding yields are in the range of 0.18 to 0.25. These aerosol yields are similar to previously reported SOA yields from monoterpenes for photooxidation and ozone experiments.

8PI8

DEVELOPMENT OF A PHOTOCHEMICAL CHAMBER FOR THE TOXICOLOGICAL EVALUATION OF COAL COMBUSTION EMISSIONS.

PABLO A. RUIZ, Joy E. Lawrence, Jack M. Wolfson, Stephen T. Ferguson, Tarun Gupta, Choong-Min Kang and Petros Koutrakis. Department of Environmental Health, Harvard School of Public Health, Boston MA 02215

This is one of a series of posters describing the TERESA study, whose objective is to evaluate the toxicity of coal-fired power plant emissions. Our approach involves: in situ sampling and dilution of emissions; chamber simulation of plume reactions for several typical atmospheric scenarios; and finally, animal exposures to the reacted aerosol. In this poster, we present a photochemical chamber that simulates the atmospheric aging of coal combustion emissions.

The main reaction that emissions undergo in the atmosphere is the oxidation of sulfur dioxide (SO2) by reaction with hydroxyl radical (OH·) to form sulfuric acid (H2SO4). To simulate this atmospheric reaction, we designed a completely-mixed continuous flow reactor. This reaction chamber has a relatively high OH· production rate, using photolysis of O3 with UV light in the presence of water vapor. Emission spectra of the light sources used are presented. A pilot chamber with a residence time of 1 hour operating at a continuous flow of 5 LPM was evaluated in the lab using a diluted power plant emission surrogate prepared from gas standards of NO and SO2. Continuous monitors for O3, NO, NO2, SO2 and particle size distribution, along with integrated filter samples of H2SO4 were used to evaluate chamber performance.

Following lab evaluation, a field chamber was built for the toxicological study performed in situ at a coal combustion power plant. This larger chamber has a residence time of 1 hour when operated at a flow rate of 7 LPM. The field work comprised 5 rounds of exposures of 4 days each, completed between April-November, 2004, at a plant located in the upper mid-west. We present a summary of chamber performance for each round in terms of upstream and downstream gas concentrations and particle production. Details of animal exposure characterization can be seen in an accompanying poster.

8PI9

UHAERO-INORGANIC MODULE: A NEW THERMODYNAMIC EQUILIBRIUM MODEL FOR MULTICOMPONENT INORGANIC AEROSOLS. Neal R. Amundson, Alexandre Caboussat, Jiwen He, ANDREY MARTYNENKO, Department of Mathematics, University of Houston, TX; John H. Seinfeld, Department of Chemical Engineering, California Institute of Technology, Pasadena, CA; Kee-Youn Yoo, Department of Chemical Engineering, Seoul National University of Technology, Seoul, Korea

A mathematically rigorous and computationally efficient model for the prediction of multicomponent inorganic atmospheric aerosol behavior is presented. The mathematical framework for the modeling of multiphase chemical equilibrium reactions is based on the canonical stoichiometry of inorganic aerosols. The numerical method for the prediction of the phase partitioning of the inorganic aerosol is based on a primal-dual active set algorithm. One of the main features of the model is its ability of predicting phase transition and multistage aerosol growth without any a priori knowledge of the behavior of inorganic aerosols. A comparison is conducted between our model and available experimental results under several conditions. Our model prediction agrees with experimental results in hygroscopic growth, temperature dependent deliquescence relative humidities, and number and makeup of multiphase aerosols. Comparisons are also conducted between our model and two other models currently in use for representative atmospheric environments over an extended composition, temperature, and RH domain. Attention is given in the modeling ability of predicting phase transition and multistage hygroscopic growth of some common inorganic salt components of individual and mixed aerosols.

8PI10

ANALYSIS AND IDENTIFICATION OF PRODUCTS FORMED DURING HYDROXYL RADICAL INITIATED PHOTO-OXIDATION OF ATMOSPHERICALLY RELEVANT HYDROCARBONS. JANEEN CASEY, Michael Mozurkewich, Don Hastie, Chemistry Department and Centre for Atmospheric Chemistry, Toronto, Canada

The hydroxyl radical initiated oxidation of hydrocarbons in the atmosphere produces a diverse range of organic products, which depending on their vapour pressures, may be found in the gas, and/or particle phase. The identities of these secondary organic products, especially those in the particle phase, are not well known. We are using a smog chamber to perform atmospherically important oxidation reactions under controlled conditions with the objective of improving our knowledge of the chemical composition of the reaction products. The chamber is an 8m3 Teflon bag surrounded by an outer shell composed of two mobile sides lined with mylar and 24 black lights. Hydroxyl radicals are produced by photolyzing isopropyl nitrite in the presence of NO, and reactions can be performed with or without pre-existing particles. So far preliminary studies on the reactions of toluene, m-xylene, 1,3,5-trimethyl benzene and ß-pinene have been undertaken. The concentrations of the hydrocarbon and NOx are followed using a gas chromatograph (GC-FID) and a chemiluminescence analyzer respectively. A tandem differential mobility analyzer (DMA) and condensation nucleus counter (CNC) are used to determine particulate size distributions, from which particle yields are obtained. Identification of gas and particulate phase products is carried out using a Sciex TAGA 6000E triple quadrupole mass spectrometer with an atmospheric pressure chemical ionization source (APCI). The 10 to 800 amu mass range available for a single MS scan allows monitoring of products with larger and smaller masses then the reagent hydrocarbon. APCI is considered a soft ionisation technique forming protonated molecular ions of products that have a greater proton affinity than water clusters, which are the reagent ions. Products are identified using the fragmentation patterns obtained by MS/MS scans. MS/MS scans also provide the ability to monitor fragmentation ions to distinguish between products of the same molecular weight. APCI-MS is showing excellent promise for product identification, requiring no chemical work up of samples prior to analysis. In the future it is desired to simplify the MS procedure by introducing online particle analysis.

8PI11

AEROSOL FLUX MEASUREMENTS FROM THE AIRPLANE. GINTAUTAS BUZORIUS, CIRPAS, Department of Research, NPS, CA, USA John Kalogiros, IERSD, National Observatory of Athens, Athens, Greece Varuntida Varutbangkul, California Institute of Technology, Department of Chemical Engineering, Pasadena, CA, USA.

Airborne aerosol flux measurements at low altitude provide an ability to study surface particle sinks and sources on regional scales. In presented study total particle number flux was measured from an aircraft flying at 30 to 40 m altitude 50 m/s velocity above Monterey Bay off central California coast. The flux was calculated using eddy correlation (EC) method, fast aerosol concentration measurements were performed with a modified condensation particle counter and wind turbulence was measured by radome. Additionally basic meteorological parameters and aerosol size distribution from 10 nm to 50 µm were measured. Measurements showed that Aitken mode aerosols dominated the total number concentration. The most likely high number (~1500 particles cm-3) of particles originated from ship emissions. Measured fluxes were dominated by vertical dilution and horizontal non-homogeneity in aerosol concentration. Case study of one flight is analyzed in more detail. Eddy correlation measurements were verified comparing EC measured and bulk derived sensible heat fluxes and using fast-transform-Fourier analysis. No sea spray emission dependence on horizontal wind speed was detected, possibly due to the fact that there were large numbers of emitted aerosol, and that this total flux was dominated by deposition and dilution-driven vertical transport. A plume was observed parallel to -122.2 longitude with consistent downward flux. It indicated that the plume was located aloft relative to the aircraft altitude.

8PI12

FILTER EXTRACTION OF ORGANIC TRACER COMPOUNDS: POSSIBILITIES AND LIMITATIONS. MICHAEL P HANNIGAN, Steven J Dutton, Gregory L Brinkman, Fatimah Matalkah, University of Colorado, Boulder, CO

Quantitative determination of the origin of ambient PM2.5 is a critical step in the development of air quality abatement strategies; after all, how can we reduce the urban ambient PM2.5 levels without a thorough understanding of where the PM2.5 is coming from? The need to reduce urban ambient PM2.5 levels stems from the knowledge that these particles are linked with adverse human health. The observed adverse effects are numerous and likely due to various types of PM2.5 exposure. Acute exposures are a primary focus, as noted by the possibility of a future reduction in the PM2.5 24-hr NAAQS. As such, quantitative determination of the origin of the ambient PM2.5--termed source apportionment--needs to be undertaken on a long, continuous time series of short-duration PM2.5 filter samples.

Effective source apportionment of ambient PM2.5 relies on the use of chemical components that are uniquely emitted by a specific source type (or emitted in a unique ratio). These unique compounds, termed tracers, can be trace metals or specific organic molecules. Organic tracers are very effective for apportioning combustion sources, as the combustion of a unique organic fuel creates unique organic molecules in the emissions. Due to limitations of the method detection limit and the resources needed for the analysis, organic tracers have not been used for source apportionment of a long time series of acute PM2.5 exposures. We are overcoming these method and resource limitations via two research tracks: (1) improvement of organic compound detection limit with the use of the Programmable Temperature Vaporization (PTV) inlet on the GC-MS, and (2) simplification of the filter extraction procedures. This presentation will focus on filter extraction procedures.

Quantification of organic tracers is typically done via GC-MS analysis of the filter extract. Numerous extraction solvents have been tried with varying degrees of success. Choice of solvent can be optimized for the analytical goals. For this work, we are tying to push the detection limits for specific compounds while reducing the resources required to do each analysis. We will present OC extraction efficiency and organic tracer reproducibility results for two solvents (dichloromethane and methanol), used individually and combined at ratio that forms an azeotrope. Both ambient and source filter samples were analyzed. Quantification procedures and tracer analysis limitation will be discussed.

8PI13

VOLATILITY AND CHEMICAL CHARACTERISTICS OF PM IN THE PROXIMITY OF A LIGHT-DUTY VEHICLE FREEWAY. THOMAS KUHN, Subhasis Biswas, Philip M. Fine, Michael Geller, Constantinos Sioutas, Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA

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.

8PI14

REGIONAL-SCALE MEASUREMENTS OF SMOKE-IMPACTED HAZE IN CALIFORNIA, OREGON AND WASHINGTON. GAVIN MCMEEKING, Sonia Kreidenweis, Jacqueline Carrillo, Jeffrey Collett, Jr., Colorado State University, Fort Collins, CO; Melissa Lunden, Lawrence Berkeley National Laboratory, Berkeley, CA; Derek Day, William Malm, National Park Service

Observations of aerosol physical, chemical and optical properties made in 38 locations in Washington, Oregon and California are presented to show the strong and regional-scale influence of wildfire smoke during the summer of 2002. Aerosol measurements made during an intensive field campaign conducted in July, August and September 2002 in Yosemite National Park indicated that smoke-impacted aerosols were present at the park during frequent haze episodes. Backward trajectory analyses showed that meteorological conditions during the study were dominated by transport from western and southern Oregon, a region which saw a high amount of fire activity during the summer of 2002. Yosemite NP observations were compared to data in California, Oregon and Washington from the IMPROVE aerosol monitoring network, sun photometer data from the San Joaquin Valley of California and aerosol measurements conducted at a remote Sierra Nevada monitoring site located just west of Lake Tahoe. Aerosol size distributions, scattering coefficients, carbon composition and ultra-violet light absorption show similar trends during the study period at many of these sites, suggesting that locations were affected by several regional-scale smoke-impacted events.

8PI15

REACTIONS OF OXYGENATED VOCS IN UT/LS AEROSOLS: LABORATORY STUDIES. LAURA T. IRACI and Rebecca R. Michelsen, Atmospheric Chemistry and Dynamics Branch, NASA Ames Research Center, Moffett Field, CA; Mads P. Sulbaek Andersen, also at Department of Chemistry, University of Copenhagen, Denmark

Several experimental studies have indicated that particle acidity catalyzes growth via condensed-phase reactions of organic species. However, a fundamental understanding of the key processes involved in the incorporation of organic material into sulfate particles is lacking. Measured solubility of the most abundant trace gases in the upper troposphere and lower stratosphere (UT/LS) does not account for the amount of organic material observed in UT/LS sulfate particles, suggesting that reactive processes are likely to generate condensed-phase organic material. Yet no reaction leading to significant accumulation of organic matter in the UT/LS has been documented.

Results of laboratory experiments will be presented for three classes of reactions which may generate low-volatility oxygenated products in acidic aerosol particles at low temperatures: aldol condensation between two aldehydes, polymerization of hydrated aldehydes, and hemiacetal formation from an aldehyde and an alcohol. In particular, the chemical behavior of formaldehyde, acetaldehyde, and propanal will be investigated. Dependence on temperature and acidity will be discussed, and implications for formation of high molecular weight organics via aerosol reactive processing will be explored.

8PI16

REAL TIME MEASUREMENT OF SILT LOADING OF PAVED ROADS IN SEOUL AND INCHEON, KOREA. SEHYUN HAN, Ki-Won Jang, Young Min Son and Yongwon Jung, Department of Environmental Engineering, Inha University, Incheon, Korea; Ji-Hyung Hong, National Institute of Environmental Research, Korea

Re-suspended dust from paved roads in Seoul and Incheon metropolitan area is one of the major PM10 sources in these areas, according to the recent emission estimates using the emission factors compiled in AP-42. It is well known that the AP -42 model for estimating PM10 emissions from paved roads requires information on silt loadings of particular paved roads along with the average weight of the motor vehicles in tons. The preliminary measurements using the conventional “vacuum swept method” clearly showed that silt loading of a specific paved road in the Incheon area varies with time and locations. Also, it was very dangerous for researchers to implement the conventional method to collect silt samples in the middle of paved roads. These drawbacks in the use of conventional method led us to develop a moving vehicle system capable of doing real time measurements of silt loading of paved roads, thereby we could get higher resolution silt loading data both in terms of time and space without too much human efforts and danger.
In this study, for the real time measurement of silt loading of paved roads, the principle used in the TRAKER method was employed and the entire sampling systems including data acquisition system were designed for this purpose and mounted on a Hyundai SUV.

From the results of real time measurements, temporal and spatial variations of silt loading data together with the existence of hot spots were observed for paved roads in Seoul and Incheon. These data will be discussed together with other useful data for analysis of fugitive dusts due to resuspension of silt deposited on paved roads in Seoul and Incheon.

8PI17

THE MAIN PRINCIPLES OF SEMI-EMPIRICAL THEORY OF STOCHASTIC CONDENSATION OF WATER VAPOUR IN THE ATMOSPHERE. OLEG SKRYNYK, Volodymyr Voloshchuk, Ukrainian Hudrometeorological Research Institute

The approximation of the semi-empirical K-theory for analysis of diffusive processes in turbulent atmosphere most frequently is used. In this case there is no opportunity to consider dynamics of processes, when space-time scales are less or comparable with appropriate scales of turbulent fluctuations of environment. The approximation of the K-theory becomes especially critical when considered phase transfers of water vapour are in turbulent mole (the problem of stochastic condensation), because under usual conditions in the troposphere of the Earth a characteristic time of condensation and evaporation of water droplets under vertical turbulent movements as a rule does not exceed a characteristic time of Lagrange scale of fluctuations of air (to). The solving of the problem of stochastic condensation had been obtained by Mazin, Sedunov, Voloshchuk and Stepanov on basis of phenomenological considerations. However represents interest to carry out the solution on a basis of deeper analysis, using models of turbulent transport which take into account parameter to.

We suppose that for solving this problem can be used two-parametric model of vertical turbulent diffusion of gas-aerosol impurity worked out by us The processes with time scales that is comparable with time Lagrange scale can be taken directly in this model. The two-parametric model is based on the assumption that turbulent diffusion of gas-aerosol impurity may be described with adequate accuracy by the Fokker-Plank's equation in phase space {r, v}, where r is radius-vector of aerosol particle and v is its random velocity. In work on basis of this idea earlier unknown equations of stochastic condensation of water vapour in the turbulent atmosphere are obtained. These equations are transformed to the known phenomenological equations of stochastic condensation by Levin-Sedunov-Voloshchuk, when assumptions of the semi-empirical K-theory are fulfilled.

Some special cases of stochastic condensation of various gases in atmospheres of planets of Solar system are considered on the basis of the obtained equations.

8PI18

CHEMICAL SPECIATION OF PARTICLE-PHASE POLYCYCLIC AROMATIC HYDROCARBONS IN MUMBAI,INDIA. RASHMI S PATIL CESE ,IIT Bombay, Mumbai,India S K Sahu and G G Pandit EAD,BARC,Mumbai, India

The high concentration of particulate matter in Indian cities presently is causing concern. The airborne particulate matter (PM) in urban atmosphere may be a complex mixture of inorganic and organic substances, and their origin can be either natural or anthropogenic, or both. Among the organic compounds of anthropogenic origin, the polycyclic aromatic hydrocarbons (PAHs) make up a significant group, because of their impact on human health and on the chemistry of troposphere. It is therefore important to measure the concentration of PAHs in particulates so as to assess their effects and possible sources. In the present study particulate matter samples consisting of PM10 and PM2.5 have been collected and analysed for particle-phase PAHs at an urban site of Mumbai, India.

PM10 and PM2.5 samples were collected using a high volume respirable dust sampler and a fine particulate sampler respectively. Sampling was done for 24 hours period at a height of 8 meters from the ground level for one year. The characterization and quantification of different PAH were carried out using a Shimadzu HPLC system (LC-10 AD) with UV-visible detector. Before analysis the filter paper samples were extracted ultrasonically for forty minutes with 50 ml of hexane as solvent. Sixteen different PAH compounds were analysed with the help of HPLC using isocratic method. A strict regime of quality control and quality assurance was followed. Meteorological parameters like wind,temperature and humidity were also measured simultaneously.

The mass concentration of the PM10 was found to be in the range of 53.5 µg/m3 to 138.4 µg/m3 whereas the PM2.5 fraction was found to have mass concentration ranging between 32.7 µg/m3 and 64.0 µg/m3 A good correlation has been observed between PM2.5 and PM10. The total PAHs level in PM10 samples ranged from 6.18 ng/m3 to 63.12 ng/m3 and the mean concentration was 28.76 ng/m3. In PM2.5 samples the total PAHs level ranged from 5.21 ng/m3 to 51.71 ng/m3 and the mean concentration was 21.30 ng/m3. It was found that 74% of the total PAH was associated with PM2.5. The lower molecular weight PAH such as naphthalene, acenaphthylene and fluorine were found to be dominant at the sampling site. Also, higher concentration of benzo(ghi)perylene was observed in both PM10 and PM2.5, which indicates significant contribution from vehicular exhaust.The diurnal variation of PAHs as well as their correlation with meteorological parameters have been analysed.

8PI19

CHAMBER STUDIES OF SECONDARY ORGANIC AEROSOL FORMATION FROM THE PHOTOOXIDATION OF BIOGENIC COMPOUNDS. NGA LEE NG, Jesse H. Kroll, Roya Bahreini, Melita D. Keywood, Richard C. Flagan, John H. Seinfeld, California Institute of Technology, Pasadena, CA; Anita Lee, Allen H. Goldstein, University of California at Berkeley, Berkeley, CA

Biogenic hydrocarbons emitted by vegetations are known to be important secondary organic aerosol (SOA) precursors. In this study, the aerosol forming potential from the photooxidation of a series of biogenic compounds (9 monoterpenes, 4 sesquiterpenes and 3 oxygenated species) as well as the gas-phase oxidation products are examined. Experiments are carried out in the Caltech indoor, dual 28m3 Teflon smog chambers, with T=20 -22oC and RH controlled at about 50%. Ammonium sulfate seed is first added to the chambers, which is followed by addition of hydrocarbons and HONO (as an OH precursor). Reaction is initiated by irradiation of the chambers with UV lights. Aerosol growth is monitored by differential mobility analyzers (DMAs) and an aerosol mass spectrometer (AMS) is used to characterize the aerosols formed. A proton transfer reaction mass spectrometer (PTR-MS) is also employed to monitor the time evolution of the parent hydrocarbon and different gas-phase products. A wide range of SOA yields is observed, with sesquiterpenes showing yields as high as 70%. The SOA yields from these photooxidation experiments are compared to results from our earlier studies of SOA formation from the ozonolysis of the same suite of compounds. Comparison of aerosol growth and hydrocarbon reacted as a function of time indicates that the oxidation of first generation reaction products also contributes to aerosol growth, and PTR-MS measurements allow for the monitoring of the evolution of such gas-phase products. The correlation between gas-phase and aerosol-phase nitrate with total aerosol growth is examined and the relationship between hydrocarbon structure and aerosol yield is discussed.

8PI20

SECONDARY SULFATE PM2.5 IN THE GREAT SMOKY MOUNTAINS AREA. EUGENE KIM, Philip K. Hopke, Clarkson University, Potsdam, NY

In recent source apportionment studies analyzing ambient PM2.5 (particulate matter less than 2.5 µm in aerodynamic diameter) compositional data sets of 24-hour integrated samples collected at Atlanta, GA, Washington, DC, Brigantine, NJ, and Bondville, IL, two or three different types of secondary sulfate aerosols were identified: summer-high, winter-high, and carbon-rich. PM2.5 carbon in the analyzed data 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, the Great Smoky Mountains area was distinguished by potential source contribution function analyses as one of the possible source areas of secondary sulfate.

The objective of this study is to identify different types of secondary sulfate aerosols in the Great Smoky Mountains area and estimate their contributions and possible source areas. In the present study, positive matrix factorization (PMF) was applied to an PM2.5 compositional data set collected at the IMPROVE monitoring site in the Great Smoky Mountains, TN. PMF identified eight sources including three types of secondary sulfates. The average contribution of three secondary sulfates to the PM2.5 concentration (8.5 µg/m3) is lower than those resolved in Atlanta (9.3 µg/m3) and Washington, DC (10.6 µg/ m3) studies. However, carbon-rich secondary sulfate accounts for 22 % of the secondary sulfate contribution, which is higher than other studies (Atlanta: 11 %; Washington, DC: 18 %).

8PI21

HETEROGENEOUS NUCLEATION OF ICE BY MINERAL DUST PARTICLES. DANIEL A. KNOPF, University of British Columbia, Vancouver, BC, Thomas Koop, University of Bielefeld, Bielefeld, Germany

Aerosol particles may induce the formation of clouds by acting as cloud condensation nuclei or ice nuclei (IN) and, therefore, may contribute significantly to the indirect aerosol effect. The formation of ice cirrus clouds may be initiated by heterogeneous nucleation of ice due to preexisting aerosol particles. Recently, the NASA-CRYSTALFACE campaign has shown that mineral dust particles emerging from the Saharan desert can act as efficient heterogeneous ice nuclei. We employed a new experimental technique to investigate the ability of mineral dust particles, effloresced (NH4)2SO4/H2O-particles containing mineral dust particles, pure solid (NH4)2SO4/H2O-particles, and H2SO4-coated mineral dust particles to act as IN.

The experimental setup allows us to control the temperature of the particles between 190-300 K and to adjust the relative humidity (RH) between 0 % and 100 % with respect to water. Supersaturations with respect to ice can be achieved in a controlled way. The instrument is calibrated by observing known phase transitions and melting points of various substances such as water or ammonium sulfate. The phase changes of the aerosol particles are observed by optical microscopy and Raman spectroscopy.

The experiments show that the investigated particle systems are very efficient IN, inducing ice formation between 100-115 % RH with respect to ice in a temperature range of 200-250 K. Below 240 K only deposition mode freezing is observed, i. e. the formation of ice directly from the gas phase. These results show that deposition mode freezing can induce ice formation at RH values 30 % lower than immersion mode freezing as observed by previous studies in which the nucleation of ice in a supercooled aqueous solution was initiated by a nucleus suspended in the solution.

Also, the effect of preactivation of mineral dust particles is observed. In this case the nucleation of ice is facilitated if the particle was previously involved in ice nucleation. Mineral dust particles in the preactivated state nucleate ice at RH 10-30 % lower compared to the non-preactivated ones.

The presented experimental results suggest that deposition mode freezing may be the dominant ice nucleation pathway for temperatures below 240 K for the particle systems studied here.

8PI22

SEASONAL VARIATIONS OF TROPOSPHERIC OZONE OVER SAJAN MOUNTAIN RIDGE (SIBERIA, RUSSIA). VLADIMIR POTEMKIN, Limnological Institute, Irkutsk, Russia

Study of minor atmospheric constituents like ozone provides an important information for modeling and prediction of future state of the earth climate system. Ozone is also of interest from the biological viewpoint due to its high toxicity and chemical activity. The issue of the tropospheric ozone still does not go beyond the scope of urban problems. In contrast to the stratospheric ozone, ground ozone concentrations increase at a rate of 1% per year. We analyze variations of total and ground ozone concentrations over Sayan Ridge. This report presents experimental data on long-term variations of total ozone concentration in the atmosphere and variations of ground ozone concentration over Sayan region.

We discuss the seasonal and diurnal variations of ground ozone. It is found that the ground ozone maximum is delayed (by 42 days, on average, with a correlation coefficient of 0.8) with respect to the maximum of total ozone, consistent with Petsold theory on vertical ozone motion, stating that the rate of ozone settling from the stratosphere is less than 1 cm/s.

8PI23

SEMI-CONTINUOUS MEASUREMENTS OF WATER-SOLUBLE ORGANIC CARBON IN THE TOKYO METROPOLITAN AREA. YUZO MIYAZAKI, Yutaka Kondo, Yuichi Komazaki, Nobuyuki Takegawa, Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan; Rodney J. Weber, Georgia Institute of Technology, Atlanta, GA

On-line measurements of water-soluble organic carbon (WSOC) were made near the urban center of Tokyo in January and August 2004. Ambient PM1 particles were continuously collected using a particle-into-liquid sampler (PILS), followed by on-line quantification of the WSOC every 6 mins using a Total Organic Carbon (TOC) Analyzer. Semi-continuous measurements of organic carbon (OC) and elemental carbon (EC), based on the thermal/optical transmission method, and those of organic aerosols measured by an Aerodyne Aerosol Mass Spectrometer (AMS) were also made. The WSOC concentrations and WSOC/OC ratio have diurnal variations showing their peaks at 12-14 LT in summer and in the afternoon (14-18 LT) in winter. On average, WSOC/OC ratio was 0.15 in winter and 0.35 in summer. The difference in the winter and summer frequency distributions of the WSOC/OC ratio suggests there are different types of OC sources for the two seasons. The WSOC mass concentrations agreed with secondary organic aerosol (SOA) concentrations estimated by using the EC-tracer method to within ±30%. The measured WSOC was also compared with some representative m/z fragments that contribute to the total AMS organic mass loadings. For the two seasons, the WSOC mass concentrations showed a tight, positive correlation (r2=0.8-0.9) with the m/z=44 (CO2+) mass fragment, which is representative of oxygenated organics. By contrast, the WSOC mass concentrations were poorly correlated with the m/z=57 (r2=0.25), an alkyl chain fragment (C4H9+), indicative of primary organic aerosol (POA). These results indicate that the WSOC measured in this study can be used as a direct marker of SOA in near real-time.

8PI24

NEAR-REALTIME MEASUREMENTS OF SPATIAL DISTRIBUTION OF AMBIENT AEROSOL IN WILMINGTON, DELAWARE. YILIN MA, Nitin Goel, Andrey Khlystov, Duke University, Durham, NC.

We report on-line measurements of spatial distribution of PM2.5 water-soluble chromium species, aerosol number size distribution, and gas-phase formaldehyde in Wilmington, DE as part of the Enhanced Delaware Air Toxics Assessment Study. A set of automated instruments is installed on a mini-van mobile laboratory and measurements are performed while driving through the city. The data set provides high time resolution temporal and spatial distribution and variation of target species, which helps better understanding of the relationships between exposure to the air toxics and the associated health risks.

An automated real time instrument has been developed for this study to measure ambient water-soluble chromium species (Cr (III) and Cr (VI)) using long path-length absorbance spectroscopy. After ambient aerosol is collected by the Steam-Jet Aerosol Collector, the collected liquid containing dissolved aerosol species is transported to the reactor for absorption measurement with a spectrometer. Cr (VI) is determined in one channel while the sum of Cr (III) and Cr (VI) is measured in the other. The Cr (III) concentration is determined as the difference between the two channels.

8PI25

MASS TRANSFER EFFECTS IN HYGROSCOPIC MEASUREMENTS OF AEROSOL PARTICLES.

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Hygroscopicity of aerosol affect many atmospheric processes such as the absorption and scattering of solar radiation, heterogeneous reactions between gas molecules and particles, and cloud condensation nuclei activity. The tandem differential mobility analyzer (TDMA) has been widely utilized to measure the hygroscopicity of laboratory-generated and atmospheric submicrometer particles. An important concern in investigating the hygroscopicity of the particles is if the particles have attained equilibrium state in the measurements. We discuss the mass transfer effects in hygroscopicity measurements.

In most TDMA studies, a residence time in the order of seconds is used for humidification (or dehumidification). Sodium chloride and ammonium sulfate particles are usually used to verify the equilibrium measurements during this residence time, which is presumed to be sufficient for other particles. There have been observations that not all types of submicrometer particles, including atmospheric particles, attain their equilibrium sizes within this time scale. We recommend that experimentation with different residence times be conducted and that the residence time should be explicitly stated in future TDMA measurements. We also point out that mass transfer effects may also complicate measurements in other types of aerosol flow-through systems that have residence times on the order of seconds for humidification (or dehumidification) (e.g., RH controlled nephelometry, ambient-dry aerosol size spectrometer, and aerosol flow tube–FTIR system) and for the activation of particles to form clouds under supersaturated conditions.

8PI26

SENSITIVITY OF CCN NUMBER TO TEMPORAL VARIABILITY OF AEROSOL SIZE DISTRIBUTION AND CHEMICAL COMPOSITION ESTIMATED USING HIGHLY TIME-RESOLVED DATA.

NITIN GOEL, Heidi Holder, Andrey Khlystov, Duke University, Durham, NC

The first aerosol indirect effect suggests that increased concentrations of atmospheric aerosol result in higher concentrations of cloud condensation nuclei (CCN) and higher cloud droplet concentrations, which lead to increased cloud reflectivity and the cooling effect on climate. The aerosol indirect effect remains one of the largest uncertainties in anthropogenic climate forcing. The number of CCN depends on the size distribution of the aerosol, its chemical composition and the maximum supersaturation in the cloud. Given the complexity of the problem, the aerosol effect on clouds is usually modeled using a few "representative" size distributions and chemical composition. The actual atmospheric aerosol, however, is highly variable in time even at one location. The effect of temporal variability of aerosol size distribution and its chemical composition on the CCN concentration was estimated using highly time resolved chemical composition and size distribution data collected during the Pittsburgh Air Quality Study (PAQS). The CCN concentration was estimated for a range of supersaturations relevant for the indirect effect studies (0.05% - 0.5%). A sensitivity analysis was performed to assess the sensitivity of CCN concentration to changes in aerosol chemical composition and the maximum supersaturation. The sensitivity of the estimated cloud reflectivity to these changes was examined. The potential effect of new particles formation events (nucleation) on the CCN number was also investigated.

8PI27

NUMERICAL STUDY FOR EFFECTS OF WIND ON AEROSOL SAMPLERS. KYOUNG SOO LIM, Young Ok Park, Fossil Energy & Environment Department, Korea Institute of Energy Research , Daejeon, South Korea, Kyoo Won Lee, Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, South Korea

A numerical simulation was conducted to determine the fluid flow and particle trajectory of aerosol sampler such as impactor and cyclone. In addition, the evaluation of the aerosol samplers was studied under a variety of wind velocities, ranging from 0 km/hr to 24 km/hr, to effect of the wind stream on the sampling efficiency during the aerosol sampling.

The numerical simulations yielded sampling efficiency and flow field that were in good agreement with the experimental data. As wind velocity increases, the turbulence flow was produced in front of aerosol samplers, and affects the flow field and sampling efficiency of the samplers

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8PI28

NUCLEATION AND GROWTH OF SECONDARY PARTICLES FORMED FROM A GASEOUS MIXTURE OF SO2/H2O/AIR BY ULTRA-VIOLET PHOTOREACTION. YOSHIKAZU KUGA, Toshiyuki Fujimoto, Kunika Hayashi, Tubasa Endoh, Takayuki Judo, Muroran Institute of Technology, Muroran, Japan

Atmospheric pollutional gases including SO2, NO2, and NO are oxidized with O2 and H2O to form H2SO4 and HNO3 molecules by UV irradiation from sunshine, and convert to the secondary particles. The investigation of the nucleation and growth of photo-produced secondary particles in the nanometer-sized range is very important to understand the mechanism on the formation of acid rain at an early stage. In this study, we experimentally investigated the UV photoreaction with use of the batch cell and the subsequent particle formation and growth with use of the flow cell experimental system.

The photo-induced reaction of gaseous mixtures of SO2/H2O/air in the cross-shaped cell attached with CaF2 windows was experimentally performed by measuring the change of their UV absorbance with use of a UV spectrophotometer. The mixture of the gases was irradiated by UV light with approximately uniform beam. The photo-dissociation reaction of SO2 in the gaseous mixtures was experimentally expressed as the 1st order reaction of SO2 concentration.

The size distributions of photo-produced particles in the flow reactor were determined by the in-line monitoring system, which consists of a low pressure differential mobility analyzer (LPDMA), electrical chargers, a Faraday cup electrometer, and a rotary pump. The total pressure and SO2 concentration were 550 Torr and 10 ppm, respectively, and H2O concentration was varied from 500 to 20000 ppm (1.16—46.4Rh%). Although the concentration of the produced particles clearly increased with the increase in H2O concentration, the particle size ranged from 5 nm to 100 nm slightly varied with the H2O concentration. The kinetic investigations of the atmospheric photoreaction and the mechanism of the subsequent particle nucleation and growth, are now under way with the detailed simulations.

8PI29

ORGANIC AEROSOL CHEMICAL SPECIATION USING SOFT IONIZATION METHODS IN AN AEROSOL MASS SPECTROMETER. Megan Northway, Achim Trimborn, John Jayne, Timothy Onasch, Manjula Canagaratna, and DOUGLAS WORSNOP, Aerodyne Research, Inc., Billerica, MA; Darin Toohey and Jose Jimenez, University of Colorado, Boulder, CO

Recent field campaigns have demonstrated that atmospheric aerosols, in particular organic aerosols, are complex mixtures of many compounds. The Aerodyne Aerosol Mass Spectrometer (AMS) has become a widely used and accepted tool for determining aerosol size distributions and chemical composition for non-refractory inorganic and organic aerosol. The current version of the AMS uses a combination of flash thermal vaporization and 70 eV electron impact (EI) ionization. EI is advantageous because it is a universally utilized and quantitative technique; however, for organic compounds the fragmentation caused by 70 eV electrons is extensive. Hence, EI mass spectra of organic aerosols are difficult to convolute because they are composites of the overlapping fragmentation patterns of all species present. Previous AMS studies have been limited to classifying organics in broad categories such as “oxidized” and “hydrocarbon-like”. Here, we present efforts to gain more information about organic aerosol composition by employing soft ionization techniques such vacuum ultraviolet (VUV) ionization, lithium ion attachment, and negative ion mass spectrometry in an AMS. The VUV source used is a low-pressure krypton lamp (emission at ~120 nm) powered by a radio-frequency discharge. This lamp is placed in direct proximity of the ionization region of the AMS, with only a window separating the lamp and the ionizer. The lithium source is a lithium oxide mixture that emits lithium ions directly into the ionization region of the AMS when heated (~1000 ºC). All of the designs allow for the alternation of the soft ionization technique with the standard electron impact ionization within the same instrument. Soft ionization spectra are compared with electron impact spectra for a number of different chemical compositions including oleic acid, polyaromatic hydrocarbons, long chain hydrocarbons, complex organic material (fulvic acids), diesel exhaust aerosol, and L.A. area aerosols. Much less fragmentation occurs with the soft ionization methods than EI ionization, and for many compounds the parent ion is the most dominant ion in the spectrum. This is particularly true when the temperature of the vaporizer is decreased, reducing thermal fragmentation of compounds. Future technical modifications for improvements to the sensitivity of the techniques and their potential for ambient measurements will be discussed.

8PI30

ESTIMATION OF SOURCE APPORTIONMENT OF PM2.5 USING THE PMF MODEL IN SAN FRANCISCO BAY AREA. INJO HWANG, Jong Hoon Lee, and Philip K. Hopke, Clarkson University, Center for Air Resources Engineering and Science and Department of Chemical Engineering, Potsdam, NY

In order to maintain and manage ambient air quality, it is necessary to identify sources and to apportion the ambient particulate matter mass. PMF (positive matrix factorization) model has been developed and widely used in receptor modeling research. This study used the data from EPA’s Speciation Trends Networks (STN). PM2.5 samples were collected in the San Francisco Bay area (San Jose-4th Street and San Jose-Jackson Street) from February 2000 to May 2002 and from October 2002 to November 2003. The samples were collected on Teflon, nylon, and quartz filters for elements, ions, and carbon analyses by a SASS (Spiral Aerosol Speciation Samplers) sampling system. A total of 54 chemical species were obtained using X-ray fluorescence (XRF), ion chromatography (IC), and thermal optical transmittance (TOT) method.

The objective of this study was to estimate the PM2.5 composition at these sampling sites by surveying concentration trends after analyzing the mass concentration of PM2.5 samples and the elements, ions, and carbon in PM2.5. PMF was applied to identify the existing sources and apportionment of the PM mass to each source. In particular, the particular emphasis of this analysis was to examine the impact of ship emissions. Conditional probability function (CPF) was applied to identify the point source relative to the wind directions.

Acknowledgment
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8PI31

SUBMICRON AEROSOL SIZE DISTRIBUTION MEASUREMENTS IN THE CITY OF SEOUL, AND COASTAL AND MARINE ENVIRONMENTS OVER SOUTH KOREA.

Seong Soo Yum, Jong-Hwan Kim, Kyungsup Choi, Yonsei University, Seoul, Korea Sung-Nam Oh, Jae-Cheol Nam, Korea Meteorological Adminstration, Seoul, Korea

Submicron aerosol size distributions and total particle (i.e., condensation nuclei, CN) concentrations were measured continuously from September 2004 at the campus of Yonsei University located at the central part of Seoul. The instruments, TSI SMPS-3936L10 and CPC-3010, were installed at an office in the sixth floor of a building and the sample air was drawn from a window. The height of the building and the relatively low traffic in the campus may qualify these measurements as a background aerosol distribution in a highly urbanized city. The highest monthly average total concentration was 37000 cm-3 in February 2005. The trend of wintertime increase was also obvious in the SMPS integrated concentrations but these were only 60-70% of the CPC concentrations. There was rather clear diurnal trend of near dawn (~4 AM) minima and morning peak (~8 AM) and a secondary peak in the evening (~8 PM). As a part of the Atmospheric Brown Clouds East Asian Regional Experiment (ABC-EAREX2005), measurements were also made on board the research vessel Kisang 2000 during the cruise from March 2 to March 10, 2005 over the South Sea of Korea and over the Korean sector of the Yellow Sea. Ship track was 60 km or more away from the coast. After the ship measurements the instruments were placed at the Gosan ABC Observatory, Jeju Island, for three weeks starting from March 11, 2005 to measure coastal aerosol distributions and inter-comparisons with other instruments. Preliminary analysis showed somewhat higher concentrations in the ship than in the coastal measurements: the average concentrations of 6700 cm-3 and 4400 cm-3 for the ship CPC and SMPS measurements, and 6000 cm-3 and 4000 cm-3 for the same two measurements at Gosan. However, when remote marine environments near Jeju Island were segregated from the ship measurements, the CPC and SMPS concentrations were 3600 cm-3 and 2400 cm-3, respectively. Further analysis will be presented in the conference. Focus will be on air mass characteristics of submicron aerosol size distributions in the marine environment of northeast Asia.

8PI32

MID-MORNING BEHAVIOR OF CONDENSATION NUCLEI AT A MOUNTAIN-TOP DURING THE WINTERTIME.

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Storm Peak Laboratory (SPL, 3210 m MSL) is at the crest of the Park Range in the northern Colorado Rocky Mountains, USA. During the wintertime, the Range and the surrounding valleys are snow-covered producing extremely stable boundary layers during storm-free periods. During these periods, mid-morning 3-nm and 10-nm condensation nucleus (CN) measurements often reveal two different patterns. The first pattern is the sudden appearance of 3-nm CN and, about 1-hour later, the sudden appearance of 10-nm CN (eg. 15 Jan 05). The second pattern is the nearly simultaneous appearance of both sizes of CN (eg. 19 Jan 05). The two patterns reflect the rates of nucleation and rates of advection from the valley below. The rate of nucleation dominated the rate of advection producing the first pattern while the rates were similar producing the second pattern. Meteorological measurements and numerical analyses with a meso-scale atmospheric model are underway to investigate the role of meteorology in the CN behavior.

8PI33

SAMPLING FROM HIGH-SPEED AIRCRAFT: NEW CORRELATIONS FOR ANISOKINETIC SAMPLING INLETS.

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A challenge in aerosol sampling is to collect particles that accurately reflect the airborne particles in concentration and size distribution. The aircraft operating conditions, inlet operation, the location of the sampler on the aircraft, the shape and size of both the sampler and aircraft all affect the inlet sampling characteristics. In our research, particle sampling characteristics of aircraft-inlets of varying dimensions and under different operating conditions is obtained using computational fluid dynamics (CFD) modeling. The particle trajectories are calculated and the aspiration efficiency of the sampler is determined in each case as a ratio of concentration of particles trapped into the sampler inlet to the free stream concentration. The effect of factors such as operating pressure, sampler wall thickness, length, tube inner diameter, sampling velocity and the presence of a blunt body behind the sampler, on the aspiration efficiency have been studied.

Aspiration efficiency for isokinetic sampling from high-speed aircraft deviates from unity for Stokes number < 10. The wall thickness of sampling inlets was seen to significant affect the inlet sampling characteristics in the Stokes number range of 0.1 -10. For Stokes number ~ 1, the aspiration efficiency for inlets with thick walls was seen to be lower than that for thin walls by ~ 30%. The presence of a blunt body downstream of the sampler can further alter the inlet characteristics in comparison with that of a thin walled inlet. The presence of a typical aircraft pod structure downstream of a particle sampling inlet can result in ~ 40% lower enhancements. The length of the sampler upstream of the blunt body also critically determines the inlet sampling efficiency. A new empirical model accounting for sampler and blunt body dimensions will be presented and compared with the existing correlations of Belyaev and Levin (1974). The correlations will be tested with published inlet characterization studies, such as that of Dhaniyala et al., 2004. The proposed model will be a critical tool for improved design and characterization of aircraft-based sampling inlets.

8PI34

DIURNAL VARIATIONS FOR VERTICAL PROFILES OF PARTICLE SIZE DISTRIBUTIONS.

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

The vertical profiles of particle size distributions were measured by optical single particle counter carried by balloon from surface to about 1500 m. The particle sizes measured by OPC were greater than 0.3 um and up to 10 um. The sampling frequency of OPC was 6 second each run and the sampling duration for each vertical profile was about 30 minutes. Therefore, vertical resolution for particle size distribution was about 10 m. In addition to the particle size distributions, the vertical profiles of ozone concentrations, the wind speed, wind directions, temperature, and relative humidity were measured simultaneously by ozonesonde and tendersonde, respectively. The particle concentrations were very uniform within the mixing layer at noon due to the effect of vertical mixing and those within the mixing layer were about two orders of magnitudes greater than those above the mixing layer. Therefore, most of the airborne particles were generated within the mixing layer locally. Significantly different diurnal variation patterns were observed for the vertical profiles for ozone and particle. For example, the ground ozone concentration depleted significantly at night due to the effects of NO titration and dry deposition. However, the ground particle concentrations might increase due to effects of temperature inversion and local emission. At about 600 m above ground, a depletion of ozone concentration was observed frequently due to the effect of NO titration, which was emitted from stationary plants. Within the plume, the particle concentrations generally increased, especially for submicron particles. The increments of particle concentrations in the morning were always later than those for ozone concentrations. Therefore, the formation of secondary aerosol was related to the photochemical reactions.

8PI35

PASSIVE AEROSOL SAMPLER FOR COARSE-MODE AEROSOL.

Darrell Sommerlatt, DAVID LEITH, Maryanne Boundy, University of North Carolina at Chapel Hill, Chapel Hill, NC

The Wagner-Leith passive aerosol sampler is small and inexpensive, but samples must be analyzed using a scanning electron microscope. Results of the analysis are used to determine the concentration and size distribution of sampled aerosol, and from these data PM10 and PM2.5 can be found.

The objective of this study was to adapt this passive sampler to the task of characterizing exposure to coarse-mode aerosols. Here, the passive samplers used glass collection substrates and particles were examined using an optical microscope. Digital images were taken and analyzed using ImageJ, software available free from an NIH website. The advantage of this arrangement is that sample analysis is fast and inexpensive; the disadvantage is that submicrometer particles cannot be measured reliably due to the limitations of optical microscopy. If the primary interest is coarse mode aerosol, the particles of interest are large enough that this limitation is not relevant.

Collocated PM10, PM2.5, and replicate passive samplers operated for periods of five, ten, and 15 days at an outdoor site. Coarse-mode aerosol concentrations were taken as the difference between simultaneous measurements with active PM10 and PM2.5 samplers. These active, coarse-mode concentrations were then compared with concentrations determined with the passive samplers. Active sampler results were consistently higher than passive sampler results, but the passive results had good precision. A correction factor can be used to bring results of the active and passive samplers into agreement. These findings suggest that passive aerosol samplers can be used to measure the concentration of coarse-mode aerosol, and that sample analyses can be done quickly and relatively inexpensively.

8PI36

A SYSTEMATIC STUDY OF LIGHT-ABSORBING PRODUCT FORMATION IN SULFURIC ACID AEROSOLS.

BARBARA NOZIERE, Williams Esteve, University of Miami / RSMAS, FL

We recently reported that some reactions of trace organic compounds in sulfuric acid aerosols produce compounds absorbing light in the near UV and Visible. We report here systematic laboratory studies of these processes: the effect of temperature (between 250 and 310 K) and acid composition (20 – 96 wt. % H_2SO_4) on the rate of formation of the products of acetaldehyde has been measured. The absorption cross-section of one of these products, crotonaldehyde, has been measured, as well as its lifetime in term of the decomposition processes that could take place in aerosols (in particular photodecomposition). Finally, the absorption indices of the products of other reactions (propionaldehyde, trifluoro acetone, acetone + acetaldehyde ...) have been measured over 200 – 1100 nm. The results from this study give a good estimate of the extent of these processes in atmospheric aerosols.

8PI37

ABSORPTION COEFFICIENTS OF CARBONACEOUS AEROSOLS AT HIGH RELATIVE HUMIDITIES UTILIZING AN OPTICAL EXTINCTION CELL (OEC). SCOTT MEYERS, Tami C. Bond, University of Illinois Urbana-Champaign, Urbana, IL

In order to determine whether carbonaceous aerosols warm or cool climate, their optical properties must be known for use in models. These properties include scattering coefficient and absorption coefficient. They have been extensively studied at low relative humidities, but how light absorption changes at high relative humidities, which frequently occur in the atmosphere, is unknown.

Modeling studies have shown changes in aerosol absorption coefficient due to changes in relative humidity (Redemann et al., 2004) , but these results have not been experimentally verified. Filter-wetting problems prevent measuring absorption coefficients at high relative humidities in many filter-based absorption measurement devices. An optical extinction cell (OEC) can be used to experimentally determine the effect of changes in relative humidity on absorption coefficient (Virkkula et al., 2005). The OEC can be used in series with a nephelometer, which measures scattering coefficient, to determine the absorption coefficient by subtraction. A three wavelength OEC was constructed, calibrated, and used to measure various biomass smokes at different relative humidities. The OEC will also be used to examine the wavelength dependence of absorption coefficient and differences in this dependency based on combustion conditions. The change in absorption coefficient with change in relative humidity will be presented.

8PI38

THE MERCURY DISTRIBUTION IN AMBIENT AIR, THROUGHFALL, WET DEPOSITION, AND SOILS. HYUN-DEOK CHOI, Thomas M. Holsen, Timothy Sharac, Soon-Onn Lai, Clarkson University, 8 Clarkson Ave., Potsdam, NY 13699

This study is the part of an NSF sponsored bio-complexity project investigating the inputs and cycling of Hg in the Adirondacks. This study includes the collection and analysis of both elemental and reactive gaseous mercury in ambient air, throughfall, and wet deposition samples. Elemental Hg, reactive gaseous Hg (RGM), and particulate mercury in ambient air are measured continuously using an automatic mercury analyzer.). This system allows fully automated, unattended operation with all three components being measured concurrently. The range concentrations of elemental Hg, RGM, and particulate Hg in ambient air are 1~2 ng/m3, 0.3~0.8 pg/m3, and 0~1 pg/m3, respectively. Three MIC-B wet deposition collectors are used for collecting throughfall and wet deposition. Precipitation is collected and the total mercury concentration in unfiltered rain water is measured by Tekran 2600. The Hg concentrations of throughfall samples are always higher than that of wet deposition samples because throughfall includes wet deposition and dry deposition. The gaseous mercury emission flux from soils is also measured using a dynamic flux chamber (DFC) consisting of polycarbonate. The flux chamber consists of an inlet part, a cylindrical body, and outlet part. Both inlet and outlet parts are connected to a Tekran mercury analyzer alternately using valve units. To make sure the factors such as flushing flow rate, time, and the size and number of the flux chamber inlet and outlet port, laboratory tests were performed under controlled indoor condition. Using the results of this study, the transport of mercury species from ambient air to soils and from soils to air will be quantified.

8PI39

PMF SOURCE APPORTIONMENT FOR PM2.5 IN FLORIDA AND MISSISSIPPI. Wei Liu, Yuhang Wang, Armistead Russell, Georgia Institute of Technology, Atlanta, GA; Eric S. Edgerton, Atmospheric Research and Analysis, Inc., Durham, NC.

ABSTRACT: Positive matrix factorization (PMF) was used to infer the sources of PM2.5 observed at four SEARCH 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. Spatial correlations of factors were investigated using the coefficient of determination (R2) calculated from the resolved G factors. Trace gases (CO, SO2, NOy) and particulate carbon fractions from TOR thermograms are used in the PMF analysis to improve factor identification. The factors resolved from this study and a previous study at Alabama and Florida (Liu et al., 2005) are compared to find the north–south changes over the Southeast. The 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 associated ammonium with a seasonal maximum in winter; (3) soil/crustals represented by Al, Ca, Fe, K, Si and Ti; and (4) wood smoke with high concentrations of EC, OC and K. An interesting disparity between the north and south sections of the Southeast will be discussed. Most of the disparity is attributed to the difference of regional primary aerosol sources.

8PI40

AMBIENT AEROSOL CHARACTERIZATION IN OXFORD, OHIO AND COMPARISON WITH THE GREATER CINCINNATI AREA. Bart Wojas, CATHERINE ALMQUIST, Paper Science and Engineering Department, Miami University, Oxford, OH

This study involves air monitoring for and characterization of ambient aerosols, or particulate matter (PM), in Oxford, Ohio. The Hamilton County Department of Environmental Services (HCDOES) is responsible for the monitoring of PM in the Greater Cincinnati area, which consists of four counties: Hamilton, Butler, Warren and Clermont; Oxford is located in the northwest corner of Butler county and the Greater Cincinnati region. The region is currently not in compliance with PM2.5 National Ambient Air Quality Standards (NAAQS) (15 ug/m3); it has an annual average PM2.5 concentration of 17.1 ug/m3. Therefore, the objective of this study was to answer two questions:

1) Will Oxford, Ohio, which is considered rural, be in compliance for PM2.5?
2) Will the addition of Oxford, Ohio to the regional PM2.5 monitoring network make a difference in the region's average annual PM2.5 concentration?
3) What are the sources of PM 2.5 particulate impacting the Oxford, Ohio site?
4) What particle constituents are generated locally versus transported to the area by prevailing winds?

The implications of these questions relate to the regional contribution to PM2.5. Since Oxford, Ohio is generally upwind of Cincinnati during daylight hours, the ambient aerosols in Oxford, Ohio represent those carried into the region rather than those generated within the region. Characterization of the ambient aerosols for particle size distribution, metals, and organic/inorganic carbon also helped us to suggest types of PM sources most affecting air quality in Oxford, Ohio.

8PI41

BINARY H_2SO_4-H_2O HOMOGENEOUS NUCLEATION BASED ON KINETIC QUASI-UNARY NUCLEATION MODEL: LOOK-UP TABLES. FANGQUN YU, State University of New York at Albany, Albany, NY

Gaseous H2SO4 and H2O have very low vapor pressure over the binary H2SO4-H2O solution and many observations indicate that most of the nucleation events observed in the atmosphere involve these two precursors. In the past half century, the classical binary H2SO4-H2O homogeneous nucleation theory has been continuously developed and improved. However, the comparisons between theories and experimental results are still not completely satisfying. Recently we showed that the binary homogeneous nucleation of H2SO4-H2O can be treated as quasi-unary nucleation of H2SO4 in equilibrium with H2O vapor and developed a kinetic H2SO4-H2O nucleation model (Yu, 2005). The kinetic quasi-unary nucleation model, which simulates cluster distributions kinetically and implicitly considers the effect of cluster hydration, is fundamentally different from the classical BHN model which assumes statistical equilibrium cluster distributions and includes the effect of monomer hydration only. The kinetic quasi-unary nucleation model gives a better agreement with recent experimental BHN results.

In this presentation, we illustrate the dependence of kinetically based H2SO4-H2O homogeneous nucleation rates on key parameters (i.e., sulfuric acid vapor concentration [H2SO4], relative humidity RH, and temperature T) and discuss under what conditions in the atmosphere H2SO4-H2O homogeneous nucleation rates may become significant. The nucleation rates look-up tables derived from quasi-unary nucleation model, which can be readily used to find the nucleation rates at a given conditions, are presented. The look-up tables cover all possible ranges of key parameters that can be found in the ambient atmosphere, in the laboratory studies, and in the exhaust plumes. The look-up tables can be easily included in multi-dimensional models to predict BHN rates with very little computing cost, and can also be used to analyze if certain observed nucleation rates can be explained by the BHN of H2SO4-H2O.

Reference: Yu, F. (2005), Quasi-unary homogeneous nucleation of H2SO4-H2O, J. Chem. Phys., 122, 074501.

8PI42

A RELATIVE RATES METHOD FOR EVALUATION OF ORGANIC AEROSOL AGING KINETICS. KARA E. HUFF HARTZ, Emily Weitkamp, Amy M. Sage, Allen R. Robinson, and Neil M. Donahue, Carnegie Mellon University, Pittsburgh, PA

Organic aerosols are processed by gas-phase oxidants in the atmosphere. Aerosol aging causes the physical and chemical properties of the organic fraction of atmospheric aerosol to change. As a consequence, the hygroscopic and cloud properties, gas-aerosol partitioning, and toxicity of organic aerosol are altered by aging. Furthermore, several chemical species commonly found in organic aerosol are used in source-receptor modeling, which assumes that the organic species are stable in the atmosphere. Our goal is to quantify the dynamics of aerosol aging.

The aerosol mixtures are prepared by atomization of the species of interest in organic solution. The aerosol consists of cosanes (pentacosane, hexacosane, and octacosane), alkanoic acids (palmitic, stearic, and nervonic acids), alkenoic acids (palmitoleic and oleic acids), dialkanoic acids (adipic and suberic acids), and sterols (cholesterol, beta-sitosterol, and campesterol). The solvent is removed by silica gel and activated carbon in diffusion tubes and the resulting aerosol is directed to a smog chamber. Gas-phase alkenes and alkanes are added so that the aerosol phase kinetics can be related to the gas-phase kinetics. Ozone is injected and the loss of gas-phase alkenes is monitored by gas chromatography with flame ionization detection. Aerosol samples are collected onto quartz fiber filters with a total mass 150-1000 micrograms. A mixture of deuterated species spiked onto the filters acts as an internal standard. The aerosol species are removed from the filter by solvent extraction and concentrated by solvent evaporation. The extract is dried using sodium sulfate. The carboxylic acid and alcohol moieties are converted to their trimethylsilyl derivatives using N,O-bis (trimethylsilyl)trifluoroacetamide with pyridine and trimethylchlorosilane catalysts. The sample is injected into a gas chromatograph for separation and mass spectrometer for detection and quantification. The precision of this method is 3% -17%. The mass recovery based on this method is estimated to be 60-85

We use this method to monitor the heterogeneous oxidation of an aerosol mixture of fourteen organic species. We find the rate of ozonolysis of organics, in order of decreasing rate constant is alkenoic acids > sterols> alkanoic acids ~ dialkanoic acids > cosanes. Binary aerosol mixtures of palmitic acid and oleic acid in different mass proportions are used to show the dependence of the processing rate on the mass composition of the aerosol.

8PI43

THE EFFECT OF AMMONIA ON NEW PARTICLE FORMATION: A KINETIC H2SO4-H2O-NH3 NUCLEATION MODEL CONSTRAINED BY LABORATORY MEASUREMENTS. FANGQUN YU, State University of New York at Albany, ALbany, NY

A clear understanding of the nucleation mechanisms is important to understand the lifecycle of atmospheric particles and to provide reliable predictions of climate change associated with aerosols. Based on the classical ternary homogeneous nucleation (THN) theory developed in recent years, the presence of ppt level NH3 concentration significantly enhances the nucleation rates. Here we compare the predicted NH3 enhancement with that derived from several reported experiments. We find that the differences between results predicted and observed are extremely large. Compared to the binary homogeneous nucleation of H2SO4-H2O (no NH3), the classical THN theory predicts a more than 30 orders of magnitude enhancement in the nucleation rates at the presence of ppt level NH3 while the laboratory measurements show only one to two orders of magnitude enhancement at the presence of NH3 range from several ppt to several ppm. Furthermore, the classical THN theory predicts a decrease in nucleation rates as RH increases but the measurements indicate an opposite trend.

Since experimental results are probably more reliable than the theoretical model, we develop a kinetic THN model so that the nucleation enhancement effect of NH3 derived from the experimental results can be included. The kinetic model assumes that H2SO4 is the principal specie dominating the cluster growth and nucleation while H2O and NH3 are secondary species influencing the cluster compositions and hence the evaporation coefficient of H2SO4 from the clusters. The kinetic model is a new approach to simulate THN and it can take into account the thermodynamic data of molecular clusters derived from density functional theory study and pre-nucleation cluster measurements. The preliminary simulations using the kinetic THN model constrained by the experimental results indicate a negligible contribution of THN to new particle formation in the boundary atmosphere. Our analysis suggests that the kinetic THN model is unlikely to under-predict too much the real ternary nucleation rates as long as there is no significant error in the experimental results. The implication of this finding and areas for further investigations are discussed.

8PI44

ESTIMATES OF AQUEOUS-PHASE SULFATE PRODUCTION FROM TANDEM DIFFERENTIAL MOBILITY ANALYSIS. JOSHUA SANTARPIA, Don Collins, Texas A&M University, College Station, TX; Dean Hegg, Kathleen Crahan, David Covert, University of Washington, Seattle, WA; Haflidi Jonsson, Gintautas Buzorius, Center for Interdisciplinary Remotely Piloted Aircraft Studies, Marina, CA

During June and July of 2004 airborne measurements of size-resolved aerosol properties were made over the coastal Pacific near Marina, California. Tandem Differential Mobility Analysis was used to determine the hygroscopic properties of these aerosols and, subsequently, to examine the change in soluble mass after the aerosol had been cloud processed. Three of the eight cases analyzed during the field campaign exhibited increased soluble mass attributable to cloud-processing. The calculated change in soluble mass after cloud-processing, derived from measurements made below and above cloud, ranged from 0.66 micrograms m^-3 to 1.40 micrograms m^-3. These values are in agreement with those determined using data collected during previous field studies in the same region. Aerosol size distributions measured throughout the study with a Passive Cavity Aerosol Spectrometer Probe were averaged to create a single representative distribution, which was used to examine the impact of the addition of sulfate to a typical aerosol measured during this project. Mass light-scattering efficiencies were calculated for both the initial and cloud-processed size distributions using Mie-Lorenz theory. These calculations show that the increase in mass light-scattering efficiency following passage through a single non-precipitating cloud is between 6% and 14%, which is in good agreement with findings of previous studies in the same region.

8PI45

THE NIST-EPA INTERAGENCY AGREEMENT ON MEASUREMENTS AND STANDARDS FOR AEROSOL CARBON: SAMPLING REGIONAL PM2.5 FOR THE CHEMOMETRIC OPTIMIZATION OF THERMAL-OPTICAL ANALYSIS.

JOSEPH M. CONNY, Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD; Gary Norris, National Exposure Research Laboratory, U.S. EPA, Research Triangle Park, NC.

In 2003, NIST and the U.S. EPA entered an agreement to measure and develop standards for carbonaceous species in ambient PM. One of the tasks specified in this ongoing agreement is to use chemometric methods to determine the extent that thermal-optical analysis (TOA) for elemental carbon (EC) might need to be variously optimized for ambient samples with predominant influences from different sources. While different TOA temperature protocols for different sample types is perhaps impractical, a chemometric assessment of protocol variation for different sample types will allow us to establish robust error limits on EC if one protocol is chosen for all samples.

Urban ambient PM2.5 was collected in three locations at different times of the year to represent regionally and seasonally distinct samples. Samples from Atlanta during July 2004 were expected to have a relatively large secondary organic aerosol (SOA) component. Samples collected near downtown Los Angeles in November 2004 were expected to have vehicle emissions as the only significant source of particulate carbon. Samples from a residential neighborhood of Seattle during February 2005 were expected to have a relatively substantial contribution from residential woodburning. Laser signal patterns and relative EC measurements from thermal-optical transmission (TOT) analyses using a test protocol suggest that the samples do exhibit the intended sources.

We sought three levels of total carbon loading at each site. Targets for the lowest level were selected such that EC might approach the TOT or thermal-optical reflectance (TOR) detection limit, particularly for the SOA- and wood-smoke-influenced samples. Targets for the highest carbon level (Level 3) were chosen to assess the instrument's laser response to OC charring and to carbon oxidation as the instrument establishes the split point. Level 3 samples from downtown LA are expected to attenuate the initial TOT or TOR laser signal such that there might be an insufficient laser response to charring. The OC in Level 3 samples from Atlanta and Seattle is expected to pyrolyze extensively such that char at this level might behave different optically than it would for the lower carbon levels.

A robust sampling protocol increased the likelihood of approximating target carbon levels and minimizing confounding effects such as changing weather. Three replicate sample suites were collected, each a randomized block of the three carbon levels. Additional within-suite replication allows for an assessment of weather effects. The preliminary test sample from each site confirmed sampling durations or prompted their modification.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

8PI47

ACCOUNTING FOR REACTIVITY USING THE CHEMICAL MASS BALANCE TOOL: METHOD DEVELOPMENT AND APPLICATION TO SOURCE RESOLUTION OF VOLATILE ORGANIC COMPOUNDS IN HOUSTON TEXAS.

ANN WITTIG, CUNY City College of New York, New York, NY; David Allen, University of Texas, Austin, TX

The ability of the Chemical Mass Balance (CMB) tool to resolve sources of reactive pollutants was assessed using simulated ambient concentrations of volatile organic compounds (VOC) typical of Southeast Texas. While this work focused on reactive gases, its findings are also relevant to source resolution of reactive aerosol components using CMB. Simulated concentrations were determined using a multistage photochemical box model which drew from the state's official gridded emission inventory of mobile and industrial sources, and used simplified reaction, convection, and dispersion schemes to describe the decay, transport and dispersion of the emissions en route to receptor sites.

This paper reports on a subset of nearly 1800 cases performed to explore the impact of reasonable uncertainties in four key assumptions implicit in the CMB formulation. These assumptions are: a) all major sources are known; and for each of these major sources, b) a single fitting species exists, which is both unique to the source and inert; c) a source profile is available and reasonably describes the distribution of pollutants in the fresh emission; and d) this source profile adequately represents the source after it has been released and photochemical reaction in the ambient air has non-uniformly distorted it. The first three assumptions were investigated by omitting or adding key sources, by varying the fitting species made available to CMB, or by using source profiles generated in one area to describe sources in another. To test the last assumption, fresh emissions profiles were supplemented with photochemically aged source profiles.

CMB model performance was assessed by comparing its source contribution estimates (SCEs) to actual emissions input to the photochemical box model. Accurate cases were those for which all of the sources were identified and assigned SCEs that were within 30% of the actual contribution. If all of the key sources were not identified or erroneous sources were assigned SCEs greater than 5%, the case was considered to be inaccurate. When typical uncertainties were introduced into the model inputs, CMB was not able to consistently allocate sources of reactive compounds: percent inaccuracy was 12% and 48% of the cases either did not converge to a solution or had performance parameters outside of acceptable ranges. When reactivity was incorporated into the model using aged source profiles, the percent inaccuracy decreased to 4% and the percent of cases that did not converge or had poor performance parameters decreased to 42%. Most of these trends were more pronounced for mobile sources than for the industrial sources.

8PI48

ESTIMATION OF MERCURY LOADINGS TO LAKE ONTARIO IN LAKE ONTARIO ATMOSPHERIC DEPOSITION STUDY (LOADS).

SOON-ONN Lai, Thomas M. Holsen, Clarkson University, Potsdam, NY; Young-Ji Han, Kangwon National University, Korea

The atmospheric mercury (Hg) loadings to Lake Ontario were estimated in the Lake Ontario Air Deposition Study (LOADS) between April 2002 and March 2003. Mechanisms of wet deposition, air-water exchange and particle dry deposition of Hg were incorporated into a total deposition model. The transfer velocities for elemental mercury (Hg0) (which was assumed to be equivalent to total gaseous mercury (TGM, defined as the sum of Hg0 ad RGM) and reactive gaseous mercury (RGM), and the dry deposition velocities for particulate mercury (Hg(p)) were modeled using meteorological data. While TGM, RGM and Hg (p) and total Hg in precipitation were measured onboard the Lake Guardian, and at two land-based sites (Sterling, NY and Point Petre, ON), a constant value of dissolved gaseous mercury (DGM) concentration (15.74 pg L-1) was assumed in the study period. The effects of the Hg emissions from different regions near Lake Ontario were investigated by using four scenarios that varyiedthe contribution percentages of Sterling, Point Petre and the urban area around the western part of the lake.. Minimum, average and maximum Hg loadings were provided to bracket the uncertainties in the models. The annual loadings of wet deposition, air-water exchange and particle dry deposition of Hg to Lake Ontario were estimated to be 170 (160 - 190) kg yr-1 (April 2002 - March 2003), -100 (-73 - -130) kg yr-1 (April 2002 - March 2003), 70 (64 - 77) kg yr-1 (September 2002 – August 2003), and 25 (17 - 34) kg yr-1 (September 2002 – August 2003). Assuming similar seasonal variations of RGM and Hg(p) in 2002 and 2003, the net Hg loading to Lake Ontario was 170 (110 – 230) kg yr-1 on average between April 2002 and March 2003. The modeled wet deposition and Hg0 emission fluxes were the largest in summer, whereas the modeled dry deposition fluxes of RGM and Hg(p) were smallest in winter. These results could be explained by seasonal variations in Hg concentrations, and meteorological parameters. The results of Hg0 emission flux and RGM deposition flux calculated with intensive cruise data indicated the importance of the sources with high TGM and RGM concentrations in the estimate of Hg loadings. The sensitivity analysis revealed that this deposition model is most sensitive to the variations in air temperature, wind speed, DGM concentration, RGM concentration and RGM transfer velocity.

8PI49

DIRECT DRY DEPOSITION MEASUREMENTS OF MERCURY (HG) WITH WATER.

SOON-ONN LAI, Thomas M. Holsen, Timothy J. Sharac, Clarkson University, Potsdam, NY

Direct dry deposition measurements of mercury are lacking due to the meteorological conditions, deposited surface characteristics and the existence of mercury in gaseous and particulate phases. Therefore, the objectives of this study are to develop and evaluate two new measurement techniques for Hg dry deposition, and to compare direct and indirect methods (i.e. a total deposition model incorporating mechanisms of air-water exchange of elemental mercury (Hg0) and reactive gaseous mercury (RGM) and dry deposition of Hg(p)). One surrogate surface was a 15 cm-diameter Petri dish filled with Milli-Q water, HCl solution or acidic halide salts (e.g. NaCl and NaBr) fitted inside a static water surface sampler (SWSS) which consists of an acrylic plate with a sharp leading edge of attack to reduce air turbulence. Samples were analyzed with a cold vapor atomic fluorescence spectrometry (CVAFS; Tekran Series 2600 Mercury Analysis System). The evasion of Hg into the atmosphere was evident when Milli-Q water was used, but 0.08 M HCl solution was able to stabilize the Hg. When different solutions were used in a laminar hood, the Hg dry deposition fluxes measured with 0.25 – 0.5 M NaCl and NaBr in 0.08 M were generally similar to those using 0.08 M HCl, and the smallest dry deposition flux was measured with Milli-Q water. In addition, the Hg dry deposition flux increased with HCl molarity. The modeled dry deposition fluxes were approximately 46% of those measured with HCl solution. The daytime fluxes were usually higher than the nighttime fluxes probably due to a larger particle deposition velocity and gas transfer velocity, and higher Hg(0) and Hg(p) concentrations. There was no significant artifact found (loss or gain) when 24 h and 12 h samples were compared. A specially designed filter holder with glass, quartz or gold filters will also be tested. The filter holder is mounted inside a knife-edge surface sampler (KSS) design similarily as the SWSS. Theoretically, glass and quartz fiber filters collect Hg(p), whereas the gold filter collects Hg0, RGM and Hg(p). However, glass and quartz fiber filters coated with KCl solution are assumed to collect Hg(p) and RGM. The glass fiber filters and quartz fiber/gold filters will be heated externally for 5 min at 500 oC and 900oC, respectively, in zero air or argon gas streams to convert all Hg species deposited onto the filters to the elemental form. The released Hg(0) will then be quantified with a Tekran Model 2537A.

8PI50

SHORT-TIME SCALE, SIZE-RESOLVED ELEMENT CONCENTRATIONS IN PHOENIX, AZ.

ANN M. DILLNER, University of California, Davis, CA, Martin M. Shafer, University of WIsconsin, Madison, WI

High concentrations of particulate matter have been shown to cause adverse health effects but the mechanisms are not well understood. Possible causes of adverse effects considered in this study are metal species concentrations, particulate size and high concentrations over time scales shorter than 24-hours. The later exposure mode has been poorly studied in an environmental context. Soil-related elements (e.g. Al, Mg, Ti), which are generally non-toxic and are larger than 1 micrometer in diameter, typically dominate the inorganic elemental components of ambient PM. However, some of the elemental concentrations, particularly in particles smaller than 1 micrometer, come from wide range of high-temperature sources and may be toxic. Time-series of element concentrations and size distributions of elements have been used to suggest specific anthropogenic sources of elements.

In this study, a method was developed to quantify size segregated elemental concentrations over short time scales. A Rupprecht and Patashnick Co., ChemVol sampler was used to collect 4-hour, size segregated samples in six size bins, particle diameters < 0.1, 0.1-0.5, 0.5 -1.0, 1.0-2.5, 2.5-10, > 10 micrometer. ICP-MS was used to determine the elemental concentrations of 29 elements. PUF and polypropylene substrates were sectioned in a trace metal clean laboratory under a HEPA hood. Typically 50 mg replicate sections were prepared - PUF masses greater than this resulted in over-pressurization of the microwave bombs. Substrates and associated PM were solubilized using a microwave-assisted acid digestion in micro-Teflon bombs. This procedure effected a total dissolution of both aerosol PM and substrate (the resulting solution is colorless with no trace of aerosol, PUF or polypropylene particulates). To minimize organic-loading to the microwave vessels, a 30-hour pre-digestion using nitric acid and peroxide was performed before bomb solubilization (hydrochloric and hydrofluoric acid completed the acid digestion mix). Element recoveries were monitored using a set 3 different NIST SRM's and spikes, and blanks evaluated with representative pre-cleaned substrates. A Thermo PQ-ExCell ICP-MS interfaced with a Cetac microconcentric desolvating nebulizer - the later provided an inert, clean, all Teflon introduction system, significantly reduced oxide and chloride interferences, and with an uptake rate of 100 µL/min., which allowed for micro-sample volumes. Reported element concentrations are method (PUF/polypropylene) blank corrected with uncertainties propagated.

Multiple uses for this data including studying short-time scales, characterizing the coarse fraction, identifying sources, and determining high abundances of potentially toxic elements in submicrometer particle sizes will be discussed. This method is a useful tool for studying the dynamic changes in a large suite of element concentrations over short-time (1-4 hours) scales.

8PI51

DENVER AEROSOL SOURCES AND HEALTH (DASH) STUDY PRELIMINARY RESULTS.

STEVEN J DUTTON, Fatimah Matalkah, Catherine A Vos, Shelly L Miller, Michael P Hannigan, University of Colorado, Boulder, CO; Sverre Vedal, University of Washington, Seattle, WA

Daily PM2.5 filter samples have been collected from a site in Denver, CO, since July, 2002 to support the Denver Aerosol Sources and Health (DASH) study. The goals of this study are to 1) obtain daily quantification of PM2.5 mass and chemistry including sulfate, nitrate, bulk elemental and organic carbon, trace metals and trace organic compounds, 2) use the mass and chemistry data as input into a source apportionment model to determine the major sources contributing to the PM2.5 in Denver and obtain a time-series for each and 3) determine if there is an association between the individual source contributions and adverse health effects including daily mortality, daily hospitalizations for cardiovascular and respiratory conditions, and measures of poor asthma control.

More than three years of daily quartz and Teflon filter pairs have been collected at this site with sampling still underway. Each Teflon sample has been analyzed for PM2.5 mass using a temperature and relative humidity controlled microbalance, and inorganic sulfate and nitrate using ion chromatography (IC). Each quartz sample has been analyzed for bulk elemental and organic carbon using thermal optical transmission (TOT). In addition, work has begun on the quantification of trace metals using inductively coupled plasma mass spectrometry (ICPMS), and speciated organic compounds using gas chromatography/ mass spectrometry (GC/MS). Up to date findings from these measurements will be presented along with some preliminary source apportionment work using Positive Matrix Factorization (PMF).

8PI52

ESTIMATION OF ORGANIC MASS TO ORGANIC CARBON RATIOS USING SOURCE APPORTIONMENT DATA. MIN-SUK BAE, James J. Schauer, Environmental Chemistry and Technology Program, University of Wisconsin-Madison, Madison, WI; Jay R. Turner, Chemical Engineering Department, Washington University, St. Louis, MO

Two independent methods are used to estimate the seasonality of the ratio of fine particulate organic matter (OM) to fine particulate organic carbon (OC) for atmospheric particulate matter collected at the St. Louis Midwest Supersite. The first method assumes that all of the fine particulate matter that cannot be attributed to sulfate ion, nitrate ion, ammonium ion, and metal oxides is organic matter. Using this method, 620 daily samples were used to estimate the annual average fine particulate matter OM/OC ratio to be 2.03 ± 0.02 with a summer average of 2.29 ± 0.04 and a winter average of 1.89 ± 0.03. The second approach to estimating fine particle OM/OC employed OC source apportionment results and estimates of source specific OM/OC, including primary sources and secondary organic aerosol. The OM/OC estimate that was based on 98 daily source apportionment calculations over a two year period yielded an annual average ratio of 1.87 with a summer average of 1.97 ± 0.09 and a winter average of 1.89 ± 0.12. A simple sensitivity analysis was used to determine the impact of the uncertainties of the estimated OM/OC ratios for primary sources and secondary organic aerosol. The results of the study provide a relatively stable annual average estimate of the OM/OC ratio for fine particulate matter in the St. Louis area. The source apportionment results indicate that the similar OM/OC ratio for St. Louis in the summer and winter results from a increased contribution of secondary organic aerosol in the summer months that is balanced by the higher woodsmoke in the winter. Although the estimated OM/OC ratios that were determined for St. Louis cannot be directly applied to other locations, the methodologies used to estimate OM/OC can be broadly applied given the necessary data for these calculations.

8PI53

MARKET SOLUTIONS TO HETEROGENEITY IN SO2 DAMAGES AND ABATEMENT COSTS. VLADIMIR HLASNY, Michigan State University

This paper evaluates the sensitivity of the net benefits of the SO2 regulation to the choice of the environmental policy in the US, when health damages from SO2 pollution vary across generators and pollution levels.

Five established types of environmental policy are compared in their effect on the aggregate health damages and abatement costs: emission caps, state-level pollution caps, emission tax, allowance trading, and exchange rates on the allowance trade. The electric industry and emissions model derives the emission levels in the trading equilibrium, and the health effects of the resultant ambient concentrations of SO2, when the marginal health damages vary across firms and regions, and increase in emissions. The critical values for the slope and curvature of the damage function are found at which alternative policies dominate the existing system of marketable allowances in the net benefits achieved.

A computable model of the electricity industry developed in this paper determines plants' production, participation in energy trade, SO2 emissions and SO2 abatement as functions of the regulatory policy. Firms' emission levels are constrained by the environmental regulation, and the trade of electricity is constrained by the pipeline capacity and the state regulation. Emission allowance market subject to endogenously given exchange rates clears simultaneously with the energy market. State regulator either allows free, competitive trade of electricity, or regulates utilities as natural monopolies with limited ability to trade. The model uses electricity generation and cost data for individual generators from the Energy Information Administration's and the Environmental Protection Agency's databases.

8PI54

A MICROWAVE PLASMA TORCH FOR THE STUDY OF ATMOSPHERIC AEROSOLS. STEPHEN MANG and Sergey Nizkorodov, University of California, Irvine

In order to simultaneously count particles and extract information about their chemical composition, it has traditionally been necessary to use mass spectrometric techniques. However, using a microwave plasma torch (MPT) as an excitation source for atomic emission spectrometry (AES), we have constructed a particle counting system that can also provide sensitive, specific chemical information with far less power, space and money required. Emission from single particles can be detected, and the wavelengths at which emission is seen is specific to the elements present in the particle. In the long term, the instrument will be made field-portable, so that it can be used in pollution and air quality monitoring applications, where real-time detection and characterization of atmospheric aerosol particles at low concentrations is desirable. The microwave plasma torch also has possible applications to mass spectrometry as an excitation source. Tests with the torch are ongoing; results from testing and characterizing the apparatus will be presented.

8PI55

COMPARISON OF CONTINUOUS SPECIATION MEASUREMENTS WITH AND WITHOUT A MANIFOLD INLET. Allen L. Williams, Michael Caughey, David Gay, Clyde Sweet Illinois State Water Survey Rahmat Ulla and Purnendu K Dasgupta, Texas Tech University

Continuous measurements of PM2.5 and gas composition taken with a gas-particle ion chromatographic sampling system with and without a sampling manifold are reported. In the sampling arrangement which included a sampling manifold, a 40 lpm air flow was drawn through a 3 meter length of 4” PVC tubing. The gas sample was then drawn from the center of the manifold through a 1/4” Teflon tube at a sampling rate of 5 lpm. In the alternative sampling arrangement without a manifold, a parallel plate denuder was placed in the free air stream adjacent to the manifold inlet and the sample was drawn into the denuder through a Teflon tube. Gas samples from both denuder arrangements were collected simultaneously over 30 minute time intervals. Over a portion of the monitoring period two other continuous gas particle ion chromatograph systems were operated simultaneously one with a similar manifold arrangement and the other in the free air stream. The gas samples were analyzed for nitric acid, sulfur dioxide, and ammonia. The effect of the manifold was noticeable in lowering the gas coincentration values by approximately 10% – 15 %. Differing manifold pumping strategies were employed to reduce the effect of fluctuations in wind speed that can destabilize the manifold flow.

8PI56

CRITICAL DESIGN VALUE AND AIR POLLUTION RISK PREDICTION. SHAO-HANG CHU, US EPA, RTP, NC

The critical design value concept developed by Chu (2000) has been proven to be a useful tool in the determination of the eligibility of States and Local environmental protection Agencies for a limited maintenance plan option for PM10. This is because it provides a good indictor of the likelihood of future violation of the National Ambient Air Quality Standards (NAAQS). Critical Design Value is a statistical prediction model based on the distribution of existing design values and their inter-annual variability in the past. It can also take into account in the prediction the effectiveness of existing control measures as reflected in the observed air pollutant concentration trend. In this paper 22 years (1982-2003) of 8-hour ozone design value data collected in the U.S. were studied. The critical design values for all available sites are calculated to identify potential high risk areas for future violation of 8-hour ozone standards. The model is evaluated through cross examinations by using the 1982-1991 data to predict the actual exceedance rate duraing the 1992-2003 period. The results showed that categorically the success of model prediction was above 85%. In this study, it demonstrates how critical design value model can be used as an air pollution risk prediction tool to identify potentially high risk areas for policy makers and environmental regulators to plan and prioritize regional emission control strategies.

8PI57

PM2.5 POLAR ORGANICS, POLYCYCLIC AROMATIC HYDROCARBONS, AND 14C MEASURED DURING THE 2003/2004 LIBBY, MONTANA WINTER. TONY WARD, The University of Montana, Missoula, MT; Lynn R. Rinehart, Desert Research Institute, Reno, NV; Todd Lange, The University of Arizona, Tucson, AZ

Except for parts of California, Libby, Montana is the only PM2.5 nonattainment area in the mid and western states. During the winter of 2003-2004, The University of Montana, Center for Environmental Health Sciences conducted a comprehensive analysis of the organics composing the fine fraction of particulate matter (PM2.5) in Libby. These data were collected to enhance a source apportionment program that identified residential wood combustion as the largest source of PM2.5 in the Libby airshed throughout the winter months. An existing Federal Reference Method PM2.5 sampler was fitted with a quartz filter to measure concentrations of polar organics every six days from November 11, 2003 through February 27, 2004. In addition, a high volume polyurethane foam sampler was installed at the Libby monitoring site to collect information on semi-volatile organic compounds (including phenolics and polycyclic aromatic hydrocarbons) associated with both the particle and vapor phases, as well as determine the concentrations of 14C in the airshed.

Results showed that levoglucosan, a well-known chemical marker for wood smoke, had the highest measured concentrations of any of the 95 polar organic compounds quantified from the fine fraction. In fact, levoglucosan accounted for over 15.5% of the measured organic carbon fraction. The semi-volatile organic compounds with the highest concentrations measured during the program were four phenolic compounds commonly found in wood smoke, including phenol, 2-methylphenol (o-cresol), 4-methylphenol (p-cresol), and 2,4-dimethylphenol. The results from the 14C analytical program indicate that a substantial fraction of the aerosol carbon (0.88 ± 0.005) comes from a modern carbon source. We further calculate that an average of 82% of the measured 14C results from a wood smoke source. These indicators support that residential wood combustion (wood stoves) is the major source of PM2.5 in Libby, Montana throughout the winter months.

8PI58

ISOTOPE RATIOS OF METALS IN AIRBORNE PARTICLES FROM SINGLE-PARTICLE LASER ABLATION MASS SPECTROMETRY.

PETER T.A. REILLY, William A. Harris, Renwu Zhang, William B. Whitten, Oak Ridge National Lab, Oak Ridge, TN

Isotopic ratios of elements in aerosols have typically been determined on bulk samples collected over a period of time. While standard isotope ratio mass spectrometry techniques have shown high accuracy for bulk samples, information about ratios in specific particle types is lost. The analysis of aerosols in real-time has been performed by single-particle laser ablation mass spectrometry. The aerosols used were laboratory-generated by nebulization followed by passage through a heater and condenser to remove solvent. Particles entered the mass spectrometer through a limiting orifice and pass through an aerodynamic lens system that collimates the particles into a tight beam for passage into the main vacuum chamber. Individual particles were sized by light scattering-based time-of-flight. The detected particles were irradiated with a focused laser when the particle reached the center of the ion trap. For the analysis of higher mass elements such as lead, the rf voltage on the ring electrode was set at a voltage where ions with masses below 150 m/z are unstable and immediately ejected. Scan speed (amu/ms) was decreased to increase isotopic separation.

Isotope ratios have been determined through laser ablation single-particle mass spectrometry. NIST standards, such as Montana Soil SRM 2710 and Urban Particulate Matter SRM 1648, were used as analytes since their composition has been well-documented. A Nd:YAG (266/532/1064 nm) is used as the ionization laser. A comparison between three different methods of laser ablation for the detection of isotopes will be discussed. The first uses standard laser fluences at 266 nm. Lead isotope ratios for lead from NIST soils demonstrated that the average isotope ratio with the standard deviation fell within the known ratio. The second employs collision-induced dissociation for the elimination of polyatomic interferences. The third utilizes high laser fluence at 532/1064 nm for the elimination of interferences. The effect of ionization fluence and wavelength on the isotope ratio will be presented. In addition, the variation of isotope ratios with particle origin will be described.

8PI59

THE EFFECTS OF CHEMICAL PROPERTIES ON TIME SCALES FOR EXPERIMENTS INVOLVING ORGANIC CONDENSATION ONTO PM.

SHING KONG, Lynn M. Hildemann, Stanford University, Stanford, CA

Research in organic aerosol growth using a TDMA is well established. In laboratory TDMA setups, however, it may be challenging to select an appropriate organic with which to conduct the TDMA experiments. When choosing an organic for TDMA work, emphasis is often placed on which organic family a compound comes from, or its presence in the atmosphere, or the historical use of the compound in other research publications. As equilibrium is the only state in which results from one experiment are comparable to results from another experiment, it is important to know what timescales are theoretically expected in order for the lab setup to be designed accordingly. Many TDMA setups have residence times on the order of 1 or 2 seconds. Our model suggests that, for most organic vapors, a significantly longer amount of time is necessary to achieve equilibrium.

A MATLAB model has been developed based on fundamental principles for heterogeneous condensation of organics onto transition-regime particles. Beginning with a single inert particle surrounded by a super-saturated organic vapor, condensation of the organic vapor onto the particle is modeled by the diffusion flux of the vapor to the particle. While this idealized model does not consider wall losses in an experimental system, it allows us to systematically examine the effect of each individual chemical property of an organic (e.g., molecular weight, density, surface tension) via a series of sensitivity analyses. We can also assess the importance of various experimental parameters in the lab setup, such as the particle concentration or the temperature used to achieve supersaturation. We are thus able to tease out the individual effect of each organic characteristic or experimental property on the timescales necessary to reach equilibrium.

Results show that the time necessary for condensation of organic vapor onto a particle typically ranges from tens of seconds to minutes. This suggests that TDMA data in the literature utilizing equilibration times of 1 to 2 seconds may not be at equilibrium. With this model, guidance can be provided to assist experimenters in the selection of appropriate organics for their particular TDMA particle growth experiments so that equilibrium is reached.

8PI60

SAMPLING CORRECTION FACTORS AND VIABLE VIRUS PARTICLE SIZE DISTRIBUTION MEASUREMENTS FOR ULTRAFINE AND SUBMICROMETER VIRUS AEROSOL PARTICLES. CHRISTOPHER J. HOGAN JR., Eric M. Kettleson, Myong-Hwa Lee, Bala Ramaswami, Largus T. Angenent, Pratim Biswas, Environmental Engineering Science, Washington University, St. Louis, MO.

The aerosolization and collection of submicrometer and ultrafine virus particles were studied with the objective of developing robust and accurate methodologies to study airborne viruses. The collection efficiencies of three sampling devices used to sample airborne biological particles, the All Glass Impinger 30, the SKC BioSampler®, and a frit bubbler, were evaluated for submicrometer and ultrafine virus particles. Test virus aerosol particles were produced by atomizing suspensions of single-stranded RNA (bacteriophage MS2) and double-stranded DNA (bacteriophage T3) viruses. Aerosol particle size distribution results show that the relative number concentration of viruses present in aqueous virus suspensions was extremely low compared to the concentration of small solutes in the suspension, i.e. virus presence or absence did not change the size distribution. None of the tested samplers were adequate in collecting submicrometer and ultrafine virus particles, with collection efficiencies for all samplers below 10% in the 30 -100nm size range at standard sampling flowrates. Furthermore, plaque assays and particle counting measurements show that all tested samplers have time varying virus particle collection efficiencies.

Despite low collection efficiencies, samplers which utilize liquid impingement have an advantage over filters in that most biological assays require samples to be stored in liquid media. To use such samplers properly, however, their low collection efficiencies and time varying performance characteristics must be taken into account. Correction factors were developed for the samplers in this study, taking into account the loss in virus viability and liquid volume within each sampler over time. A method to determine the size distribution function of viable virus containing particles utilizing differential mobility selection was also developed. To effectively determine airborne virus concentrations and applied dosages in respiratory challenges, the methods reported here must be used to determine sampler correction factors and viable virus particle size distributions.

8PI61

GENERATION AND MEASUREMENT OF PARTICLE SIZE DISTRIBUTION OF ECTROMELIA VIRUS AEROSOL. DIVEY SAINI, Mark Buller, St Louis University, St Louis, MO; Myonghwa Lee, Pratim Biswas, Washington University in St Louis, St Louis, MO

Due to the concern over potential for bioterrorism there is renewed interest in development of prophylactics and therapeutics to protect humans from respiratory tract infections with CDC/NIAID Category A infectious agents. Because these bio-agents do not normally circulate in the human population, efficacy testing of potential vaccines or anti-microbials must take place in animal models using respiratory challenges. Pulmonary exposures to infectious agents can best be modeled under experimental conditions by challenging with aerosols. These bio-agents can be aerosolized by different types of aerosol generators such as single or multi-jet atomizers, ultrasonic aerosol generator, spinning disk aerosol generator, electrospray aerosol generator, or vibrating orifice aerosol generator. A 1-jet atomizer, vibrating mesh aerosol generator, and electrospray aerosol generator were evaluated in this study to generate an aerosolized ectromelia virus. To predict the anatomical site of particle deposition in the respiratory tract, the particle size distribution of the aerosol was measured using a particle size measurement instrument (TSI: SMPS Model 3080). The real time instrument measured mobility equivalent particle size diameters of the aerosol. The results from the instrument were compared to that measured by using the SEM and TEM imaging instruments. The size of the ectromelia virus measured by microscopic measurements was 350-400 nm in length and 200 -300 nm in thickness. This was higher than that the mean size measured by the SMPS instrument. The difference in size is due to the formation of high number concentration of crystal particles from the buffer solution in which the virus particles were suspended. The geometric mean diameter of the aerosol from the ectromelia virus in tris buffer generated by the one-jet aerosol generator was measured to be 38 nm (GSD: 1.8). Also studied was the stability of ectromelia virus in the buffer solutions (tris, ammonium acetate) and DI water. Bio-aerosol sampling for size analysis was done using an electrostatic collection technique. Since the ectromelia virus has a delicate structure, direct high velocity impaction on to the TEM grid might cause damage to virus, therefore the electrostatic collection technique was used. This approach will help to evaluate the different generators used to aerosolize ectromelia virus. Aerosols with higher viability and optimum particle size distribution are necessary requirements for the development of the animal models to mimic human respiratory disease.

8PI62

A FIELD STUDY OF NEW PARTICLE FORMATION IN THE MIDWEST UNITED STATES. ALICIA KALAFUT, Charles Stanier, University of Iowa, Iowa City, IA Allen Williams, Illinois State Water Survey, University of Illinois, Champaign, IL

The creation of new atmospheric particles via nucleation is an important source of atmospheric particles and may influence climate by altering the aerosol size distribution. While there are many theories to describe the process of nucleation, there are still significant gaps in the knowledge of new particle formation. Due to this lack of knowledge, current models used to predict this phenomenon are inaccurate. This research will focus on measurements to better constrain new particle formation models based on the "ternary" ammonia-sulfuric acid-water system. We are particularly interested in quantifying (1) the role of ammonia in enhancing new particle formation rates and (2) the vertical structure of continental new particle formation. We have completed a preliminary field study to gage the suitability of rural Midwestern sites for studying these two processes.
New simulations of particle formation for central Illinois have been performed assuming ternary nucleation with a high sensitivity to NH3 concentrations (Napari, Noppel et al. 2002; Gaydos, Stanier et al. 2005). The simulations show that new particle formation should be frequent (due to high NH3 levels), but the growth of the particles should be limited due to relatively low SO2 levels (approximately 4 µg m-3 / 1.54 ppb). These preliminary simulations were tested during a 2 month field deployment at the Bondville Atmospheric Research Site near Urbana, Illinois. A mobile laboratory for studying atmospheric new particle formation was constructed and tested. Using this setup, several weeks of simultaneous SO2, NH3, particle count and particle size distribution measurements were monitored at a Midwest sampling location to gage the frequency, intensity and dependence of the nucleation events on NH3 levels.
Meteorology and aerosol chemistry data were monitored during the same period by colleagues.

Gaydos, T. M., C. O. Stanier, et al. (2005). \Modeling of in situ ultrafine atmospheric particle formation in the eastern United States.\ Journal Of Geophysical Research-Atmospheres 110(D7).
Napari, I., M. Noppel, et al. (2002). \Parametrization of ternary nucleation rates for H2SO4-NH3-H2O vapors.\ Journal Of Geophysical Research-Atmospheres 107(D19).

8PI63

FLOWRATES, CUTPOINTS, AND CONCENTRATIONS IN THE IMPROVE NETWORK. NICOLE HYSLOP, Warren White, Chuck McDade, University of California, Davis, CA

The Interagency Monitoring for Protected Visual Environments (IMPROVE) program utilizes PM2.5 samplers with passive flow control. The flowrate is passively controlled using critical orifices located downstream of the sample filter. Critical orifices are insensitive to downstream pressure changes but sensitive to upstream pressure changes. As the filter loading increases, the pressure drop across the filter increases, lowering the pressure upstream of the critical orifice, and thereby reducing the flowrate. The decrease in flowrate varies significantly among samples depending on the sample deposit area, the PM2.5 concentration, and the particle size distribution. These changes in flowrate result in changes in the particle-size cutpoint of the cyclone. Depending on the particle size distribution, the amount of particulate matter collected can change as a result of the shift in cyclone cutpoint.

The uncertainty of IMPROVE sample concentrations is increased by varying flowrates during sample collection, and this uncertainty must be considered in analyses of the IMPROVE data. The 24-hr average sample flowrates for each filter (nylon, quartz, and Teflon) are included in the IMPROVE database. In addition, new validation flags have recently been implemented to convey flowrate problems more succinctly and consistently. Three different validation flags are used to indicate flowrate problems in the IMPROVE dataset. Approximately 1% of filters/year are invalidated (concentrations replaced with missing values indicators) as a result of severe decreases in flowrate. Approximately 1 -4% of filters/year are flagged as clogging, which is defined as having the cutpoint rise above 4 um. A significant number of samples (4-10% of filters/year) is flagged as having a 24-hr average flowrate 7% below or above the nominal flowrate, which corresponds to a cutpoint above 3 or below 2 um, respectively.

Samples with severe flowrate problems are flagged as described above but even minor deviations from the nominal flowrate can affect the data quality. At the Mesa Verde site in Colorado, two collocated Teflon sample modules were operated for several months with filter cassettes having differing flow resistances. The flowrate in one of the collocated modules regularly decreased more during each 24-hr sampler period than the flowrate in the other module. These differences in flowrate resulted in differences in cutpoint and ultimately differences in the concentrations measured by the two modules. This paper documents the resulting differences in reported concentrations.

8PI64

SUSPENSION VELOCITY MODEL FOR LARGE PARTICLES ENTRAINED IN THE ATMOSPHERIC CIRCULATION PATTERN THAT INCLUDES INERTIAL EFFECTS.

Kenneth Noll, OBATOSIN ALUKO, Illinois Institute of Technology, Chicago, IL

Suspension velocities are provided for large particles entrained in the atmospheric circulation pattern. The transport and fate of large particles in the atmosphere depend in part on their inertial properties. Particles in the 10 to 100 micron size ranges are unique due to the importance of inertial properties relative to gravitational settling. Accurate models that include inertial effects for large particles after they have become entrained in the major circulation patterns of the atmosphere are important in understanding the transport and fate of airborne particles.

Experiments that focus on measurement of upward and downward large particle suspension velocities have been conducted for entrained atmospheric particles. These experiments were conducted in an urban area, removed from point sources of particles and at an elevation of 12 meters so that only particles well entrained in the atmosphere would be measured. These measurements are compared with theory and incorporated into a particle suspension model that includes the effects of both particle settling velocities due to gravity and vertical velocity fluctuations due to inertial effects and allows estimation of the effective suspension velocity of large particles for use in transport models. By adding the upward and downward inertial velocities to the gravitational settling velocity, effective upward and downward particle fluctuations result. The upward fluctuations will carry some large particles upward and promote their ability to remain suspended in the atmosphere. Application of the model demonstrates that at higher wind speeds upward and downward particle inertial velocities are comparable to gravitational settling velocities for particles in the 15-30 micron size range and this allows entrained particles of this size to be transported great distances. Model results for even larger particles (30-100 microns) that are characteristics of source area wind erosion do not have large upward velocities are therefore short lived and are not capable of being transported over large distances.

The mass-size distribution of atmospheric large particles has also been measured and was correlated with the upward and downward flux of particles. The peak in the mass-size distribution was observed to vary between 15 and 30 microns diameter with larger sizes related to higher wind speeds. The peak concentration in the mass-size distribution corresponded to the particle size that had the maximum upward particle velocity. The general form of the mass-size distribution in many locations on the earth has been observed to be similar to the results reported here. The distributions possess a log-normal shape with a mode in the 10-30 micron range regardless of their origin. The reason for this similarity in shape may be due to the particle carrying capability of the atmosphere for entrained particles. Other large particle modes are only apparent near sources when the wind speed increases above the threshold value for erosion and these particles are not transported over large distances.

8PI65

QUANTIFYING PM2.5 SOURCE CONTRIBUTIONS DURING CALIFORNIA REGIONAL PM10/PM2.5 AIR QUALITY STUDY (CRPAQS) WITH RECEPTOR-BASED MODELS.

L.-W. Antony Chen, Judith C. Chow, John G. Watson, Desert Research Institute, Reno, NV, USA

The persistent high particulate concentrations in the San Joaquin Valley (SJV) and the associated environmental and health effects triggered the California Regional PM10/PM2.5 Air Quality Study (CRPAQS). This study integrated a comprehensive ambient sampling strategy, innovative sampling and analytical techniques, and updated source emission characterization to understand the origins of elevated PM10 and PM2.5 and to evaluate ways for remediation. Conventional receptor model approaches for PM source apportionment focus on single-site measurements which are usually in the span of a few to several years. The change of source characteristics over a long term poses a risk to the analyses. CRPAQS acquired 24-hour speciated PM2.5 measurements at 32 sites across central California within 14 months, with two thirds of them considered in the same airshed. Since these sites are likely influenced by the same source or source categories but at variable degrees, receptor models can be applied to the multiple site measurements that span a relatively short period of time.

Following the guidance of existing emission inventories and chemical source profiles for this region, seven to nine sources were recommended by two multi-variant receptor models, UNMIX and PMF. Commonly among them, by the order of significance, are secondary aerosol, residential wood combustion (RWC), motor vehicle exhaust (gasoline and diesel), dusts, agriculture emission, and sea salt. At the Fresno Supersite, the motor vehicle exhaust contributed to 40 – 50% of total carbon and 10 – 20% PM2.5 mass during non-winter seasons, while in winter these fractions became 15 – 20% and 5 – 10%, respectively. This is consistent with the increase of RWC and secondary aerosol contributions in winter. RWC contributed to 70 – 80% of total carbon and 35 – 45% of PM2.5 at Fresno in winter, consistent with the observation of high levoglucosan, a wood burning marker, in the urban air. These results are supported by the similarity between source profiles resolved by UNMIX and PMF. These profiles are compared with those from recent source tests, and the causes of discrepancies will be discussed.

8PI66

CLIMATE-AIR POLLUTION INTERACTIONS DURING SUMMER AND WINTER: A SENSITIVITY STUDY. JOHN P. DAWSON, Spyros N. Pandis, Peter J. Adams, Carnegie Mellon University, Pittsburgh, PA

High concentrations of fine particulate matter (PM2.5) and ozone (O3) are two major air pollution problems in the United States. The goal of this modeling study is to determine how concentrations of PM2.5 and ozone will respond to future changes in climate over the eastern United States and to determine the most important links between pollutant concentrations and meteorology. The sensitivities of PM2.5 and ozone concentrations to temperature, wind speed, absolute humidity, cloud liquid water content, precipitation, cloud cover, and mixing height are investigated. Sensitivities to boundary and initial conditions of the pollutants and their precursors are also examined. The scenarios simulations include a summertime period (July 2001) and a wintertime one (January 2002) with the modeling domain covering the Eastern United States. Sensitivities are determined by the systematic perturbation of meteorology from the base case values. Simulations were run using the Chemical Transport Model PMCAMx v. 4.0 (Gaydos et al., 2005), which incorporates the aerosol chemistry and physics modules developed at Carnegie Mellon University into the CAMx v. 4.02 chemical transport model of ENVIRON Corp. (ENVIRON, 2004).

Simulation results suggest that the effects of small changes in the meteorological parameters are complex in both space and time. Both average and peak summertime ozone concentrations increased nearly linearly with increasing temperature. This was mainly due to the chemistry of peroxyacetylnitrate (PAN) and its homologues. Average and peak summertime PM2.5 concentrations decreased rather linearly with increasing temperature, though different aerosol species had different responses to temperature change. Generally, ozone and PM2.5 concentrations decreased with increased wind speed due to the accelerated removal of pollutants. The seasonal differences of these responses and the relative magnitudes of the sensitivities to different meteorological variables are investigated. This study is part of a larger effort to determine how pollutant concentrations will respond to future changes in climate and emissions at both the global and regional scales.

ENVIRON (2004) User's guide to the Comprehensive Air Quality Model with extensions (CAMx), Version 4.02, ENVIRON Int. Corp., Novato, CA.

Gaydos T., R. Pinder, B. Koo, K. Fahey, G. Yarwood, and S. N. Pandis (2005) Development and application of a three-dimensional Chemical Transport Model, PMCAMx, Atmospheric Environment, submitted.

8PI68

BIOLOGICAL AND METAL AEROSOL SOURCE EMISSION RATES PRODUCED DURING LAND APPLICATION OF PROCESSED SEWAGE SLUDGE. TANIA PAEZ-RUBIO, Abel Ramarui, Jeffrey Sommer, Ronald Calhoun, Jordan Peccia, Arizona State University, Tempe, AZ

The flow regime of contemporary wastewater treatment plants requires a constant demand, market, or disposal method for the resultant sludge. Sewage sludge that has been stabilized to reduce the concentration of pathogens and indicator organisms, reduce odors, and reduce putrefaction potential is termed biosolids. Greater than seven million dry tons of biosolids are generated in the U.S. annually. Approximately 60% of biosolids are reused through application to agricultural land. Due to persistent, anecdotal health complaints from residents living near land application sites, the U.S. EPA sponsored a 2002 independent study by the National Research Council (NRC) on the management of biosolids land application. Under the topic of on-site and off-site exposure, the NRC report highlighted that exposure pathways such as inhalation were not adequately evaluated by the Part 503 rule and that the knowledge about pathogen transport and survival needed to link the potential for biosolids to cause on-site worker and off-site health impacts, was lacking. The purpose of this research was to determine the aerosol source emission rates of pathogens, pathogen indicators and metals that are emitted during biosolids land application and their incorporation into the soil through disking. The source emission rate is a required input for pathogen aerosol fate and transport models that predict an absolute concentration at a specified distance and ultimately the health risk. In addition to a suite of culture-based and molecular- based bioassays, real-time PM 10 monitors and LIDAR remote sensing was used to determine spatial concentration profiles of the aerosol source area.

Source emission rates for total microorganisms, sulfur-reducing clostridia, total coliforms, heterotrophic plate counts and, endotoxins were 1.3x109 total number of cells/s, 4.7x103 CFU/s, 2.5x103 CFU/s, 3.86x107 CFU/s and, 2.1x104 EU/s, respectively. All measurements were done immediately downwind from the biosolids spreader and concentrations were 2 to 3 order of magnitude higher than background. The origin of the bioaerosols was confirmed by comparative analysis of Clostridia spp. 16S rRNA sequences present in the biosolids and in the aerosols. A ratio between biosolids and bioaerosol total microorganisms, Clostridia spp., total coliforms and, heterotrophic plate count concentrations was found and can be used to predict pathogenic bioaerosol concentration as a function of pathogen concentration in biosolids. This novel method for estimating the source emission rate represents a fundamental improvement for measuring the fate and transport of pathogenic aerosols.

8PI69

OLIGOMER FORMATION IN SECONDARY ORGANIC AEROSOL DERIVED FROM THE PRIMARY PRODUCTS OF A-PINENE OZONOLYSIS.

KATHERINE J. HEATON; Michael Tolocka; Murray V. Johnston, University of Delaware, Newark, DE

The goal of this study is to determine how secondary organic aerosols are formed from primary products of α-pinene and what conditions affect their formation. Secondary organic aerosols (SOA) are known to cause environmental effects as well as health problems within the population. Several studies have shown oligomers to be significant components of SOA. The reaction of α-pinene, a biogenic SOA precursor, with ozone is one type of reaction that has been known to produce oligomeric SOA. It has previously determined that when α-pinene reacts with ozone, six primary products are formed including pinonaldehyde, pinonic acid, norpinonaldehyde, pinic acid, norpinonic acid, 10-hydroxypinonaldehyde, norpinic acid. These primary products further react to form SOA that contains oligomers. By studying the formation of oligomers from these precursors, we hope to provide insight into the mechanism of SOA formation.

This study focuses on three of the primary products of α-pinene ozonolysis: pinonaldehyde, pinonic acid and pinic acid. Secondary reactions of these primary products were performed in a 0.5 m3 reaction chamber to determine how ozone and acid seed affected SOA production. The SOA was collected on a filter and then extracted. The extracted products were analyzed using electrospray ionization with a quadrupole time of flight mass spectrometer. Preliminary results show that the primary products are able to form oligomers in the absence of α-pinene. Many oligomers observed in the reaction of α-pinene and ozone are also observed in the direct reaction of the primary products. It is also observed that the primary products do not require ozone and acid seed for the formation of some oligomers.

8PI70

THE CHEMICAL COMPOSITION OF FINE PARTICLES AND QUANTITATIVE RELATIONSHIP BETWEEN THE MASS CONCENTRATION AND METEOROLOGICAL CONDITION IN BEIJING.

JINGLI WANG, Institute of Urban Meteorology, CMA, Beijing, Xulin Liu, Beijing Meteorological Information and Network Center, Beijing, China

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. The results also showed that precipitation had great washout effect on mass concentration of fine particles, but the drizzle had some washout effects to remove fine particles. And the synoptic regime had relatively great influence upon the mass concentration of fine particles.

The monitor results showed that PM2.5 had higher concentration in summer and winter. In summer time, the PM2.5 may mainly come from secondary reaction that makes serious pollution at regional scale, while in winter AEBCMA at southern part of Beijing had much higher level of PM2.5 because of more coal burning in that area.

The chemical compositions of PM2.5 showed very similar pattern at different site in Beijing. The annual average chemical composition in 2001 at PKU and DS indicated that the organics and crustal elements at both sites were the largest contributors to the PM2.5 mass, sulfate and nitrate had also significant portion. The nearly identical chemical composition in figure 2 hinted that the PM2.5 pollution was a regional issue.

However, the chemical composition of PM2.5 seemed to change with season. Using the data measured at AEBCMA as an example, the major chemical species in PM2.5 showed different contribution to PM2.5 in summer, autumn and winter. Organics, sulfate and nitrate were main species in PM2.5, the organics (OC) was the largest contributor also, the ratios of OC/EC were 7 to 11, much larger than the critical value of 2, showing the existence of secondary pollution in Beijing.

8PI71

SEASONAL VARIABILITY IN THE OPTICAL PROPERTIES AT BIG BEND AND GUADALUPE MOUNTAINS NATIONAL PARKS. Christopher L. Allen, Don R. Collins, Texas A&M University, College Station, TX

The Reconstruction equation used to describe the impairment in visibility is identical for all Class I visibility areas. There is concern that the aerosol particles in Big Bend and Guadalupe Mountains National Parks may differ sufficiently from those for which the default values of the coefficients in the Reconstruction equation pertain to cause considerable error when relating current and projected class-resolved aerosol mass concentrations to the expected extinction coefficient. To understand this, two-week sampling periods during the spring, summer, and fall of 2003, and the winter of 2004 where conducted at Big Bend, while sampling in Guadalupe Mountains has been on going since April 2005 to describe the seasonal variability in both Class I locations. Submicron aerosol size distributions were measured using a differential mobility analyzer (DMA). An aerodynamic particle sizer (APS) was used at both sampling sites to measure the supermicron size distributions, for Big Bend it was only employed during the spring and summer sampling periods only. Size-resolved hygroscopic growth was measured using a tandem differential mobility analyzer (TDMA) both to improve the estimate of the f(RH) in the Reconstruction equation, and to constrain the aerosol composition. Additional measurements were done each day at both locations wherein the size-resolved aerosol was exposed to a varying RH or temperature, allowing us to conclude the aerosols deliquescence, efflorescence, and volatility properties. Implications concerning the differences between the calculated mass scattering efficiencies and the default values used by the IMPROVE (Interagency Monitoring of Protected Visual Environments) network will be presented.

8PI72

COMPARISON OF ACTIVE AND PASSIVE SAMPLERS FOR MONITORING AMBIENT AIR. ZHONG-MIN WANG, David Leith, University of North Carolina at Chapel Hill, Chapel Hill, NC

The passive aerosol sampler described by Wagner and Leith is a simple device about the size and weight of a dime that is used to monitor aerosol exposures. In this device, particles collect passively on a substrate and are later characterized by microscopy. In addition to particle concentration and size distribution, the passive sampler can evaluate particle morphology and composition when the analysis is done using an electron microscope with XRD.

The objectives of this study were: (1) to evaluate the effect of exposure time on the precision of passive sampler measurements, and (2) to compare results of passive and active samplers. Outdoor air was continuously drawn into a chamber that contained both active and passive samplers. A dichotomous sampler, a TEOM with WINS impactor, and an APS each sampled continuously through independent PM10 sampling heads; data from these instruments were then used to determine PM10, PM2.5, PM Coarse, and the size distribution of the aerosol in the chamber over time. Replicate passive samplers were exposed simultaneously for periods of one, three, seven, 14 and 21 days. Analyses of the passive samples were done using SEM, TEM, and optical microscopy.

Results of this study describe the time necessary to obtain a reliable passive sample and the level of agreement between passive samplers and active samplers at determining PM exposure. The ability of the passive sampler to determine particle size distributions is also discussed, along with its potential to assess exposure to ultrafine particles.

8PI73

EFFECT OF CONDENSABLE SPECIES ON SOOT PARTICLE MORPHOLOGY. JAY SLOWIK, Jeong-Ho Han, Jennifer Kolucki, Paul Davidovits, Boston College, Chestnut Hill, MA; Leah Williams, Timothy Onasch, John Jayne, Charles Kolb, Douglas Worsnop, Aerodyne Research, Inc., Billerica, MA

In a previous study, two types of soot particles distinguished by morphology and composition were produced from a propane flame depending on the fuel equivalence ratio (phi) (Slowik et al. 2004). For phi < 4.0 (low fuel/O2), the particles were irregular fractal agglomerates, composed mostly of black carbon (BC). For phi > 4.0 (high fuel/O2), compact, near-spherical particles consisting of approximately equal amounts of BC and polyaromatic hydrocarbons (PAHs) were produced. It was hypothesized that the differences in morphology between these two types of soot were due to the increased condensation of PAHs on the near-spherical soot compared to the fractal soot. Here we explore this proposed mechanism by investigating the effect of condensation and evaporation on the two soot types.

Soot particles were generated in an ethylene flame, size-selected by a Differential Mobility Analyzer (DMA), and passed through a reaction zone in which the particles are coated by either oleic acid (liquid) or anthracene (solid). Following the reaction zone, the particles can be heated to evaporate flame- or laboratory-generated coatings. The processed particles are analyzed by an Aerodyne Aerosol Mass Spectrometer (AMS) and a Scanning Mobility Particle Sizer (SMPS). The AMS quantitatively measures the mass spectrum of the non-refractory components of the particles and also provides the vacuum aerodynamic diameter. The DMA and the SMPS provide the mobility diameter of the unprocessed and processed particles, respectively. These measured quantities are used to determine the total particle composition, mass, density, dynamic shape factor, and fractal dimension.

Both fractal and near-spherical particles become spherical upon coating with oleic acid and near-spherical upon coating with anthracene. For particles of the same initial mobility diameter, the relationship between shape and volume is the same regardless of coating type or equivalence ratio. When the coating is subsequently removed, the final morphology of the particles depends on the amount and type of the deposited coating and on the composition of the original particle. For an oleic acid coating and phi = 2.05, the recovered particles are more spherical than the original particles. However, for anthracene coatings and higher equivalence ratios the original particle morphology is recovered. Further evaporation of flame-generated PAHs produces particles composed of more than 95% BC. The relationship between shape and volume of these particles is consistent with an increase in BC spherule size as the equivalence ratio increases.

These results suggest that both fractal and near-spherical soot particles may originate in the flame as fractal particles. The difference in their morphology is due to increased PAH content and increased BC spherule size in the near-spherical soot.

8PI74

STATUS OF THE IMPLEMENTATION OF THE DECOUPLED DIRECT METHOD FOR PARTICULATE MATTER IN A THREE-DIMENSIONAL AIR QUALITY MODEL. BONYOUNG KOO, Greg Yarwood, Gary Wilson, Ralph Morris, ENVIRON International Corporation, Novato, CA; Alan M. Dunker, General Motors R&D Center, Warren, MI

The Decoupled Direct Method (DDM) is a powerful and efficient sensitivity analysis tool to predict the response of air quality models to input data and model parameters. The DDM was previously implemented in the Comprehensive Air Quality Model with extensions (CAMx) for ozone sensitivity to emissions and initial and boundary concentrations (Dunker et al., 2002). This study extends the DDM implementation in CAMx to particulate matter (PM). Equations for sensitivities are derived for each of three PM modules in CAMx: inorganic thermodynamics (ISORROPIA), secondary organic aerosol partitioning (SOAP), and aqueous chemistry (RADM). The sensitivity coefficients calculated by the DDM are then compared with those obtained by the brute-force method. The computational efficiency of the DDM is also discussed.

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8PI75

STUDIES ON SOA FORMATION FROM OH-OXIDATION OF TOLUENE. GANG CAO, Myoseon Jang, The University of North Carolina at Chapel Hill, Chapel Hill, NC

The objective of this study is to investigate the effects of acid-catalyzed heterogeneous reactions on the SOA formation from the OH-oxidation of toluene. Experiments are conducted in a 2 m3 indoor Teflon Film chamber in the presence of nonacid seed ((NH4)2SO4) or acid seed (NH4HSO4/H2SO4) under NOx free condition. 2-methyl-2-butene and ozone reaction is used to generate the OH radicals in the study. Experimental observations indicate that the SOA yield is higher in the presence of acid seed. The acid-catalyzed reaction mechanisms are proposed for explanation of excess heterogeneous SOA production from the oxidation of toluene.

8PI76

GAS/SOLID PARTITIONING OF CHLOROACETANILIDE AND DINITROANILINE HERBICIDES AS A FUNCTION OF RELATIVE HUMIDITY IN THE PRESENCE OF SURFACTANTS. WENLI YANG, Britt A Holmén, University of Connecticut, Environmental Engineering Program, Storrs, CT

Gas/particle partitioning of herbicides plays an important role in herbicide mobility in the gas phase of air-dried soils and their volatilization from the soil surface into the atmosphere, and also affects the atmospheric transport of herbicides. Most herbicides used in the field are applied as formulations that consist of adjuvants (surfactants and solvents) in addition to the active ingredients. Surfactants are the most essential formula components, providing special functions such as emulsification, wetting and dispersal of the herbicide. Our previous study showed that the gas/particle partitioning of metolachlor and pendimethalin were enhanced in the presence of formulation surfactants. In addition to the effects of temperature and compound properties, relative humidity has a strong effect on gas/particle partitioning of semivolatile organic compounds. For example, in the atmosphere, the sorption of PAHs to urban particulate matter may decrease by a factor of two as relative humidity increases from 40% to 95%. However, up to date little is known about the magnitude of relative humidity effects on gas/particle partitioning of herbicides in the presence of surfactants.

The gas/particle behavior of seven herbicides from two families—chloroacetanilide and dinitroaniline—were examined with and without two surfactants commonly used as adjuvants—nonylphenol ethoxylate and calcium dodecylbenzene sulfonate. Air-dried Connecticut clayey loam soil spiked with pure herbicide and herbicide-surfactant was loaded in a stainless steel filter holder, a vacuum pump pulled clean and particle-free air through the treated soil at 4L/min and polyurethane foam (PUF) plugs were used to capture the gaseous herbicides desorbed from the particulate matter. The desorption experiments were performed at constant room temperature (25.0°C) and five different relative humidities (from <10% to >90%) adjusted by Perma Pure MH humidifier. The PUF and soil samples were extracted by supercritical fluid extraction (SFE) and analyzed by GC/MS to quantify herbicide concentration in the gas and particle phases, respectively. Preliminary experimental results show that over 48 hours of desorption the herbicides partitioned more readily to gas phase in the presence of surfactants.

8PI77

MEASUREMENTS OF HETEROGENEOUS ICE NUCLEI: RESULTS FROM INSPECT-II. MATHEWS RICHARDSON, Paul DeMott, Sonia Kreidenweis, Anthony Prenni, Markus Petters, Department of Atmospheric Science, Colorado State University; Daniel Cziczo, Department of Environmental Sciences, Swiss Federal Institute of Technology; Jose Jimenez, Edward Dunlea, Department of Biochemistry, University of Colorado; Sarah Brooks, Department of Atmospheric Sciences, Texas A&M University; Jefferson Snider, Department of Atmospheric Science, University of Wyoming; Dan Murphy, Aeronomy Laboratory, National Oceanic and Atmospheric; Randolph Borys, Storm Peak Laboratory, Division of Atmospheric Science, Desert Research Institute; Chuck McDade, Crocker Nuclear Laboratory, University of California, Davis;

During the spring of 2004, researchers from several institutions participated in the Ice Nuclei Spectroscopy (INSPECT-II) field campaign. This campaign was conducted at Storm Peak Laboratory atop Mt. Werner (3210 m above MSL) in Northwest Colorado. The primary aim of this campaign was to determine the chemical and physical characteristics of ice nuclei (IN) active at supercooled cloud temperatures, with an emphasis on determining the impact of Asian dust on IN concentrations. Colorado State University's continuous-flow diffusion chamber (CFDC) was used to determine the concentration of particles with an initial aerodynamic diameter less than 1 micron that act as IN as a function of temperature and relative humidity. A laboratory counter-flow virtual impactor (LCVI) was used to separate ice crystals from inactive aerosol immediately downstream of the CFDC. Downstream of the LCVI, the chemical composition of the IN was measured using several techniques. These techniques included single particle mass spectrometry as well as collection of particles on transmission electron microscope grids (TEM) for subsequent analysis. Bulk collections for compositional analysis, measurements of size distributions of the ambient aerosol population and water-uptake and CCN measurements were taken concurrently.
Typical IN concentrations active at temperatures as low as -50°C were one to ten per liter. However, there were several periods of enhanced IN concentration. According to the bulk compositional analysis, these periods correspond to periods of elevated soil levels. This presentation examines in detail two days which showed significantly elevated IN concentrations. The physical and chemical composition of the active IN and the ambient aerosol population of those days will be compared with days during which typical concentrations were measured. These comparisons allow us to make inferences regarding the properties of those particles serving as active IN and their relationships to other ambient aerosol characteristics.

8PI78

SINGLE DIAMETER REAL TIME ULTRAFINE NUMBER CONCENTRATION MEASUREMENTS AND RELATIONSHIPS TO METEOROLOGY AND TRAFFIC VOLUMES FOR A NORTHERN CALIFORNIA FREEWAY. Kathy Nanzetta, Deb Niemeier, University of California; Britt Holmen, University of Connecticut

Roadside measurements of single diameter particle number concentrations at five diameters (10, 20, 30, 40, 70 nm) and meteorological and traffic volume data were measured in northern California in July 2002. By applying constant voltage to a differential mobility analyzer (DMA, TSI, Inc.) in panel mode, continuous number concentrations in a narrow diameter range were obtained. Panel mode data are collected continuously at a single diameter, as opposed to scanned data that measure each diameter on set time intervals by a specified scan time. In prior studies, high variability of roadside number concentrations computed from the continuous panel mode data has been observed, which clearly illustrates the dynamic character of roadside number distributions. This characteristic of high variability reinforces the importance of collecting panel mode data when measuring roadside ultrafine particle numbers. We explored daily trends by particle size and compared the panel mode data to scanned data collected at the same location to examine size-resolved relationships between number concentrations and meteorology and traffic volumes. Results from the panel mode data indicate that nucleation rates decreased and particle growth rates increased over the day. Number concentrations of 10 nm particles decreased with increasing temperature and decreasing relative humidity in a curvilinear fashion and similar relationships were observed in 20 nm particles in the afternoon. Additionally, greater vehicle volumes corresponded to increases in 10 nm number concentrations. For 10 nm number concentrations, temperature was the best meteorological predictor variable and total vehicles the most important vehicular parameter in an estimated multivariate regression model, second order in temperature. Higher wind speed generally corresponded to lower number concentrations of 30, 40 and 70 nm particles.

8PI79

IN-SITU MEASUREMENTS OF AEROSOL MICROPHYSICAL PROPERTIES AND EVOLUTION IN NORTH CENTRAL OKLAHOMA IN MAY, 2003. JIAN WANG, Brookhaven National Laboratory, Upton, NY; Robert Elleman, David Covert, University of Washington, Seattle, WA; Haflidi Jonsson, Naval postgraduate School, Monterey, CA

During May of 2003, aerosol size distributions, optical properties, and hygroscopicity were measured on board the CIRPAS Twin Otter aircraft during 17 flights at the Southern Great Plains (SGP) site in north central Oklahoma as part of the Aerosol Intensive Operation Period. At the same time, sub micrometer aerosol size distribution and total particle concentration were characterized continuously at a surface site. High particle concentrations were observed mostly during sunny days; these high concentrations are well correlated with the simultaneously measured sulfur dioxide concentrations, suggesting the nucleation involving sulfuric acid is likely the main source of newly formed particles. On cloudy days, when the boundary layer was well mixed, vertical profiles measured onboard Twin Otter showed increasing dry aerosol scattering coefficient and volume with increasing altitude within the boundary layer. The increases are attributed to in-cloud production of sulfate at the top of the boundary layer through the aqueous reactions of sulfur dioxide with peroxide and ozone. The in-cloud production of sulfate is sufficiently fast compared to the mixing process within the boundary layer, and accounts for the observed vertical gradients of aerosol scattering coefficient and volume. This conclusion is supported also by the humidigraph measurements, which show aerosol hygroscopicity increasing with increasing altitude. Detailed growth law analyses carried out using the continuous aerosol size distributions measured at the surface, suggest the growth of aerosol size distribution is controlled mainly by volume-based reactions, consistent with the in-cloud production of sulfate.

8PI80

MODELING ANALYSIS OF THE IMPACT OF FIREWORK EMISSIONS ON PM2.5 LEVELS IN CORPUS CHRISTI, TEXAS. Rohan Bakane, KURUVILLA JOHN, Texas A&M University - Kingsville, Kingsville, TX

The National Ambient Air Quality Standard (NAAQS) for fine particulate matter (PM2.5) is 65 µg/m3 for the 24-hour averaging period. During an unusual air pollution episode during Dec 31, 2002 through January 1, 2003, extremely high levels of PM2.5 were observed at an air monitoring site in Corpus Christi. It was noted that following a pyrotechnic display celebrating the New Year event, a significant increase in the PM-fine concentrations was observed at an air monitoring site downwind of the event. The highest observed level of PM2.5 (771.25 µg/m3) was recorded around 1:00 a.m. on January 1, 2003. During this period, stagnant wind conditions along with an unusually shallow boundary layer exaggerated the impact of local PM emissions and resulted in a violation of the 24-hour PM2.5 standard. However, this event alone did not result in an excursion of the annual averaged PM2.5 standard of 15 µg/m3 for the Corpus Christi area.

The objective of this study was to evaluate the impact of increased particulate matter emissions during firework events held during holidays like the 4th of July and the New Year eve periods. To accomplish this work, air emission from the fireworks and pyrotechnic display was estimated using a stoichiometric approach along with survey-based data and empirical estimation techniques. In addition, parameters like the fine particulate matter concentrations, wind directions, wind speeds and radio sounding data were obtained from various federal and state monitoring agencies in the region and the data was analyzed. The mixed layer height was computed for the episode period to get a better understanding of the boundary layer transport conditions within the urban airshed. The pyrotechnic emissions and the plume transport during this episode was simulated using AERMOD, a Gaussian dispersion model, and the observed concentrations for the New Year eve of 2002-03 were compared with the model output. The model predicted concentrations were then compared to PM2.5 data obtained from air monitoring site downwind of the firework event. The maximum ground-level concentration predicted at the monitoring site for this event was 653 µg/m3 and the model simulated a narrow plume extending over the urban area of Corpus Christi. The modeling analysis captured the spatio-temporal characteristics of the plume of pollutants associated with this firework event. Analysis of similar air quality episodes during firework events will allow planners to assess the impact of various anthropogenic sources of air pollution on an urban airshed.

8PI81

ENVIRONMENTAL AEROSOL AND CARBON DIOXIDE CONCENTRATIONS DUE TO BIOMASS BURNING. T. S. VERMA, T. A. Thomas, Department of Physics, University of Botswana, Pvt Bag 0022, Gaborone, Botswana

In Southern Africa, savanna fires, domestic cooking and heating, during winter in particular, contribute to environmental aerosol concentration. Estimates suggest that the African continent alone shares about 47% of the world's burnt biomass. This biomass burning releases particulate matter in the sub micrometer size range particles and various polluting gases such as carbon dioxide, carbon monoxide, nitric oxides, methane etc. these gases may turn into airborne particles by gas-to-particle conversions.

Lower atmosphere aerosols vary over a wide range in sizes generally from 0.01µm to 5µm in size and in concentration from about 102 to 105cm-3. Gaborone has been noticed to be one of the fast developing cities in the world. Today it is a clean city but tomorrow, with the current rate of increase in constructional and industrial activities, it may stand in the queue of polluted cities of the world.

A comprehensive study to monitor concentration of environmental aerosol produced as a result of biomass burning have been conducted during year1999-2000. In the current study to monitor aerosol concentration, we have used two automatic particle counters from RION, Japan. These counters work on the light scattering principle. The counters can measure over a wide size range of particles from 0.1 to 5 µm in eight channels altogether. In the last year, we have added a Scanning Mobility Particle Sizer (SMPS) from TSI, USA, which can detect particles of size 0.01 µm and above, to our list of monitoring equipments.

In the present context, we found the mean variation of aerosol concentration for each month of the year. The mean monthly concentration of aerosols of size larger than 0.1µ;m was compared and for the years 1999 – 2000, 2002 – 2003 and 2003 - 2004. The most noticeable observation we could see was that the aerosol concentration was found to be the highest in the winter season. During these periods, it has been documented that there is an increased biomass burning taking place in the Southern African region.

CO2 is one of the minor greenhouse gases, a heavy gas, which settles closer to the earth's surface and hence affects human health, plants and animals. It is well understood that CO2 contributes to the global warming. A gaseous analyser (HORIBA) measuring carbon dioxide was used in this study. The CO2 concentration was measured and results were analysed. The study was conducted over a year and some interesting results were seen on an annual scale. One observation was that concentration of CO2 increased in winter.

Both studies are ongoing and the additional results will be presented at the conference.

8PI82

OLIGOMER FORMATION IN SECONDARY ORGANIC AEROSOL AQUEOUS PHASE REACTIONS. KATYE E. ALTIERI, Sybil P. Seitzinger, Institute of Marine and Coastal Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ; Annmarie G. Carlton, Barbara J. Turpin, Department of Environmental Science, Rutgers, The State University of New Jersey, New Brunswick, NJ

Oligomer formation in aerosol-phase reactions has recently been shown to contribute to gas phase secondary organic aerosol (SOA) formation. The heterogeneous polymerization reactions between semi-volatile condensed products yield compounds of lower volatility. The lower volatility favors partitioning into the particle phase causing the total SOA yield to exceed that predicted by models using single compound vapor pressures.

Isoprene is responsible for over half of non-methane volatile organics emitted globally. Isoprene is not usually considered an SOA precursor. However, in-cloud processing of water soluble products of isoprene oxidation can yield low volatility carboxylic acids (e.g. oxalic acid) as predicted by Lim et al. (2005) and demonstrated in laboratory experiments in a companion paper by Carlton et al. These low volatility acids remain largely in the particle phase when the cloud droplet evaporates, forming SOA. The formation of oligomers in this process was investigated using photochemical batch aqueous phase reactions of pyruvic acid and hydrogen peroxide.

Electrospray ionization mass spectrometry (ESI-MS) was used to identify monomers and oligomers in the cloud water SOA formation experiments. ESI-MS is a "soft" ionization tool that does not fragment compounds. The ESI-MS provides molecular weight information as mass to charge ratio (m/z). In the negative ionization mode, compounds with acidic functional groups are deprotonated and appear in the spectra as the molecular weight minus one.

Heterogeneous and homogeneous dimer formation was found to occur throughout the experiment but was not found in standards analyzed using the same instrument conditions. Pyruvic acid and glyoxylic acid were present in the samples primarily in their homogeneous dimer forms [2MW-H+]. Preliminary interpretation of the ESI-MS data indicates heterogeneous dimers of glyoxylic and oxalic acid, pyruvic and oxalic acid, and acetic and glyoxylic acid were formed [(MW1 +MW2)-H+] during the experiment. Because the oligomers have lower vapor pressures than their monomer components, they are more likely to stay in the particle phase and the total SOA yield will be higher than predicted. The formation of oligomers in cloud processing could warrant further experimental investigation and inclusion in cloud processing models.

8PI83

INFLUENCE OF WOOD SMOKE EMISSIONS ON SECONDARY PARTICLE FORMATION IN HOUSTON, TEXAS.

BIRNUR BUZCU, Zhiwei Yue, Matthew P. Fraser, Civil and Environmental Engineering Department, Rice University, Houston, TX; Uarporn Nopmongcol, David T. Allen, Department of Chemical Engineering, University of Texas at Austin, Austin, TX.

To further examine the significance of fires as a source of particulate matter during a regional haze episode period, source apportionment calculations for three sites in Houston during a period influenced by wood smoke emissions and during a background period. The analysis of ambient samples using organic molecular makers to determine source contributions are reported for days when particulate matter concentrations were greatly influenced by forest fires, and separately on other days not influenced by wood smoke. Chemical mass balance (CMB) and positive matrix factorization (PMF) approaches were used to estimate the contributions of primary and secondary sources to PM2.5 levels. The results indicated that, in addition to being a significant source of carbonaceous aerosol, fires can lead to significant enhancements of particulate sulfate concentrations, and that this excess sulfate can only be accounted for if heterogeneous sulfate formation reactions are occurring on the wood smoke surfaces. Regional photochemical modeling of days with and without significant concentrations of wood smoke particles was performed to assess the impact of heterogeneous reactions on sulfate concentrations. The results of this study can be used to isolate the impact of direct emissions from biomass combustion from the effects of primary emissions on secondary sulfate formation.

8PI84

ON THE RELATIVE IMPACTS OF ONROAD AND NONROAD HEAVY-DUTY DIESEL EMISSIONS.

DAVID R. COCKER III, Aniket A. Sawant, Abhilash Nigam, Sandip D. Shah, Ajay K. Chaudhary, Bill Welch, J. Wayne Miller, University of California, Riverside

The promulgation of increasingly stringent emissions regulations for on-road heavy-duty diesel vehicles has brought the relatively unregulated nonroad sources into sharper focus. Nonroad sources, such as backup generators, construction equipment, locomotives, and ships are estimated to contribute significantly to the national emissions inventory (U.S. EPA AP-42)—however, these estimates have not been updated for several years. Further, the U.S. EPA has announced its intent to formulate more stringent emission standards for nonroad sources, and intends to require the use of current on-highway (500 ppm S) fuel for future nonroad applications.

Therefore, there exists a need to characterize and quantify emissions across multiple nonroad sources, with the objective of understanding the relative contributions of each to local and regional inventories. In the present work, we investigate emissions obtained from a matrix of Class 8 heavy-duty diesel tractors, backup generators and switching locomotives, all on the same test stand, the UCR/CE-CERT Mobile Emissions Laboratory (MEL). These sources are compared against emission measurements made by our group on commercial aircraft, container ships, and construction equipment. Specifically, we discuss emission factors for regulated (THC, CO, NOx, PM) and non-regulated (EC/OC, carbonyl) emissions on a per kg CO2 basis to allow for comparison across sources. We also develop an estimate for an urban community with typical concentrations of all these sources and estimate the impacts of current and future regulations on local emissions inventories.

8PJ1

ASSESSMENT OF GREENHOUSE GASES AND AEROSOL CLIMATE EFFECTS BY ASSIMILATION OF SATELLITE RADIANCE DATA INTO A GLOBAL CHEMISTRY AND AEROSOL MODEL. Robert Bergstrom, Hong Guan, Howard Houben BAER Institute, Sonoma CA; Robert Chatfield, Philip Russell, NASA Ames Research Center, Moffett Field, CA

We are combining a global chemistry and aerosol transport numerical model with a sophisticated radiative transfer model to improve the application and interpretation of satellite data using advanced data assimilation techniques. We are incorporating satellite data into our modeling to obtain substantially better scientific understanding of aerosol and combustion product sources and transport. A new technique is available which allows the assimilation of observations with little foreknowledge of the observed system. The new methodology requires that the observed quantity (in this case satellite radiances) be the primary assimilation variable.

We are utilizing an existing aerosol transport model (the NCAR CAM global numerical model), adapting its assimilation methodology slightly to get the benefits of the new technique, and adding our radiative transfer model to predict satellite radiances at each model node (i.e., to produce synthetic satellite images for each model timestep). We are also adding the aerosol parameterizations from the NCAR MATCH model and focussing on the transport mechanisms into the troposphere. The result should be much improved and better constrained aerosol modeling, which will give more insight into questions of the climatic impact of aerosols.

We are investigating the biomass burning regions of South America and Africa and the outflow from East Asia. The first test area is the biomass burning regions of South America and Africa for the years 2000 and 2002. We will estimate emissions based on the assimilation of the VIRS and MODIS satellite products. The second test area will be the ACE-Asia field experiment region and time frame of April 2001. We are using the geosynchronous GMS-5 satellite data for our data assimilation. The East Asian area is of great current interest and has been the subject of a number of studies. We will show some preliminary results from the simulations.

8PJ2

WEB-ACCESSIBLE DATABASE WITH EMBEDDED ANALYTICAL TOOLS FOR THE MANAGEMENT AND VISUALIZATION OF AIR QUALITY DATA. DR. ROBINSON KHOSAH, Charles Crawford, ATS-Chester Engineers, Pittsburgh, PA; Dr. Kevin Crist, Ohio University, Athens, OH; Dr. Kuruvilla John. Texas A&M University - Kingsville, Kingsville, TX

The U. S. Department of Energy (NETL) has funded several research projects targeted towards the characterization of fine particulate (PM2.5) and co-pollutants present in ambient air along the Upper Ohio River Valley (UORV) corridor. Exposure to PM2.5 species has been linked with mortality incidences involving people with upper respiratory ailments. These studies have produced large data sets that are resident in disparate locations with limited access by the sponsors and interested stakeholders. This project involves the development of a comprehensive, computer-based system for (1) integrating the ambient air quality data being collected under multiple ongoing DOE-sponsored monitoring programs in the UORV region, and (2) creating a publicly-available, user-friendly tool for accessing, displaying, analyzing and interpreting these air quality data. The resulting database will provide timely data analysis for the sponsors, stakeholders and the community-at-large through an easy-to-use web-based data management system that will have graphical analytical tools for displaying, analyzing and interpreting the archived air quality data. One benefit derived from this project is that it will be used to support scientifically-sound policy decisions by regulatory agencies. This system's data storage, retrieval and analysis tools are easily adaptable in the environmental field, including water quality data management

8PJ3

EVALUATION OF A THREE-DIMENSIONAL CHEMICAL TRANSPORT MODEL (PMCAMX+) IN THE EASTERN UNITED STATES FOR ALL FOUR SEASONS. VLASSIS A. KARYDIS, Alexandra P. Tsibidi, Spyros N. Pandis, Dept. of Chemical Engineering, University of Patras, Patras, Greece

Atmospheric aerosols have adverse effects on human, animal, and plant health, contribute to the acid rain and visibility reduction and influence the energy balance of the planet. A three-dimensional chemical transport model (PMCAMx+) (Gaydos et al., 2005) is used to simulate particular matter (PM) mass and composition in the eastern United States during the four seasons of the year (July 2001, October 2001, January 2002, April 2002). PMCAMx+ uses the framework of CAMx (ENVIRON, 2002) modelling the processes of horizontal and vertical advection, horizontal and vertical dispersion, wet and dry deposition, and gas-phase chemistry. In addition to the above, PMCAMx+ includes three detailed aerosol modules: inorganic aerosol growth (Gaydos et al., 2004; Koo et al., 2003), aqueous-phase chemistry (Fahey and Pandis, 2001), and secondary organic aerosol formation and growth (Koo et al., 2004). The model predictions are evaluated against hourly measurements of PM and gas-phase data collected during the Pittsburgh Air Quality Study (PAQS) (Wittig et al., 2004), as well as daily average PM measurements taken throughout the eastern United States by the IMPROVE (IMPROVE, 1995) and STN (U.S. EPA, 2002) monitoring networks. The strengths and limitations of current modelling approaches for this modelling domain and for the different seasons are discussed.

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8PJ4

GLOBAL DISTRIBUTION OF AEROSOL INDEX CLIMATIC NORMS AND LONG TERM EVOLUTION. IRYNA KALININA, Sergiy Snizhko, Department of Meteorology and Climatology,Kiev Shevchenko University, Kiev, Ukraine; Grigoriy Kruchenitsky, Central Aerologic Observatory, Moscow, Russia

Atmospheric aerosol is the important constituent of earthly atmosphere. It takes part in optical and chemical atmosphere?s properties forming. Therefore research of its dynamics is very important for climatic investigations. The object of submitted work is a calculation of climatic norms of atmospheric aerosol and finding its long-term changes. We have used global fields of aerosol index monthly averaged values obtained by TOMS measuring from 1978 November. As a result of researches was found climatic norms, the determination coefficient of seasonality and the field of trends.

Main results:

1. All indexes of climatic norms change zonal, however the maximal values in Western Sahara are expressly selected.

2. The mean value of aerosol index has zonal distribution: from the maximal values in a tropical area (to 22) to minimum (about zero) in moderate and arctic regions. However, the maximal values in the districts of most deserts of our planet are separately selected and especially in the district of Western Sahara.

3. The determination coefficient has changes according to the zonal law from 90% to 0%.

4. Amplitude of seasonal going also is most in a tropical area and has the maximal value in the region of Western Sahara (more than 9). 5. Trends values are changes from most in a tropical area (to 7% per decade) to the lowest in an Antarctic continent (-2% per decade)

8PJ5

OPTICAL SCATTERING AND ABSORPTION CLOSURE FOR DRY AND HYDRATED AEROSOL AT THE GOSAN SUPERSITE DURING ACE-ASIA.

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A major goal of the ACE-Asia study was to understand how the microphysical and chemical properties of Asian aerosols control ambient light extinction, particularly during time periods impacted by heavy dust loadings and anthropogenic sources. One technique for probing the relationships among aerosol physical, chemical and optical properties is so-called closure studies, whereby detailed information about the aerosol size distribution and chemical composition is used to derive light extinction coefficients that can be compared with direct measurements.

The goal of this work is to use number size distribution, chemical composition, and size-resolved water uptake measurements made at the Gosan supersite during ACE-Asia to calculate aerosol light extinction coefficients for ambient conditions. Derived light scattering and absorption coefficients for ‘dry’ and ‘wet’ cases are compared with measurements to assess if aerosol optical properties can be predicted within the measurement and model uncertainties. Size-resolved chemical composition data are used to assess the impact of external versus internal mixing state on aerosol water uptake and light extinction. New thermodynamic models are applied to predict the water activity and hygroscopic growth of Asian aerosol, including water soluble and insoluble components. Observed compositional differences between particles of different hygroscopic growth determined by simultaneous water uptake and composition measurements are used to test the models of water activity. The relative impact on derived optical properties of changes in size distribution mode diameter, concentration, size-resolved chemical composition, and external versus internal mixing state are examined for dust and non-dust periods. The sensitivity of derived extinction coefficients to assumptions on particle shape is explored.

Total ($Dp<10$ micron) scattering and absorption were observed to increase by factors of 3 and 4, respectively, during dust events compared to non-dust periods. Scattering by super-micrometer particles was found to comprise 90% of the total scattering during dust events compared to 50% during other periods. Calculated and measured extinction coefficients typically agree within 20% for dry aerosol. Preliminary results suggest that during dust input periods also associated with higher pollution loading, shifts in the dominant modes of the size distribution play a larger role in controlling integrated scattering than concentration increases. The proposed closure studies will also reveal the influence of dust composition on ‘wet’ scattering closure when more and less-pollution input is associated with sampled dust.

8PJ6

CHARACTERISTICS OF AEROSOL OBSERVED DURING SEVERE HAZE EVENTS OCCURRED IN JUNE AND OCTOBER 2004 OVER KOREA.

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Two seasonal haze episodes occurred 9~12 June and 5~8 October 2004 over Korea have been studied using satellite and ground based sunphotometer observation data to estimate the effects of long range transported aerosol. Semi-real time organic and elemental carbon (OC and EC) concentration data were also analyzed to investigate the contribution of the transported fine particles to local atmospheric burden. Physical and optical characteristics of aerosols of the two haze events were related to their transport pattern. Based on the satellite data and backward trajectory analysis contributions of primary and secondary carbonaceous particles to local air quality have been evaluated. During the first haze event of June 2004 very high aerosol optical thickness (AOT) up to 2.0 was observed due to the influence of the long-range transported haze plume from the burning areas in Eastern China, resulting in an elevated surface PM10 concentration up to 250 . Also the organic compounds were enriched due to the accumulation of long-range transport of OC plus primary local emission. Secondary OC concentration increased to 12.6 during daytime by photochemical reaction under high ozone concentration (~76ppb). Satellite image and backward trajectory results showed that the haze plume originated from the Chinese urban area near Beijing in October 2004. Compared to the first haze event the contribution of SOA was much lower during the second haze event; ~70% vs. ~45%. Contribution by the transport of primary carbon particles increased during the second haze event. It can be concluded that the observed differences in the aerosol chemical characteristics account for the influence by different types of sources and air mass pathway.

8PJ7

EVIDENTIARY SUPPORT OF POLLUTED CLOUDS IN THE SIERRA NEVADA: AEROSOL-CLOUD INTERACTIONS DOWNWIND OF METROPOLITAN COASTAL AREAS. CRYSTAL REED, Don Collins, Texas A&M University, College Station, TX; Duncan Axisa, Southern Ogallala Aquifer Rainfall Program, Plains, TX; Daniel Rosenfeld, The Hebrew University of Jerusalem, Jerusalem, Israel

Measurements made on board the SOAR Cheyenne II aircraft during February and March 2005 were used to quantify the impact of pollution aerosols on the microphysics of clouds present over the Sierra Nevada in California. This study was designed to examine the role of emissions from the major metropolitan areas in California on winter precipitation in the Sierra. Of particular interest were shallow orographic clouds associated with cyclones, which are believed to be most sensitive to enhanced aerosol concentration. Aerosol size distributions and size-resolved hygroscopicity were measured using a differential mobility analyzer / tandem differential mobility analyzer. These data were coupled with measurements made using a DMT CCN counter to assess the extent to which upwind emissions influenced CCN concentration. The manifestation of any change in CCN concentration was examined through measurements of cloud droplet size distributions using a DMT cloud droplet probe (CDP) and a DMT cloud imaging probe (CIP). Meteorological data and satellite images were used to interpret the in situ measurements. The implications of the observed impact of pollution on cloud microphysics and on precipitation will be discussed.

8PJ8

EXPERIMENTAL AND NUMERICAL STUDIES OF NEAR-SOURCE FUGITIVE DUST TRANSPORT. JOHN VERANTH, Department of Pharmacology and Toxicology, Scott Speckart, Eric Pardyjak, Department of Mechanical Engineering, University of Utah, Salt Lake City, UT, Vic Etyemezian, Desert Research Institute, Las Vegas, NV

Surface roughness and atmospheric stability are important factors affecting the near-source transport of fugitive dust from unpaved roads and similar sources. These factors are not considered in current dust inventory models but many result in significant redeposition of the initially suspended dust within the first 100 m of the source. Field studies of particle deposition on surfaces and of dust flux downwind of a source are compared to computational model predictions. The experiment conducted under daytime conditions with sparse vegetation showed no measurable dust removal, but a study conducted at night time under simulated urban conditions showed 85% dust removal. A computational model that considers advection, diffusion, and deposition on surfaces accounts for the differences observed between these two field studies. The results can be used to improve estimates of personal exposure to people living near dust sources and suggest that windbreaks can be used as a dust mitigation strategy.

9A1

AN INTEGRATED SYNTHESIS OF KEY AND POLICY RELEVANT FINDINGS FROM EPA'S PM SUPERSITES PROGRAM AND RELATED STUDIES. Paul A. Solomon, US Environmental Protection Agency, ORD/NERL, Las Vegas, NV; Philip K. Hopke, Clarkson University, Potsdam, NY; John R. Froines, University of California Los Angeles, Los Angeles, CA

The Particulate Matter (PM) Supersites Program is a multi-million dollar, multi-institutional program of methods development and evaluation, air quality measurements, data analysis, and modeling. The three major objectives include: 1. Developing information that will reduce uncertainties in our understanding of PM accumulation in air on urban and regional scales; 2. Advancing and evaluating PM measurement methods; and 3. Supporting health effects and exposure studies.

The Supersites Program consists of eight projects located across the US in urban areas with different source mixes and meteorological conditions leading to diverse atmospheric chemical conditions. These conditions allow the program to meet its three major objectives. Each project is considered a regional study extending well beyond the boundaries of their particular urban environment. Integration of the projects coupled with related studies has lead to a true national program. From this standpoint, the PM Supersites Program is enhanced and enhances air quality and meteorological data collection activities across the country as well as SE Canada, during the period 1999 to 2005. EPA-funded field and laboratory efforts are complete and project data analysis efforts are underway.

A synthesis of key and policy relevant findings was initiated by EPA to further integrate findings from the program and related efforts that occurred during the last 5-7 years. The AAAR PM Supersites Program and Related Studies International Conference in February 2005 is part of the synthesis process. The goal of the synthesis is to provide key stakeholders and relevant scientific communities' information that would ultimately reduce uncertainties in our understanding of atmospheric PM accumulation on urban and regional scales, and therefore, provide information to assist in the development of effective emissions management programs to reduce the impacts of PM-related pollution on humans and ecosystems. In 2004, EPA in conjunction with state, regional planning organizations, other Federal agencies, and the private sector has developed a set of 17 key and policy relevant questions to be addressed by the Supersites Program principal investigators and other key individuals. These questions form the basis for the integrated synthesis of atmospheric sciences findings, from which, policy relevant and health relevant findings will be derived. The purpose of this presentation is to provide initial insights into the findings based on the initial drafts of the technical papers due in July 2005.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

9A2

SYNTHESIS OF SUPERSITE PROGRAM FINDINGS: REGIONAL TRANSPORT OF FINE PM. Ann Wittig, CUNY City College of New York, New York, NY; Jay Turner, Washington University, St. Louis, MO; DAVID ALLEN, University of Texas, Austin, TX

Recent scientific field studies of fine particulate matter (fine PM), conducted as part of the Particulate Matter Supersites Program and related field measurement programs, are producing information of broad relevance that can help inform public policy decisions. This paper presents the synthesis of recent scientific findings concerning regional transport of fine PM. Parallel efforts are examining intra-urban and continental scale transport of fine PM.

This work examines the extent to which regional pollutants influence both urban and downwind regional levels of PM. This work initially compares composition of fine PM mass experienced in major cities across the United States, drawing from recent results of the Supersites Program. The sources of the fine organic PM in these cities are also presented. Measurements of fine PM mass made by the Supersite Program and IMPROVE network are compared to assess the extent to which differences in composition can be explained by differences in local sources (natural and man-made), by the regional transport of pollution from one location to the other, or simply by differences in monitoring techniques. Finally, modeling scenarios which illustrate episodic impacts of urban plumes on regional pollutant levels are presented.

9A3

MODELING AIR QUALITY DURING THE CALIFORNIA REGIONAL PARTICULATE AIR QUALITY STUDY (CRPAQS) USING THE CIT/UCD SOURCE-ORIENTED AIR QUALITY MODEL – PART I: MODEL PERFORMANCE EVALUATION. QI YING, Michael J. Kleeman, Dept of Civil and Environmental Engineering, UC Davis, Davis CA; Ajith Kaduwela, Planning and Technical Support Division, Air Resources Board, California Environmental Protection Agency, Sacramento, CA

The National Ambient Air Quality Standards for particulate matter smaller than 10 micrometers in diameter (PM10) and for particulate matter smaller than 2.5 micrometer (PM2.5) are consistently exceeded in central California, especially during the winter season. A database containing measured gaseous and particulate matter concentrations, meteorological measurements, and emissions estimates has been constructed to support an evaluation of the underlying cause for this severe air quality problem. In this study, the CIT/UCD source-oriented air quality model is applied to the extensive CRPAQS data set to verify the ability of the model to predict gas and particulate matter concentrations in central California during a winter stagnation event. Model simulation is carried out for the time period December 15, 2000 to January 31, 2001 for an area of approximately 210,000 km2 which includes the major urban areas of San Francisco, Sacramento, Fresno and Bakersfield. This is the first application of a full scale, source-oriented external mixture air quality model in central California with high temporal (1hr) and spatial (4km) resolution. Both diagnostic and prognostic (MM5) meteorology fields are used to evaluate the uncertainty in model calculations associated with meteorological inputs. Likewise, calculations are performed using a grid with 4km x 4km horizontal resolution and 8km x 8km resolution to determine the sensitivity to scale. The predicted and measured concentrations of carbon monoxide (CO), nitrogen oxides (NOx), ozone (O3), elemental carbon (EC), organic compounds (OC), nitrate, sulfate and ammonium ion are compared using model performance statistics. The verified CIT/UCD source oriented air quality model will be used in the second part of the modeling study to identify the sources that contribute to the primary and secondary particulate matter in central California.

9A4

THE ROLE OF RESUSPENDED SOIL IN LEAD FLOWS IN THE CALIFORNIA SOUTH COAST AIR BASIN. ALLISON HARRIS, Cliff Davidson, Carnegie Mellon University, Pittsburgh, PA

We have constructed a mass balance for airborne lead in the South Coast Air Basin of California (SOCAB). Sources include emissions from stationary point sources, gasoline- and diesel-powered vehicles, and piston engine aircraft which still use leaded fuel. Sinks include deposition and advection out of the Basin. As an additional source we consider resuspended soil, which is not usually considered in emission inventories. However, given that over 10 metric tons of lead was deposited on SOCAB soil each day for years during the peak use in leaded gasoline, we expect that some of this lead is still available for resuspension.

Using 2001 as our base year, we calculate that approximately 44500 kg of lead are advected from the Basin each year, and dry deposition totals about 11300 kg/year. Thus the total lead removed from air in the Basin is around 55800 kg/year.

Emissions from point sources in 2001 total 5410 kg/year, although there is significant uncertainty associated with this value. Using unleaded gasoline and diesel consumption data with small (but nonzero) lead mass fractions, we estimate that on-road traffic generates an additional 850 kg/year. Piston engine aircraft run on fuel containing tetraethyllead additives, and for the SOCAB area, this results in emissions of about 270 kg/year below the mixing height. Thus emissions of lead from these traditional sources total about 6500 kg/year. The net result from the mass balance outlined above is that lead removed from the Basin each year exceeds the quantity of lead added to the Basin by about an order of magnitude.

To resolve this discrepancy and to calculate the contribution of resuspended particles, we propose a model based on the differential changes to soil and air concentrations. The fraction of soil particles resuspended by wind is proportional to a resuspension rate. Using appropriate resuspension rates for wind and soil conditions in southern California as model input provides values that are in reasonable agreement with measured air and soil concentrations for lead between 1970 and 2001.

Additionally, the model confirms that soil lead concentrations have remained high despite the drop in airborne concentrations since the elimination of lead in gasoline. The model suggests that soil concentrations will remain high well into the future, and that resuspension of soil lead will continue to be a significant source of lead for years to come.

9A5

THE IMPACT OF AMMONIA EMISSIONS ON ATMOSPHERIC PARTICULAR MATTER FORMATION IN TEXAS.

THOMAS PAVLOVIC, David Allen, Yosuke Kimura, Uarporn Nopmongcol, University of Texas at Austin, Austin, TX

SO2 emissions, which lead to sulfate formation, are known to be a major source of atmospheric particulate matter. Reducing SO2 emissions generally leads to reductions in sulfate formation, however, reducing SO2 emissions in regions with high ammonia concentrations can lead to additional formation of ammonium nitrate. In this paper we report on the impact of ammonia emissions on atmospheric particular matter formation in Texas, as SO2 emissions are reduced. The response of particulate matter concentrations to emission reductions was estimated for a summer 2000 episode using a three dimensional photochemical model (the Comprehensive Air Quality Model with extensions, CAMx). Emissions inventories for ammonia, used in the modeling, were developed based on local land cover and activity data; point source SO2 emissions were projected based on announced emission reductions associated with the Clean Air Interstate Rule (CAIR). Simulations were performed for a variety of ammonia and SO2 emission scenarios and the response of ammonium nitrate concentrations to these emission reduction scenarios will be reported.

9A6

MODELING NEW PARTICLE FORMATION IN THE MEDITERRANEAN AREA.

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The air quality model UAM-AERO has been modified to cover the main processes leading to new particle formation. Briefly, new clusters are assumed to be formed through ternary nucleation of sulfuric acid, ammonia and water, and the subsequent growth of clusters to large sizes is driven by condensation of sulfuric acid and organic vapors. Both of these processes were parameterized allowing a computationally efficient calculation of the flux of new particles to the smallest size bin used for particles in UAM-AERO. The modified version of UAM-AERO is used to investigate the effects of new particle formation on air quality in two representative Mediterranean areas, the Athens, Greece (GAA) and the Marseille, France (GMA) Greater Areas. The application of the model reveals higher sulfuric acid condensation sink and higher remaining quantity of sulfuric acid, available for the nucleation, in the GMA. This is due to the substantially higher SO2 emissions in the GMA. As a result, the nucleation rate and, consequently, the number of clusters formed are greater in the GMA. The estimated by the model growth rates of nuclei as well as the estimated condensation sinks are within the corresponding higher and lower values that have been measured during the extensive field campaigns in the above mentioned areas. However, due to the limited quantities of organic vapors in the GMA, which limit the growth rate of the clusters, more mass crosses the lower diameter used for aerosol treatment by UAM-AERO in the GAA. Since the available organic carbon in both areas of interest is the same for the same time step of the simulation with and without the nucleation module, the nucleation and growth processes do not change the total mass of particulate matter in the entire domains. What changes is the number concentration and the mass in each size bin of the particle's size distribution, as the newly formed particles enter the lower bin of the size distribution. As the particle transport rate is proportional to the difference in the particle concentrations in the corresponding size bins belonging to adjacent cells, the inclusion of the nucleation module affects the spatial distribution of particulate matter, by modifying the distribution of the mass in each size bin in the domain.

9B1

USING AEROSOL MASS SPECTROMETRY TO STUDY RADICAL-INITIATED REACTIONS OF ORGANIC AEROSOL PARTICLES.

GEOFFREY D. SMITH, John D. Hearn and Kylee List, University of Georgia, Athens, GA

Atmospheric aerosol can contain a significant fraction of organic material consisting of hundreds of different species. These particles are aged, or “processed,” in the atmosphere through reaction with trace gas-phase species, such as O3 and OH. Recently there has been a substantial effort undertaken by multiple groups to study the reactions of O3 with unsaturated organic species in condensed-phase particles or films. However, despite the importance of the OH radical for oxidation in the troposphere, there have been relatively few studies of OH reactions with organic films or particles.

We have begun to explore such radical-initiated reactions of organic particles using Aerosol CIMS (chemical ionization mass spectrometry) and SPMS (single-particle mass spectrometry). These complementary methods are particularly well-suited to the study of organic species since the mass spectra contain very little fragmentation. In particular, the reactions of Cl and OH radicals with particles comprising various organics have been studied by monitoring changes in the particle composition. These experiments have been carried out both in the absence and in the presence of O2, thereby providing insight into the oxidative processing which may potentially alter many critical properties of organic particles, including hygroscopicity and the ability to act as cloud condensation nuclei. The significance of these findings for the processing of atmospheric organic aerosol will be discussed.

9B2

PHOTOCHEMISTRY OF OXIDIZED ORGANIC AEROSOL PARTICLES.

JIHO PARK, Anthony Gomez, Maggie Walser, Ao Lin, Nicole Britigan, Sergey Nizkorodov, Department of Chemistry, University of California at Irvine, Irvine, CA

Chemical and photochemical aging of organic species adsorbed on aerosol particle surfaces is believed to have a significant effect on cloud condensation properties of atmospheric aerosols. This work focuses on photodissociation processes occurring in organic solid-air and liquid-air interfaces representative of atmospheric aerosol particles. A thin film of organics coated on the surface of an inorganic substrate, e.g., a sub-monolayer of partially oxidized unsaturated fatty acids on quartz nanoparticles, is excited at various UV wavelengths, and escaping gas-phase photochemical products are monitored using cavity ring-down spectroscopy. Products in the film are probed by mass-spectrometry. The reaction mechanism and its implications for photochemical aging of atmospheric aerosol particles will be discussed.

9B3

HETEROGENEOUS REACTIONS OF O3 WITH MULTICOMPONENT AND MULTIPHASE MIXTURES CONTAINING OLEIC ACID. DANIEL A. KNOPF, Lori M. Anthony, Allan K. Bertram

Condensed phase organic material is abundant in the atmosphere. Fieldwork has shown that pure organic particles consist most likely of a variety of organic compounds which may form in some cases multiphase mixtures. Organic aerosols, while in the atmosphere, experience reactions with gas-phase species which potentially lead to the modification of the particle composition and morphology. Heterogeneous reactions may also change the hygroscopic properties and optical properties of organic particles, and, therefore, influence the ability of these particles to act as cloud condensation nuclei and to scatter and absorb solar radiation. The purpose of this study is to gain a better understanding of heterogeneous reactions on multicomponent and multiphase organic particles.

The heterogeneous reaction of O3 with lauric acid/oleic acid (LA/OA) mixtures and myristic acid/oleic acid (MA/OA) mixtures were studied as a function of composition, physical state, and microstructure at 298 K. Also, the uptake of O3 by multicomponent mixtures representing closely the composition of meat cooking aerosols was investigated. A rotating wall flow tube reactor coupled to a chemical ionization mass spectrometer was employed to measure the reactive uptake coefficients ( ) of the various systems.

The reactive uptake coefficients of O3 on liquid LA/OA and MA/OA solutions range from 4x10-4 to 7.2x10-4. The values measured for solid-liquid LA/OA and MA/OA mixtures range from 2x10-5 to 1.7x10-4. Our experiments show that only 7 % solid by mass in the solid-liquid mixture can decrease by an order of magnitude compared to the liquid mixtures. The experiments employing mixtures which correspond closely to the composition of meat cooking aerosol derive values from 1.5x10-5 to 6.9x10-5. We found that the obtained values of the solid-liquid mixtures depend strongly on the microstructure which in turn depends on the method of preparation. We also observed that increases with film age of the solid-liquid mixture. This can be explained either by the formation of a non-equilibrium phase followed by its relaxation to the stable phase or Ostwald's ripening. The obtained values were used to estimate lower limits of the atmospheric OA lifetime under typically polluted conditions. The OA lifetimes of liquid mixtures are in the order of minutes. The lifetimes derived for solid-liquid mixtures range from 20 to 124 min,significantly longer than for liquid solutions.

9B4

MECHANISM OF OLEIC ACID OZONLYSIS ELUCIDATED BY COMPARISON STUDIES WITH METHYL OLEATE AND MIXED OLEIC-ACID/STEARIC-ACID PARTICLES. Yasmine Katrib, Stephanie M. King, SCOT T. MARTIN, Division of Engineering and Applied Sciences, Harvard University, Cambridge MA, 02138, USA; Michihiro Mochida, Institute of Low Temperature Science, Hokkaido University, Sapporo, 060-0819, Japan; Paul Davidovits, Chemistry Department, Boston College, Chestnut Hill MA, 02467, USA; John T. Jayne, and Douglas R. Worsnop, Aerodyne Research, Inc., Billerica MA, 08121, USA

The impact of chemical structure on the products and kinetics of condensed-phase ozonolysis reactions is employed to elucidate the chemical mechanism. Results are compared for oleic acid (C18 compound with double bond and carboxylic acid group), methyl oleate (carboxylic acid group of oleic acid replaced by methyl group), and stearic acid (double bond of oleic acid replaced by saturated bonds). The ozonolysis of methyl oleate leads to the formation of long chain hydrocarbons in the condensed-phase even in the absence of the functional group COOH. The ozonolysis of mixed oleic-acid/stearic-acid particles shows that stearic acid is also lost, which implicates the coupling of the oleic acid Criegee intermediate to the carboxylic acid group because stearic acid alone does not react with ozone. In both sets of experiments, compounds with molecular weights greater than the primary ozonolysis products are detected. The results therefore show that polymerization occurs and that parallel pathways, including radical addition across the double bond and linkage via the carboxylic acid group, simultaneously occur in significant yields. More specifically, our previously proposed mechanism suggesting the addition of the Criegee intermediate to the double bound is supported by the experimental results.

Results are also obtained concerning the effect of the matrix on reactivity. Namely, the study of mixed oleic-acid/stearic-acid particles shows that oleic acid does not decay exponentially with increasing ozone exposure. Rather, the decay occurs in two steps: there is an initial fast decay followed by an absence of further reaction. For example, 30% of oleic acid remains unreacted in particles initially of 50% oleic acid and 50% stearic acid. We hypothesize that the morphology of the particles could explain these results if, for example, stearic acid and the initial ozonolysis reaction products form an outer shell around the particle which serves to seal the residual oleic acid and prevent reaction with ozone. Changes in the particle bream width inside the Aerosol Mass Spectrometer support this hypothesis because defocusing of the mixed particles shows that the particles are non-spherical prior to reaction and become further defocused after ozonolysis.

9B5

FORMATION OF METHYL TETROLS IN SECONDARY ORGANIC AEROSOL FROM LABORATORY IRRADIATED ISOPRENE/NOX/SO2/AIR MIXTURES.

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Recent observations in ambient PM2.5 of 2-methylthreitol, 2-methylerythritol and 2-methylglyceric acid, proposed isoprene oxidation products, suggest the contribution of isoprene to SOA formation, long thought to be relatively unimportant, should be reexamined. An experimental study was initiated whereby isoprene/NOx/air mixtures were irradiated in a flow reactor smog chamber in both the absence and presence of SO2 to measure the SOA yield of isoprene and to establish whether the two 2-methyl tetrols and 2-methylglyceric acid are present in isoprene SOA and could serve as SOA indicator compounds. In the absence of SO2, the SOA yield of approximately 0.002 was low, as expected, although uncertain because the SOA concentration was near chamber background levels. (This finding is consistent with the earlier chamber-derived SOA yields by Pandis and co-workers.) Measurements were then taken for SO2 concentrations ranging from 40 to 290 ppb. SOA yields increased monotonically from zero SO2 and reached a plateau at approximately 200 ppb. The secondary organic carbon yield reached a value 0.007 at the highest SO2 concentrations. Analysis of the trimethylsilyl derivatives of the SOA samples by gas chromatography/ mass spectrometry showed chamber concentrations of the two 2-methyl tetrols totaling 0.1 µg/m3 and a 2- methylglyceric acid concentration of 0.3 µg/m3 in the absence of SO2, with the levels increasing significantly to 4.8 µg/m3 and 0.9 µg/m3, respectively, when SO2 was added. The laboratory data suggest that these compounds are possible indicator compounds for isoprene SOA and that the presence of SO2 enhances significantly SOA formation from isoprene photooxidation, with acid catalyzed reactions possibly playing a role. The importance of these findings was supported by the detection of the two 2-methyl tetrols and 2-methylglyceric acid in summertime ambient PM2.5 samples collected at three locations in the eastern United States in 2001. However, additional mechanistic studies are required to predict the contributions of the SO2- assisted isoprene SOA formation to ambient PM2.5 concentrations.

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9B6

NEUTRAL AND ACIDIC FRACTIONS OF ORGANIC AEROSOL COMPLEX MIXTURES FROM PM2.5 IN THE NEW YORK CITY AREA.

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; Stephen R. McDow, Human Exposure and Atmospheric Sciences Division, National Exposure Research Laboratory, U.S. EPA, Research Triangle Park, NC; Claire Belisle, Department of Civil & Environmental Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ

Organic molecular markers were measured in airborne fine particulate matter (PM2.5) from four New York metropolitan area sites to determine the seasonal distributions of the acidic and neutral organic fraction over the carbon number range of C10 to C36. The ambient PM2.5 sample collection ran from May 2002 to May 2003 following the 1-in-3 day schedule prescribed by the U.S. EPA Speciation Trends Network (STN) air monitoring protocol. Forty sample composites each containing 6 to 10 filters were extracted with organic solvent (1:1 methylene chloride: acetone) and analyzed for both acidic and neutral components by gas chromatography/mass spectrometry (GC/MS). The acidic organic components were derivatized with freshly prepared diazomethane to convert carboxylic acid and aromatic hydroxyl groups to the corresponding methyl ester and methoxy derivatives. Mass distributions of the total neutral and acidic fractions were plotted in reference to the n-alkane series (C10 to C36). Relative responses of the n-alkane homologs were used to determine the mass of components eluting between two adjacent homologs. Seasonal abundances of the neutral and acidic fractions mass distributions were compared among the four receptor sites (Chester, NJ upwind; Elizabeth, NJ traffic dominated; Queens, NY densely populated urban; and Westport, CT). These spatial and seasonal distributions of the acidic and neutral fraction will improve current understanding of the relative importance of primary sources versus secondary photochemical sources of fine carbon particles in the NYC metropolitan area. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

9C1

CABIN AEROSOL EXPOSURES IN CONVENTIONAL SCHOOL BUSES WITH AND WITHOUT RETROFIT EMISSIONS CONTROLS.

L. BRUCE HILL, James Gooch, Clean Air Task Force, Boston, MA Neil Zimmerman, Purdue University, West Lafayette, IN

Previous studies have documented potentially harmful aerosols in the cabins of yellow school buses. This study investigated: 1) causes of in-cabin diesel particulate matter exposures in conventional school buses, 2) cabin air quality in buses retrofit with emissions controls.

Testing was conducted on school buses in three U.S. cities—Chicago, IL and Atlanta, GA and Ann Arbor, MI in 2003 and 2004. Buses were tested during: a) idling, b) queuing, and c) on typical hour-long bus routes. During bus routes, windows were closed. A lead car with identical instrumentation was used as a control to characterize ambient air in the roadway in front of the bus, as a potential source of cabin aerosol. Actual school bus routes were followed twice in largely residential neighborhoods with few nearby diesel sources.

PM2.5, ultrafine particles, black carbon and particle-bound PAH were found to routinely build up in the cabin due to emissions from the tailpipe and engine. Aerosol emissions generally entered the bus through the front door, when open, during bus routes, idling, and queuing. Ultrafine particles, black carbon, and particle-bound PAH were associated with the tailpipe emissions. In contrast, fine mass (PM2.5) concentrations were associated with crankcase emissions that typically vent under the hood through a “road draft” or “blow-by” tube, subsequently entering the bus through the front door. Aerosol build-up was dependant on relative wind direction between the two identified emissions sources and the front door.

Ultrafine particles, black carbon, and PAH dropped to near limits of detection in the cabin following installation of a diesel particulate filter (DPF) and ultralow sulfur diesel fuel (ULSD). However, DPFs did not significantly reduce PM2.5 mass in the cabin as expected. Instead we found that PM2.5 was predominantly a result of strong crankcase PM2.5. Following installation of a closed-crankcase filtration device, the Donaldson Spiracle, PM2.5 was largely eliminated in the cabin. The combined use of the DPF, Spiracle and USLD resulted in near elimination of measured aerosols in the bus cabin.

In other experiments, significant ultrafine particles, black carbon and PAH remained in a bus retrofit with a diesel oxidation catalyst. A compressed natural gas bus showed little build up of PM2.5 and limited ultrafine particle self-pollution.

This research suggests that the combination of a catalyzed diesel particulate filter, ultralow sulfur fuel and a closed crankcase filtration device provides effective mitigation of cabin aerosols on conventional school buses.

9C2

PREDICTORS OF IN-VEHICLE ULTRAFINE PARTICULATE MATTER CONCENTRATIONS AND OTHER VEHICLE-RELATED POLLUTANTS ON LOS ANGELES FREEWAYS.

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Time spent in vehicles is an important route of exposure to air pollution, but few studies of ultrafine particle (UFP) concentrations on roadways have been conducted. In this study, a Toyota RAV 4 electric vehicle was used to house and power a collection of real-time or near real-time particle measurement instruments including two condensation particle counters (TSI Model 3007 and TSI 3022A) and two Scanning Mobility Particle Sizers for UFP measurements. In addition, real-time measurements were made of NOx (by chemiluminesence), CO/CO2, black carbon (by light absorption), particulate matter-phase PAH (by UV ionization), and particle length (by diffusional charging). Measurements were conducted on a variety of streets and freeways in Los Angeles from February through April, 2003. High correlations between UFP numbers and diesel vehicle-related pollutants were observed (e.g., Pearson’s r2~0.8 for NO, 0.8 for black carbon, 0.7 for PAH, and 0.9 for particle length). While diesel-powered vehicles were often a major source of high UFP count concentrations (e.g., >100,000 per cm3) when followed directly, gasoline-powered vehicles were sometimes observed to produce comparably high UFP counts when the vehicles were older or underwent hard accelerations. After compiling a video-assisted, real-time record of location, speed, acceleration, congestion, diesel truck density, and the vehicle-followed, multiple regression and ANOVA analyses showed that 60 to 80 % of the variability (i.e., R2 of 0.6 to 0.8) in UFP count, black carbon, NO, and particulate-bound PAH concentrations was explained by the particular freeway segment or diesel truck densities. In addition, annual average diesel truck counts for each freeway segment were found to be highly linearly correlated with UFP concentrations (Pearson’s r2~0.9), indicating good estimates of in-vehicle and roadway UFP concentrations can be made from existing truck counts. Other measures such as speed, total congestion, and vehicle followed were much less predictive of concentrations of these pollutants, although congestion was a decent predictor of CO and CO2. UFP concentrations on freeways were more than an order of magnitude higher than in residential locations, indicating that urban freeway commuters likely receive the majority of their daily UFP exposure during their drive time.

9C3

IN-CABIN AND OUTDOOR NANOPARTICLES, AND ULTRAFINE PARTICLES I: SIZE DISTRIBUTION MEASUREMENTS ON LOS ANGELES ROADWAYS.

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On-road exposure to nanoparticles (NPs, dp < 50nm) and ultrafine particles (UF, dp < 100nm) is of growing concern worldwide in megacities and other large urban centers as a result of increasing traffic congestion. Such particles represent an important component of PM2.5, and show high toxicity in laboratory animals. Human exposure to high concentrations typically found near major freeways and roadways lead to concern about adverse human health impacts. NPs and UF particles are capable of entering the circulatory system when inhaled and exert adverse pulmonary effects by generating airway inflammation. Increasing evidence suggests that the toxicity of these particles may result from their small size, large number concentration, high organic carbon content (including polycyclic aromatic hydrocarbons and quinones), and their ability to localize in subcellular organelles such as mitochondria (Li et al., 2004, Miguel et al., 2005).

We report in-cabin and outdoor measurements of particle size distributions while driving on Los Angeles roadways in a 2003 VW Jetta Wagon 1.8T equipped with a factory-installed HEPA-activated carbon particle filtration system. Outdoor particles, sampled through a 3 mm (id) probe mounted on the window, were measured in the 7 nm – 300 nm diameter range (1-min scans) using a TSI model 3785 water-based condensation particle counter (WCPC), a TSI model 3080 scanning mobility particle sizer (SMPS), and a TSI model 3081 electrostatic classifier and differential mobility analyzer. In-cabin and outdoor particle size distributions were measured under different operating conditions of vehicle speed, air conditioning and ventilation system settings. Observed in-cabin and outdoor particle size distributions in the 7 – 300 nm range were observed to be mostly bimodal, with peaks occurring at 20-30 nm (Aitken size range) and 80-90 nm (ultrafine range). At times, outdoor particles showed an additional mode centered at ~200 nm. The HEPA-activated carbon filter offered an in-cabin protection of up to 70% for particles in the Aitken size range, but only 10-30% for particles in the 30-120 nm size range.

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9C4

CHARACTERIZATION OF THE MECHANISM OF DIESEL PARTICULATE MATTER PENETRATION INTO SCHOOL BUSES.

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In a previous study, we found that concentrations of diesel vehicle-related pollutants such as black carbon and particle-bound PAHs were significantly higher on board conventional diesel school buses when windows were closed compared with ambient background or with windows open. This was due to the intrusion of the bus's own exhaust, as demonstrated through the use of a tracer gas added to each bus's exhaust. In a related study we found that even higher transient peak concentrations were observed with windows open when following a diesel-powered school bus or other diesel vehicles.

In our present research, the mechanism and degree of exhaust penetration into the cabin of school buses was evaluated using tracer gases injected into the exhaust pipe and monitored in the cabin. We simultaneously measured total particle number concentration in the cabin, using a condensation particle counter, and the concentration of particle-bound polycyclic aromatic hydrocarbons, using a photoionization detector. The tracer gases, propylene and sulfur hexafluoride (SF6) were metered into the exhaust pipe in proportion to the flow rate of air into the intake manifold of the engine. Tracer gas concentrations were measured in real time using photoionization detection for propylene and electron capture detection for SF6.

We also conducted "leader-follower" experiments in which an instrumented bus was used to characterize self- pollution using one tracer while following another bus that released a different tracer gas to characterize the penetration of the leader's exhaust into the following bus. The degree of exhaust intrusion due to each of the buses was evaluated through this simultaneous release of two different tracer gases.

The effectiveness of two methods to reduce exposure to diesel particulate matter was also evaluated. In the first method the exhaust outlet from near the rear bumper was redirected to above the bus cabin (still at the rear of the bus). In order to directly compare the benefit, the exhaust pipe was split so that half of the exhaust was directed upwards, while the other half exited at the usual bumper location. A different tracer gas was used for each split. The second mitigation method was to use a high capacity blower to pressurize the bus (with windows closed) with air obtained from above the roof near the front of the bus. The effectiveness was determined by repeatedly turning the blower on and off while measuring the tracer gas concentrations and particulate matter concentrations. All tests were conducted on loops of public roads from 5 -10 miles in length and tests were conducted with windows both open and closed. Buses were chosen to represent a wide variety of "tightness" using a pressurization test.

The results showed that self-pollution of diesel particulate matter could be reduced, with varying degrees of effectiveness, by either raising the exhaust or using a blower. Using both methods together increased self-pollution under stationary conditions when the exhaust from the high release was blown towards the inlet of the blower. For all test conditions and scenarios (windows open or closed, blower on or off, and leader bus exhaust high or low), there was significant intrusion of leader bus exhaust into the follower bus.

9C5

ASSESSING EXPOSURE TO AIR TOXICS IN MICROENVIRONMENTS DOMINATED BY MOBILE SOURCES. Eric M. Fujita, David E. Campbell, Barbara Zielinska, William P. Arnott and Judith C. Chow, Desert Research Institute, Reno, NV

The Desert Research Institute conducted field measurements in California's South Coast Air Basin during summer 2004 and winter 2004/5 of volatile air toxics, PM2.5 mass, black carbon and polycyclic organic matter (POM) to characterize and assess exposures to air toxics in microenvironments dominated by mobile sources. These exposure measurements are being compared to the annual and seasonal average concentrations derived from MATES–III, which is being conducted by the South Coast Air Quality Management District (SCAQMD) from February 2004 to March 2005. Our study focuses on two specific exposed populations – 1) in-cabin exposure of commuters traveling by automobile and 2) residents living near major roadways. In-cabin measurements were made along three freeway routes in the western and central SoCAB during the morning commute period and along truck routes later in the morning. Residential exposures were measured at three locations with varying proportions of diesel and gasoline vehicle traffic. The time-integrated methods included: pumped whole-air canister samples (with upstream NOx denuder) for benzene, toluene, ethylbenzene, xylenes, styrene, 1,3 butadiene, MTBE and n-hexane; 2,4-dinitrophenylhydrazine (DNPH) cartridges for acrolein, formaldehyde and acetaldehyde; Teflon filters for gravimetric mass, quartz filters for organic and elemental carbon (IMPROVE protocol); Teflon-impregnated glass fiber filters with backup XAD resin for speciated particulate and semi-volatile organic compounds. Continuous methods include: both an active non-dispersive infrared (NDIR) and a passive electrochemical cell device for CO; NDIR for CO2; chemiluminescence analyzer for NO and NOx; nephelometer for PM2.5 mass, photoacoustic analyzer for black carbon; an active photo-ionization detector (PID) for volatile organic compounds; and optical particle counter for particle size distribution. The continuous measurements were also used to characterize the gradients in pollutant concentration from the residential sampling sites to nearby roadways and MATES regional and microscale sites.

This presentation summarizes the results from the summer and winter field studies. The ranges in observed in-cabin and near-roadway residential exposures are compared to the annual averages from the local air toxics and PM monitoring programs. The microenvironment/ambient ratios will be compared to the default values that are used in exposure models. We will also characterize and estimate contributions of gasoline- and diesel-powered vehicles to exposures to gaseous air toxics and carbonaceous particulate matter in various vehicle-dominated hotspots in the SoCAB using chemical mass balance and multivariate analysis approaches. The study is funded by the Health Effects Institute.

9C6

IN-CABIN AND OUTDOOR NANOPARTICLES, AND ULTRAFINE PARTICLES II: COLLOCATED NUMBER CONCENTRATION MEASUREMENTS ON LOS ANGELES ROADWAYS. ARANTZA EIGUREN-FERNANDEZ, Yifang Zhu, Antonio H. Miguel, William Hinds, Southern California Particle Center and Supersite, University of California, Los Angeles, CA; Susanne V. Hering, Aerosol Dynamics Inc. Berkeley, CA; William W. Nazaroff, Department of Civil & Environmental Engineering, University of California, Berkeley, CA.

In part I, we pointed out the importance of human exposure to nanoparticles (NPs, dp < 50 nm), and ultrafine particles (UF, dp < 100 nm) with respect to increasing concern related to human exposure and their toxicity, and presented our observations of in-cabin and outdoor particle size distribution measurements in the 7 - 300 nm size range, carried out on Los Angeles roadways. We now describe our observations of simultaneous in-cabin and outdoor measurements of number concentration observed while driving in the same 2003 VW Jetta Wagon 1.8T equipped with a factory-installed HEPA-activated carbon particle filtration system.

The number concentration of in-cabin particles was determined by means of sampling air through a 3 mm (id) probe and measuring particles in the ~ 5 nm - 2 micrometer diameter range using a TSI model 3785 water-based condensation particle counter (WCPC), with 1-s time-resolution. Outdoor particles were sampled through a 3 mm (id) isokinetic probe mounted on the window and measured in the 5 nm - ~ 600 nm diameter range using a Quant model 400 WCPC (distributed by TSI). Similar to part I, in-cabin and outdoor particle number concentrations were measured under different operating conditions of vehicle speed, air conditioning and ventilation system settings. Particle number concentrations measured simultaneously in-cabin and outside showed that transient changes in outside levels cause corresponding in-cabin changes approximately 30 s later, indicating rapid air-exchange in the automotive cabin. We also observed that, in general, for particles detected by the WCPC, in-cabin concentrations were ~ 70% of the outdoor levels. We will present a preliminary model that aims to predict indoor particle concentrations based on outdoor levels, taking into account vehicle and ventilation system operating parameters.

9D1

LABORATORY STUDY OF MINERAL DUST AEROSOL: HETEROGENEOUS CHEMISTRY AND PHASE TRANSITIONS.

VICKI GRASSIAN, Department of Chemistry, University of Iowa, Iowa City, IA

Mineral dust aerosol can impact a wide range of global processes including the chemistry of the Earth's atmosphere, the Earth's climate and human health. Atmospheric processing of mineral dust through heterogeneous chemical reactions and will alter how these particles impact global processes. Laboratory studies can provide a framework in which to understand the molecular-level details of the changes in the properties of mineral dust aerosol as these suspended particles are processed or aged in the atmosphere. A combined approach of applying state-of-the-art probes, including ones based on microscopy and spectroscopy, and kinetic measurements allows for a greater understanding of heterogeneous chemistry and phase transitions that can occur for mineral dust aerosol in the atmosphere.

9D2

IMPACT OF THE ORGANIC AEROSOL FRACTION ON AEROSOL HYGROSCOPICITY IN THE LOWER FRASER VALLEY: REGIONAL AIR QUALITY MODELLING RESULTS DURING THE PACIFIC 2001 FIELD PROGRAM.

CRAIG STROUD, Paul Makar, Michael Moran, Sunling Gong, Wanmin Gong, Richard Leaitch, Srinivasan Venkatesh, Air Quality Research Branch, Meteorological Service of Canada, Downsview, Ontario; Veronique Bouchet, Canadian Meteorological Centre, Meteorological Service of Canada, Dorval, Quebec; Yayne-Abeba Aklilu, Michael Mozurkewich, Department of Earth and Space Science and Centre for Atmospheric Chemistry, York University, Toronto, Ontario

Back trajectories and aerosol composition measurements in the Lower Fraser Valley, British Columbia during the PACIFIC 2001 field program show that air originating from the Vancouver plume had higher organic to sulfate aerosol ratios than air originating southwest of the valley from the coal-burning power plant source region. Concurrent aerosol hygroscopicity measurements with a tandem differential mobility analyzer showed diameter growth factors at relative humidity of 80%, GF (80%), of 1.0-1.2 during sampling from the Vancouver plume and 1.3-1.4 during sampling from the coal-burning power plant source region. This work evaluated the ability of a Unified Regional Air Quality Modelling System (AURAMS) to predict the trend and magnitude of aerosol liquid water for selected case study periods during PACIFIC 2001. A new secondary organic aerosol parameterization based on the Jiang (2004) instantaneous organic aerosol yield (IAY) approach was implemented AURAMS. Water uptake was predicted based on an iterative solution to the Köhler equation. Unfortunately, the thermodynamic parameters for the organic components in the Köhler equation are highly uncertain due to the complex speciation of the organic aerosol fraction. A series of simulations were performed with varying thermodynamic parameters (e.g. organic-phase osmotic coefficient parameterizations, Van't Hoff factors, assumptions regarding stability of meta-stable state, and deliquescence and efflorescence points) to assess the sensitivity of modelled aerosol water to estimated upper and lower limits for these parameters. Based on an optimized set of hygroscopic parameters for the organic fraction, we use the regional air quality model to estimate the impact of the organic aerosol fraction on overall aerosol hygroscopicity for summertime conditions in the Lower Fraser Valley.

9D3

GAS-PHASE MOLECULAR HALOGEN PRODUCTION FROM SEA-SALT AEROSOL PARTICLES VIA INTERFACE REACTIONS: A MODELING STUDY.

JENNIE THOMAS, Angel Jimenez-Aranda, Barbara Finlayson-Pitts, Donald Dabdub

Chamber experiments showed molecular chlorine was produced when deliquesced NaCl aerosol was exposed to ozone and light. Similarly, molecular bromine production was observed when NaBr aerosol particles above the deliquescence point interacted with ozone. For both cases, interface reactions explained observed gas-phase halogen levels.

A new interface reaction rate and a new expression for mass accommodation of gas phase species involved in interface reactions have been developed. These changes have been incorporated into an updated version of the Model of Aerosol, Gas, and Interfacial Chemistry (MAGIC 2.0).

The sensitivity of gas-phase halogen production to interface reaction probability is investigated using MAGIC 2.0. Results confirm that the interface process involving surface chloride and gas-phase OH is the dominant pathway for gas-phase molecular chlorine formation. The interface process involving surface bromide and gas-phase OH is studied for the first time showing the relative importance of interface halogen production. In this case, molecular bromine is mainly formed in the aqueous phase and transfered across the interface. For surface bromide interacting with gas-phase ozone, model results confirm that both aqueous-phase and interface chemistry contribute to gas-phase bromine formation. The effect of interface processes on pH and potential atmospheric implications will be discussed.

9D4

UNDERSTANDING THE EFFLUORESCENCE OF SUPERSATURATED AEROSOLS USING FLUORESCENCE SPECTROSCOPY.

Man Yee Choi and CHAK K. CHAN, Department of Chemical Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

The knowledge of the state of water molecules, particularly the amounts of solvated water and free water in aqueous droplets, is valuable in understanding the hydration properties of atmospheric aerosols. A novel technique combining the use of an electrodynamic balance (EDB) and a fluorescence dye, 8-hydroxyl-1,3,6-pyrenetrisulfonate (pyranine), was used to study the state of the water molecules in single levitated aqueous droplets from subsaturation to supersaturation concentrations. The steady state fluorescence spectra of NaCl, (NH4)2SO4, Na2SO4, MgSO4, Mg(NO3)2 and mixed NaCl and Na2SO4 (in 1:1 mole ratio) solutions doped with 100 ppm pyranine were measured. The fluorescence emission of pyranine is sensitive to the proton transfer capacity of its microenvironment. When excited by radiation at around 345nm, pyranine fluoresces and the spectrum consists of two peaks, one at about 440nm and the other at about 510nm, which correspond to the presence of solvated and free water, respectively. The fluorescence peak intensity ratios of the 440nm peak to the 510nm peak and the hygroscopic measurements were used to calculate the amounts of solvated and free water in the droplets as a function of relative humidity (Zhang et al., 2004). We found that the equality of the amounts of solvated and free water is a necessary but not sufficient condition for efflorescence. For efflorescing compounds such as NaCl, Na2SO4, (NH4)2SO4, and a mixture of NaCl and Na2SO4, the amount of free water decreases, while that of solvated water is roughly constant in bulk measurements and decreases less dramatically than that of free water in single-particle measurements as the relative humidity (RH) decreases. Efflorescence of the supersaturated droplets of these solutions occurs when the amounts of free and solvated water are equal (Choi and Chan, 2005). This study demonstrates that fluorescence spectroscopy is a unique tool in understanding the hydration properties, the efflorescence and the structural heterogeneity of aqueous droplets.

References:
Choi M.Y., Chan C.K. and Zhang Y.H. (2004) “Application of fluorescence spectroscopy to study the state of water in atmospheric aerosols” J. Physical Chemistry A, 108, 1133-1138.
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9D5

CHARTING WATER-AEROSOL INTERACTIONS TO INFER CHEMICAL COMPOSITION AND AGING OF AMBIENT AEROSOLS. SARA LANCE, Athanasios Nenes, Georgia Institute of Technology, Atlanta, GA; Matthew J. Dunn, James N. Smith, National Center for Atmospheric Research, Boulder, CO

While inorganic salts, such as ammonium sulfate and sea salt, are known to control the uptake of water by ambient aerosol particles at below 100% relative humidity (RH), organics and other slightly soluble compounds can substantially affect the interaction of aerosols with water vapor when they activate into cloud droplets (RH > 100%). Concurrent observations of aerosol hygroscopic uptake and cloud droplet activation can provide unique insight on the chemical composition of the aerosol as it ages and transforms in the atmosphere. The combined measurements quantitatively characterize the ability of ambient aerosols to become cloud droplets; this yields a powerful dataset useful for testing the theory used to study aerosol-cloud interactions as well as providing constraints for modeling studies of the aerosol indirect effect on climate.

We present laboratory and in-situ results from this aerosol-water interaction measurement technique. We use a Droplet Measurement Technologies Cloud Condensation Nucleus counter (CCNc) to obtain the activation potential and droplet growth kinetics of an aerosol sample, while the hygroscopic water uptake is measured with a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA). Laboratory-generated single and multi-component aerosol are used to test the methodology. Following this, ambient measurements are performed at the Marshall Field Site, located in a rural area SE of Boulder, CO. These measurements are supplemented with those of chemical composition using the Thermal Desorption Chemical Ionization Mass Spectrometer.

9D6

FORMATION OF HYDROXYL RADICAL FROM THE PHOTOLYSIS OF NITRITE, NITRATE, AND HYDROGEN PEROXIDE ON ICE. CORT ANASTASIO and Liang Chu, Atmospheric Science Program, Department of Land, Air & Water Resources, University of California, Davis, CA

The photolysis of nitrite, nitrate, and hydrogen peroxide generates hydroxyl radicals (OH) in ice and snow. In snow these reactions are important because the photoformed OH reacts with trace species, such as organics or halides, to form volatile reactive products, such as formaldehyde and reactive halogen gases, which are released to the atmosphere and thereby alter atmospheric chemistry. Similar reactions likely occur on atmospheric ice particles, such as in upper tropospheric stratus ice clouds and perhaps on polar stratospheric clouds as well. However, the impacts of these photolysis reactions on atmospheric ice particles are currently unknown. In any case, understanding the effects of the photoformed OH requires knowing the quantum yields of OH from nitrite, nitrate, and hydrogen peroxide.

Over the past five years we have worked to determine these quantum yields on ice using benzoate as a chemical probe. For this presentation we will discuss the molar absorptivities of each chromophore (nitrite, nitrate, and hydrogen peroxide), the efficiency of each photolysis and its temperature dependence, and its pH dependence. In all cases the temperature dependence experiments reveal that the activation energy for photolysis on ice is very similar to the value in aqueous solution, suggesting that these reactions occur in a “quasi-liquid layer” on the ice. Furthermore, our results indicate that hydrogen peroxide is generally the dominant OH source of these three chromophores, although this is dependent upon their concentrations. The implications of this OH formation, and its possible effects on atmospheric chemistry, will be discussed.

9E1

FIELD MEASUREMENT DATA OBTAINED WITH A PORTABLE AEROSOL MEASUREMENT SYSTEM.

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INTRODUCTION The need to measure the full Aerosol Size distribution with one instrument will give a better informa-tion about particles in ambient air and therefore a better assessment of the possible impact on human health. There is a need for more information. To get a deeper insight in the composition of the particles, it is necessary to measure the aerosol spectrum in combination/addition with different speciation technologies. This will not only result in a better dust mass value, through the detailed knowledge the wider size distribution, it also allows a differen-tiation technology combined with a polycyclic aro-matic hydrocarbon (PAH) sensor.

METHODS Optical particle counter (particle counting with the method of orthogonal light scattering) are widely used to measure particle counts and calculate the mass of ambient aerosols. For this new approach an OPC (optical particle counter), a Grimm dust monitor #1.109 has been used, which measures the particle size distribution in over 30 different sizes channels as counts and/ or particle mass distribution (or as different PM values). This instrument has been combined with an SMPS permitting to meas-ure the aerosol size distribution from 350 to 3 nanometer again in over 40 size channels, thus in-creasing the total particle size distribution from 3 to 30.000 nanometer.

In the sample air stream outlet of the OPC, behind the measuring chamber, a new kind of PAH (Poly-cyclic Aromatic Hydrocarbons) sensor has been at-tached, to measure the amount of particle bound PAH in the ambient air. The results of this sensor is the amount of particle bound PAH in the same sample air, which has been previously monitored to determine the particle size/mass distribution. So a correlation can be made between these mass/count distributions. This permits a further speciation dur-ing the continuous monitoring of all the aerosol par-ticles. As a further option there is a heater included in the sample pipe, which can be powered to heat up the sample air until most SVC/VOC (Semi-Volatile Compounds) have vaporised. It is possible to switch between heated and unheated mode and to process the measured values. By doing so the SVC/VOC fraction in the ambient air can be determined as well. The whole system configuration is made for the mobile use. This allows for mobile measuring campaigns, hotspot measuring or source apportionment.

RESULTS AND DISCUSSION The obtained values are correlated with a new kind of software for a total distribution curve. However, when the sample pipe was heated, the mass values dropped in some cases down to 2/3 of the previous values. This phenomena is related to the amount of VOC fraction the ambient air. In order to quantitatively evaluate the correlation, other methods were used, results will be reported.

SUMMARY The combination of different continuous monitor-ing methods into one portable Environmental sys-tem will not only permit access to particle size dis-tribution and particle adsorption values, it may also be a very useful tool for atmospheric airborne parti-cle studies. Especially for field campaigns, hotspot measurements or source apportionment will this be a preferred technology.

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9E2

RAPID CHECK OF CASCADE IMPACTOR CUT SIZES USING A POLYDISPERSE CHALLENGE AEROSOL.

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A technique has been developed to rapidly check the cut sizes of cascade impactor stages. The technique involves generating a polydisperse aerosol that covers the range of the cut sizes for the impactor being tested. The amount of deposit on each impaction plate is analyzed. A histogram of the resulting aerosol size distribution is then plotted, using the amount of aerosol collected on each impaction plate and the published values for the cut sizes of the impactor in question. It is first assumed that the polydisperse aerosol is log-normal, and if the particle size distribution indicated by the histogram does not result in a log-normal distribution, one or more of the assumed cut sizes of the impactor are in error. The incorrect cut sizes of the impactor can then be adjusted until the curve is log-normal.

This calibration technique was applied to the Micro-Orifice Uniform Deposit Impactor (MOUDI) to check the published calibrated cut sizes (Marple et al, 1991). At the time of the original MOUDI calibration, the generation of monodisperse particles in the sizes near 1.0 ?m was difficult. The rapid check of the cut size for this stage showed a cut size of 0.82 ?m. This stage was then calibrated with monodisperse particles and a value of 0.85 ?m was obtained. The difference between the two values may be due to the challenge polydisperse aerosol not being truly log-normal.

To further test this new technique, the calibrated cut size values of the recently developed, and calibrated, Next Generation Pharmaceutical Impactor (NGI) (Marple et al, 2003) was checked. The resulting histogram was log-normal, indicating that a well calibrated cascade impactor needs no adjustment to stage cut sizes. This result was not unexpected, since the NGI was calibrated in just the past two years under \Good Laboratory Practice\ procedures with the latest equipment and techniques currently available.

Marple V.A., K.L. Rubow and S.M. Behm, "A Microorifice Uniform Deposit Impactor (MOUDI): Description, Calibration and Use," Aerosol Sci. and Technol., 14:434-446, 1991.

Marple, V.A., B.A. Olson, K. Santhanakrishnan and J.P. Mitchell, "Next Generation Pharmaceutical Impactor (A New Impactor for Pharmeceutical Inhaler Testing) - Part II: Archival Calibration," Journal of Aerosol Medicine, Vol. 16, No 3: 301 -324, 2003.

9E3

DESIGN AND EVALUATION OF A COARSE PERSONAL EXPOSURE MONITOR (CPEM).

JONATHAN THORNBURG, Charles Rodes, Phil Lawless, J. Randall Newsome, RTI International, RTP, NC

Interest in the particulate matter coarse fraction (PM2.5-10) is increasing due to possible health risks from elevated exposures to this component. However, the size and expense of existing dichotomous samplers prohibits their use in personal exposure studies. RTI developed an innovative impactor insert for the Marple 2 Lpm PM10 PEM to collect the coarse and fine fractions separately in a small, inexpensive package suitable for use personal and residential monitoring. Coarse and fine particulate matter fractions are collected on 25 mm and 37 mm filters, respectively.

Laboratory testing of the Coarse PEM (CPEM) was conducted with mono- and polydisperse aerosol to validate the design. The PM10 impaction plate d50 cutpoint was not affected by the additional impactor insert. The d50 cutpoint of the 25 mm filter was 2.5 micrometers. Internal losses within the CPEM were less than 3%.

CPEMs were added to the sample matrix for the DEARS Winter 2005 season for field testing. Units were deployed at residential indoor, residential outdoor, and ambient locations. CPEM, 4 Lpm PEM, and Andersen Dichotomous samplers were deployed at the ambient monitoring site. Fine fraction concentrations from the CPEMs were compared against fine fraction data measured by 4 Lpm PEMs collected at the residential indoor and outdoor locations. Linear regression of the Coarse PEM data against the other two metrics was performed. The CPEM fine fraction concentrations agreed well (R2 > 0.9, slopes = 1.0 to 1.1) with those from other metrics. A positive bias of 2.1 to 4.1 micrograms per cubic meter existed for the Coarse PEM fine fraction; possibly indicating some carryover of coarse particles to the 37 mm filter. Agreement between the coarse fraction concentrations measured by the Coarse PEM and Dichot was not as strong. The R2 was 0.44, the slope was 0.8, and the intercept was -0.9. The broader PM2.5 cutpoint on the Dichot virtual impactor probably affected the comparison. CPEM precision and accuracy goals of +/- 20% were achieved. Additional CPEM precision data, comparison of the CPEM against other dichotomous samplers, and data from DEARS Summer 2005 also will be presented.

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9E4

NUMERICAL CHARACTERIZATION OF THE FOCUSING PERFORMANCE OF AERODYNAMIC LENSES FOR NANOPARTICLES.

XIAOLIANG WANG, Ashok Gidwani, Steven L. Girshick, Peter H. McMurry, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN

We have recently reported guidelines for designing aerodynamic lenses to focus nanoparticles (Wang, et al., 2005a). In that work it was found that lighter carrier gases helped to achieve focusing of nanoparticles with larger Stokes numbers, and that maximizing the operating pressure minimized the detrimental effects of Brownian motion. We also found that a lens system having multiple lenses in series could focus particles having Stokes numbers below the optimal value. Both theoretical and empirical relations were applied when we developed these guidelines. In this presentation, we describe a numerical simulation method that can accurately characterize the focusing performance of aerodynamic lenses for nanoparticles. We use these simulations to validate the guidelines described by Wang et al. (2005b).

The numerical model utilized the commercial CFD software FLUENT version 6.1.22. We first solve the Navier-Stokes equations to obtain the particle-free gas flow (axisymmetric, steady, compressible, laminar and viscous) assuming that the particle loading is low enough so that particle-particle interactions are negligible and that the presence of particles does not affect the gas flow. Then particles are introduced into the system to obtain their trajectories and velocities by solving the Langevin equations. To account for Brownian diffusion, we include the random Brownian force along with the deterministic drag force in the Langevin equations. We applied this numerical tool to model an aerodynamic lens system designed to focus 3-nm-diameter particles of unit density. Both diffusional particle loss and beam broadening inside the lens system and in the downstream expansion are addressed. Four critical performance characteristics of this lens assembly are considered: particle penetration, beam width, terminal axial velocity, and divergence angle. With the help of this numerical tool we also compare the effects of carrier gas, particle density and lens design on the focusing performance of aerodynamic lens systems.

Wang, X., F. E. Kruis and P. H. McMurry (2005a). Aerosol Sci. Technol.: submitted.
Wang, X., A. Gidwani, S. L. Girshick and P. H. McMurry (2005b). Aerosol Sci. Technol.: submitted.

9E5

PARTICLE FOCUSING USING AERODYNAMIC LENS WITH SLITS. RAVI S CHAVALI, Goodarz Ahmadi, Suresh Dhaniyala

Ability to produce tightly packed particle beams is very useful in aerosol measurements. Conventionally, this is done by passing the particle laden gas through a series of orifices and hence forming a highly collimated beam (Liu et al. 1995a,b). This assembly is referred to as the aerodynamic lens. In this presentation, a new conceptual design of aerodynamic lens is developed and its performance for focusing of particle ranging from 10-1000 nm is studied. The new aerodynamic particle focusing system consists of a sequence of rectangular slits arranged orthogonal to their adjacent slits. This slit arrangement permits the focusing of particles alternatively into perpendicular sheets and eventually to a narrow beam. The flow fields and particle trajectories in this lens system are evaluated and the system performance for application in aerosol mass spectrometry is studied. The simulations are performed using the CFD software FLUENT® under laminar flow conditions and Lagrangian particle trajectory analysis. The particle equation of motion used includes Stokes drag and accounts for local non-continuum effects.

The performance of this system is compared to an equivalent aerodynamic lens system with orifices (Liu et al., 1995; Zhang et al., 2002). It is observed that for a given pressure drop, the assembly with slits has much higher sampling flow rate and a higher net particle number transported in a typical beam diameter of ~ 1mm compared to the orifice lens system.

9E6

USING THE ELPI TO MEASURE PM MASS. MATTI MARICQ, Ning Xu, and Richard Chase, Research and Advanced Engineering, Ford Motor Company, Dearborn, MI

The tightening of ambient and source related PM emissions has generated considerable interest in the development of on-line, real-time instrumentation. A major driver for this is the increasing desire for data with high spatial and temporal resolution that gives us the ability to perform stringent tests of atmospheric models, investigate source apportionment, carry out higher quality epidemiological studies, and develop reliable engine / aftertreatment systems. Interest is particularly high in the case of motor vehicle emissions because of the impending reductions imposed by EPA Tier II and the 2007 heavy duty regulations. PM mass data remain the center of attention, because the regulations are mass based. Unfortunately, the regulations require filter collection of the PM, which is both costly and time intensive. The present paper examines how one recent instrument, the electrical low pressure impactor (ELPI), can be used for quantitative PM mass measurements in motor vehicle exhaust. The methods that are presented should extend to other applications as well.

The standard reduction of ELPI data for submicron aerosols overestimates the PM mass by a factor of two or more. A number of reasons for this are discussed including, the response of the upper stages, loading effects, and the interplay between aerodynamic and mobility diameter. This paper introduces a model approach which assumes a lognormal size distribution and fractal-like effective density to describe the soot emissions, and then fits the ELPI currents to derive the best fit particle number concentration and mean size. This approach overcomes the issues with the standard data analysis and achieves quantitative PM mass measurement with an accuracy of about 20%. When applied to low emitting vehicles, the ELPI measurement can be many times smaller than the filter collected mass because of gas phase adsorption by the filters. The paper also discusses the extension of the model to a bimodal distribution that describes a combination of soot and nucleation modes.

10A1

GLOBAL MODELING OF NITRATE AND AMMONIUM: HETEROGENEOUS INTERACTION OF AEROSOLS AND TROPOSPHERIC CHEMISTRY.

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Global radiative forcing of nitrate and ammonium aerosols has mostly been estimated from aerosol concentrations calculated at thermodynamic equilibrium or using approximate treatments for their uptake by aerosols. However, the equilibrium assumption and other approximations can lead to important inaccuracies in the calculation of nitrate and ammonium aerosol concentration and their size distribution. In this study, a more accurate hybrid dynamic approach (DYN) was used to simulate the uptake of nitrate and ammonium by aerosols and heterogeneous interaction with tropospheric chemistry in a three-dimensional global aerosol and chemistry model, IMPACT, which also treats sulfate, sea salt and mineral dust aerosol. The agreement between the modeled and observed surface concentrations of sulfate, nitrate and ammonium aerosols falls within a factor of 2, for three sets of ground-based measurement data over oceans and polluted continents. Global annual averages show that 48% of nitrate aerosol burden, 0.165 TgN, and 90% of ammonium aerosol burden, 0.225 TgN, exist in the fine mode (D < 1.25µ;m) that scatters most efficiently. This differs substantially from the results of an equilibrium calculation where the fraction of fine-mode nitrate to total nitrate (gas plus aerosol) is 9.8%, much less than that computed by the hybrid dynamic method (14%). Our results suggest that the estimates of aerosol forcing from equilibrium concentrations will be underpredicted. Furthermore, approximations that are commonly used to treat nitrate and ammonium in aerosol, including a method using a first-order gas-to-particle loss rate determined by uptake coefficients (UPTAKE) and a hybrid method that combines the former with an equilibrium model (HYB), were also examined in sensitivity studies. It is found that both approximations, UPTAKE and HYB, significantly overpredict the nitrate uptake by aerosols especially that by coarse particles, resulting in nitrate aerosol burdens higher than that of DYN by +112% and +53%, respectively. Although HYB (0.075 TgN) predicts a similar nitrate aerosol burden as DYN (0.079 TgN) in the size range that scatters most efficiently, a much higher fine-mode nitrate burden, 0.133 TgN, was computed by UPTAKE. These results suggest the importance of using the more accurate hybrid dynamic approach in the calculation of nitrate and ammonium aerosol in global models. The use of the DYN method would not only improve the estimate of anthropogenic aerosol forcing, but would also improve the calculation of the tropospheric ozone decrease due to heterogeneous reactions on aerosols in current global gas-phase chemistry models.

10A2

A MODELING STUDY OF PARTICULATE MATTER AND ITS SENSITIVITY TO EMISSIONS UNDER INFLUENCE OF CLIMATE AND EMISSION CHANGES.

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Climate change induced by emissions of gases and particulate matter, modified land use, and other human activities has a potential feedback and can affect regional air quality. Changes in regional air quality may also impact climate at similar scales. In this work, a future climate scenario is adopted based on a simulation generated by a global climate model and downscaled to a regional scale through the MM5 modeling system. In addition, a scenario of anthropogenic emissions are likewise forecast, accounting for climate, population and emissions control changes. Effects of climate change in the future on fine particulate matter levels in the continental U.S. are assessed using the MODELS-3 system, with emphasis on sulfate and nitrate. Modeling results of particulate matter levels for a summer period are compared between a base year of 2001 and future year 2050. The sensitivity of particulate matter levels to emission controls is calculated using the Direct Decoupled Method (DDM) and is useful in that it helps indicate if current strategies on emission control should be maintained or adjusted to account for climate change.

10A3

SURFACE AND AIRCRAFT CCN MEASUREMENTS AND INSTRUMENT COMPARISONS. JAMES G. HUDSON, Subhashree Mishra, Desert Research Institute, University of Nevada, Reno, NV, Seong Soo Yum, Yonsei, University, Seoul, South Korea

Simultaneous detailed surface and airborne measurements of cloud condensation nuclei (CCN) spectra from the two Desert Research Institute (DRI) CCN spectrometers (Hudson 1989) are presented. Unlike other CCN instruments the DRI spectrometers have enough channels to provide differential CCN spectra as well as traditional cumulative CCN spectra. In order to more accurately cover the entire cloud supersaturation (S) range (1.0-0.02%) these instruments were operated over different S ranges. Measurements below the lower limit of other CCN instruments (< 0.1%, which are large CCN) are needed because:

1) Cloud S can be less than 0.1%.
2) Static CCN closure requires complete spectra.
3) Dynamic CCN closure requires complete CCN spectra.
4) Large CCN may be drizzle embryos.
5) Cloud droplet spectral width depends on complete CCN spectra.
6) Giant nuclei (diameter > 1 μm) measurements would be more credible if consistent with Large CCN measurements.
7) Wider CCN spectral measurements are needed to obtain accurate measurements of CCN sizes (Hudson and Da 1996).

Agreement between these two instruments in the overlapping S range between 0.3 and 0.1% provides confidence in these difficult measurements. This agreement for wide ranges of ambient concentrations, environments, spectral shape, and operating conditions suggests that the problems noted by Chuang et al. (2001) and Nenes et al. (2002) may have been exaggerated.

Extensive temporal measurements are presented from the rural surface ARM site in Oklahoma. These showed mostly polluted continental concentrations with some occasional low concentrations typical of maritime air masses.

Spatial and temporal measurements are presented from two aircraft field projects: one continental, AIRS2 over the Great Lakes area, and one maritime, RICO over the Caribbean. Both of these show extensive evidence of cloud scavenging. In the Caribbean concentrations were consistently maritime in the lower layers (less than 200 cm-3) where most of the clouds formed, but concentrations were rather continental (several hundred per cm3) at higher altitudes.

These measurements add to the CCN climatology that has been compiled by these instruments (e.g., Hudson and Yum, 2002; Yum and Hudson, 2005). CCN spectral measurements are essential for evaluating the largest climate uncertainty --the indirect aerosol effect.

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10A4

CLOUD CONDENSATION NUCLEI (CCN) BEHAVIOR OF PURE ORGANIC AND MIXED ORGANIC/INORGANIC PARTICLES. TRACEY A. RISSMAN, Fred J. Brechtel, Richard C. Flagan, John H. Seinfeld, California Institute of Technology, Pasadena, CA

The activation properties of particles of known organic and mixed organic/inorganic composition were studied using the Caltech cloud condensation nuclei (CCN) instrument (CCNC3). Aerosols of known chemical composition were created using an aerosol atomizer, dried in a silica gel drier, and then sent to a DMA for dry-size selection. After the DMA, the size selected aerosol is sent to a Condensation Particle Counter (CPC) and the CCNC3. The organic and inorganic species were dissolved in ethanol, instead of water, for atomization, to ensure that no water was present in the particles before size selection in the DMA and subsequent growth in the CCNC3. The organic compounds include organic aerosols that have been found to be important in the atmosphere, such as glutaric acid, oleic acid, and organic nitrates, and that vary in solubility and surface tension activity. These organics were studied in pure particles and mixed particles with inorganic salts, ammonium sulfate ((NH4)2SO4) and sodium chloride (NaCl). Aerosol particles of varying inorganic/organic and soluble/partially-soluble/insoluble composition were studied in an attempt to understand and develop the theory behind their CCN behavior.

10A5

STUDYING THE ACTIVATION BEHAVIOR OF MULTICOMPONENT ORGANIC AEROSOLS.

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Understanding the interactions of aerosol with water vapor is a major step towards quantifying the aerosol indirect effect. Yet, the amount of experimental data on the activation of carbonaceous aerosol (a major component of global aerosol) into cloud droplets is still sparse. Most available data focuses on quantifying the critical supersaturation (i.e., the level of water vapor supersaturation needed for an aerosol particle to become a cloud droplet) alone; very little experiments explore the actual growth kinetics of the droplets, as they form. Both can have a strong impact on cloud droplet formation in clouds and need to be constrained.

In this study, we will present the results from a series of activation experiments, in which laboratory-generated aerosol is exposed to a water vapor supersaturation and allowed to activate into cloud droplets. The aerosol is composed of ammonium sulfate mixed with a variety of organic acids, sugars and amino acids. The relative amounts of organic and inorganic compounds is varied, as well as the water vapor supersaturation, exposure time to supersaturation and temperature. To complement the activation experiments, we also measure the surface tension of the multicomponenet mixtures. From the experiments, we determine the activation properties of the laboratory-generated aerosol, and also determine the timescale of droplet growth. This information will give a unique insight towards the mechanisms responsible for the cloud droplet formation.

10A6

GLOBAL EVALUATION OF CCN FORMATION BY DIRECT EMISSION OF SEA-SALT AND GROWTH OF ULTRAFINE SEA-SALT.

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The contribution of sea-salt emissions and specifically the ultrafine (dry Dp < 0.1 micron) component of these emissions to CCN concentrations was assessed with a global model of aerosol microphysics. Four sea-salt emissions parameterizations were incorporated into the GISS II-prime general circulation model with the size-resolved aerosol microphysics module, TOMAS. The four simulations were compared to observations of monthly average PM10 sea-salt mass at several locations, sea-salt mass size distributions from several field campaigns and marine aerosol number distributions from an array of sources. The agreement of the simulations with the observations varied greatly based on the sea-salt emissions parameterization used. The impact of sea-salt aerosols on CCN(0.2%) concentrations was assessed by looking at the percent change in their concentrations between simulations with both sea-salt and sulfate and with sulfate alone. Two of the emissions parameterizations included ultrafine sea-salt particles, and their contribution to CCN(0.2%) formation was assessed by sensitivity studies. Depending on the emissions parameterization, the addition of sea-salt increased CCN(0.2%) over the Southern Ocean by 150% to 500%. The highest increases resulted from incorporation of ultrafine emissions. It was found that ultrafine sea-salt can increase CCN (0.2%) concentrations over both the Southern Ocean and Antarctica by over 50% relative to the same parameterizations with ultrafine sea-salt excluded. The sensitivity to ultrafine sea-salt emissions enhances the importance of reducing the uncertainty in sea-salt emissions parameterizations.

10A7

MESOSCALE AEROSOL MODELING FOR GLOBAL CLIMATE PREDICTION: MODELING THE AGING PROCESS OF SOOT. NICOLE RIEMER, Marine Sciences Research Center, Stony Brook University, Stony Brook, NY; Heike Vogel, Bernhard Vogel, Institute for Meteorology and Climate Research, Forschungszentrum Karlsruhe, Germany;

In recent years it has become evident that aerosol particles play a key role for the global climate. An important example for the complexity of aerosol-climate interactions is the aging process of soot.

Soot particles contribute both to the direct and indirect climate effect. While freshly emitted soot is initially hydrophobic and externally mixed, it can be transferred into an internal mixture by coagulation, condensation or photochemical processes. These aging processes affect the hygroscopic qualities and hence the growth behavior, the optical properties and eventually the lifetime of the soot particles. Our understanding of these processes is still fragmentary. The aging process of soot is therefore one of the key uncertainties concerning the burden and effect of black carbon.

In this study results are shown of 3D simulations with the coupled mesoscale-gamma model KAMM/DRAIS, which provides a highly resolved boundary layer and allows for an explicit treatment of the aging process of soot by coagulation and condensation. Based on the results of the simulations, the time scale on which soot is transferred from an external to an internal mixture is derived. The focus is on continental conditions in an industrialized environment, and two different meteorological scenarios are investigated, that is a summer and a winter episode.

Generally, the derived aging time scales are smaller than most of the value currently used in global climate models. A considerable variability in space and time is found suggesting that using one constant value to describe the aging process may be an oversimplification.

10B1

INVESTIGATION OF ATMOSPHERIC AEROSOL MIXING STATES USING SCANNING TRANSMISSION X-RAY MICROSCOPY. MARY GILLES, Alexei Tivanski, Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA; Bryan Marten, Lowell High School, San Francisco, CA; Lynn Russell, Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA.

Atmospheric aerosols influence the atmospheric radiative budget by directly scattering and absorbing solar radiation or by forming cloud condensation nuclei. How combustion products, such as soot, are mixed within an individual aerosol strongly affects its radiative properties. Spectromicroscopic near edge x-ray absorption fine structure (NEXAFS) studies using Scanning Transmission X-ray Microscopy (STXM) of individual particles permits probing of multiple elements and oxidation states within a particle without the requirement of a UHV environment. The sensitivity of electronic transitions to the local coordination environment is used to identify organic functional groups. In atmospheric aerosols, the intensity of the 285 eV peak is strongly dependent upon particle size for particles known to contain combustion products. Aerosols from a variety of sources (biomass burns, aircraft samples) and geographical locations (Urban US, Asia, Africa), along with soot surrogates such as n-hexane soot, resistively heated graphite, and Monarch Black carbons are examined to ascertain the variation of their NEXAFS spectra. Aerosol samples with and without combustion products are investigated to determine the potential of this method for distinguishing mixing states in atmospheric particles.

10B2

MEASUREMENTS OF SIZE-RESOLVED PARTICULATE ORGANIC TRACERS OF VEHICULAR EMISSIONS AT ROADSIDE AND TUNNEL LOCATIONS.

HARISH PHULERIA, Michael D. Geller, Constantinos Sioutas, Philip M. Fine, University of Southern California, Los Angeles, CA

Individual organic compounds found in particulate emissions from vehicles have proven useful in source apportionment of ambient particulate matter. Species of interest include the hopanes, originating in lube oil, and selected PAH generated via combustion. Most efforts to date have focused on emissions and apportionment PM10 or PM2.5. However, examining how these compounds are segregated by particle size in both emissions and ambient samples will help to apportionment of size-resolved PM, especially ultrafine particles which have been shown to be more potent toxicologically. To this end, high volume size-resolved (coarse, accumulation and ultrafine) PM samples were collected inside of the Caldecott tunnel in Orinda, CA to determine the relative emission factors for these compounds in the different size ranges. Sampling occurred in two bores, one off-limits to heavy-duty diesel vehicles, which allows determination of the different emissions characteristics for diesel and gasoline vehicles. Although tunnel measurements do not allow for a full engine duty cycle, they do provide an average emissions profile over thousands of vehicles that can be considered characteristic of “freeway” emissions. In addition, samples were collected over two seasons immediately adjacent to a Los Angeles freeway on which heavy-duty diesel vehicles are also prohibited. The emissions characteristics of gasoline vehicles determined in the tunnel were then compared to these roadside samples. Results include size-fractionated emission rates for hopanes, PAH, elemental carbon, and other organic species from both diesel and gasoline vehicles. The results are compared to previously conducted PM2.5 emissions testing using dynamometer facilities and other tunnel environments.

10B3

EXPERIMENTAL AND MATHEMATICAL ANALYSIS OF NANOPARTICLES IN THE ROADSIDE ENVIRONMENT.

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Nanoparticles have been getting much public attention recently. They are emitted from automobiles in the roadside environment. Their evolution during the transport from the roadside to the background is quite uncertain. We conducted a chamber experiment to examine the evolution of nanoparticles emitted to the roadside environment. This experiment is effective because the influence of dispersion can be excluded. A chamber of 3.0m x 5.3m x 1.9m was installed along a major road in Tokyo, Japan in February, 2004. Air was introduced into the chamber, and the evolution of particle number size distribution inside the chamber was measured by SMPS for an hour.

The chamber kept being sealed completely according to measured gaseous concentration inside it. Particle number size distribution having two peaks around 20nm and 80nm was often observed. A peak around 20nm gradually shrunk and was shifted to around 30nm and a peak around 80nm also shrunk for an hour. We examined the influence of wall loss, coagulation and condensation/evaporation on the evolution by using theoretical equations and the mathematical simulation. Shrink rate of peaks was too fast and its dependence on diameters was also different from theoretical rates of wall loss. Similar shrink of a 20nm peak was reproduced in case of considering coagulation, but not enough to explain the entire evolution. In addition to that, measured particle volume concentration decreased while it does not in principle by coagulation. When assuming components with vapor pressure similar to SOF around a 80nm peak and vapor pressure a order lower than SOF around a 20nm peak, evolution of particle number size distribution was reproduced well. In this case, the evolution was due to coagulation and evaporation.

Hydrocarbon in exhaust gas condenses on particles due to decrease of temperature inside a tailpipe and during dispersion from a tailpipe. Components with relatively high vapor pressure tend to condense on larger particles because of the Kelvin effect. It seems that evaporation of hydrocarbon condensed as described above caused the evolution of particle number size distribution. However, evolution rate is relatively slow so dispersion seems to be the major mechanism which can alter particle number size distribution in the roadside environment. Coagulation may have little influence in the actual roadside environment because air is further dispersed during the transport to the background.

10B4

DIURNAL AND SEASONAL CHARACTERISTICS OF PARTICLE VOLATILITY AND CHEMICAL COMPOSITION NEAR A LIGHT-DUTY VEHICLE FREEWAY.

THOMAS KUHN, S. Biswas and C. Sioutas, Department of Civil and Environmental Engineering, University of Southern California, Los Angeles, CA

Volatility properties of ultrafine particles were analyzed next to State Route 110 (Pasadena freeway in Los Angeles, CA USA), 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 January 12 to 25 2005, 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.

These measurements repeated a campaign during summer 2004 to study seasonal effects which are of interest since changed conditions in winter, such as a lower temperature, are likely to have an effect on nucleation of ultrafine particles from fresh vehicular emissions. Although seasonal variations are not very large in Los Angeles, changes in PM properties were observed. The conditions differed most during the evening rush-hour traffic, which in the winter campaign was after sunset with the lowest temperatures.

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 in a coarse, accumulation, and ultrafine mode. Alternately, a tandem differential mobility analyzer (TDMA) was used at the two sites. The first DMA of the TDMA selected particles of a certain diameter, while the second DMA analyzed the losses of volatile components after heating the monodisperse aerosol.

Size distributions of the ambient aerosol were measured in the two TDMA sites using one of the two DMAs. The average total ultrafine number concentrations next to the freeway were 80,000 1/cm3 during the sampling period, while they dropped to 26,000 1/cm3 at 50 m distance. These values were higher than in summer, where 46,000 and 14,000 1/cm3 were measured.

The measured volatility ranged from about 55% volume losses of 120 nm particles heated to 110 °C, to 95% losses of 20 nm particles next to the freeway. Volume losses were higher during the evenings, e.g. 53% volume losses of 120 nm particles before sunset and 61% after. The 20 nm aerosol was only internally mixed, whereas increasing non-volatile fractions were found for 40 nm (8% of particles), 80 nm (32%), and 120 nm (39%). The non-volatile fraction was lower in the evenings.

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10B5

DISPERSION OF TRAFFIC EMISSIONS IN A ROADSIDE ENVIRONMENT: MOBILE LABORATORY MEASUREMENTS AND MODELLING.

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In urban environments traffic emissions are the main source of fine particles, and due to large number of emission sources coupled to low source heights they might cause severe air quality problems in big cities. Besides continuously monitoring stationary measurement sites also mobile laboratories with higher temporal and spatial resolutions are needed to measure rapidly changing concentrations of exhaust pollutants on roads and in their vicinity.

In this study we analysed the data collected by the mobile laboratory (Pirjola et al., 2004) on a busy highway Itäväylä and nearby in the Helsinki city area during the Finnish national LIPIKA-project. The two-week winter and summer campaigns were conducted in both years 2003 and 2004. During rush hours the van was driving back and forth on Itäväylä, standing at different sites downwind on the way of 140 m away from the highway, and occasionally measuring urban background concentrations at a site 600 m northwest of the highway. The size distribution of particles in the size range of 7 nm to 10 microns was measured by the Electrical Low Pressure Impactor (ELPI) and the nucleation mode particle (3-50 nm) size distribution by the Scanning Mobility Particle Sizer (SMPS). Also concentrations of traffic exhaust gases (CO, CO2, NO, NO2), along with meteorological and geographical parameters were recorded.

The atmospheric chemistry and aerosol dynamics box model MONO32 (Pirjola and Kulmala, 2000; Pirjola et al., 2003) was applied for predicting the time development of the number concentration, size distribution and chemical composition of various particle size classes. The model uses monodisperse representation for particle size distribution; in this work we used six modes. The modal emission factors were estimated based on the LIPIKA-measurements. The dilution rate of particles was obtained from the roadside dispersion model CAR-FMI (Härkönen, 2002).

The variation of the number concentration as a function of distance from the road was well predicted. The most important process that reduced the number concentration was dilution with background air. On the other hand, the concentration of condensable vapours is the main factor in controlling the particle growth and size distribution.

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10B6

SIZE AND COMPOSITION OF PARTICULATE MATTER IN A FREEWAY ENVIRONMENT. MICHAEL ROBERT, Chris Jakober, Michael Kleeman, Dept of Civil and Environmental Engineering, UC Davis, Davis CA

Transportation is one of the major sources of particulate air pollution in urban areas. Of special interest are the size and composition characteristics of particulate matter (PM) emissions from freeways and how these characteristics change spatially and temporally. Fresh combustion particles emitted in the freeway environment are in the fine (Dp < 2.5 microns) and ultrafine (Dp < 0.1 microns) size range, exposing a large human population to potentially harmful chemical components in these particles. The evolution of transportation particles in the freeway environment must be understood to fully evaluate the potential health consequences of these particles.

In the present study, the size and composition of particles emitted from transportation sources in six size fractions between 0.056-1.8 microns particle diameter are reported from field and laboratory studies. Field measurements were made at background, adjacent, and downwind sites near the I5 freeway in San Diego, CA, during summer conditions. Laboratory measurements of tailpipe emissions from light duty gasoline vehicles and heavy duty diesel vehicles were made using chassis dynamometers operated under realistic driving cycles and load conditions. Measurements during both field and laboratory studies were made with filter-based samplers, cascade impactors, and Scanning Mobility Particle Size / Aerodynamic Particle Size instruments. The size distribution of carbonaceous (EC, OC) and ionic (SO42-, NO3-, Cl-, PO42-, Na+, NH4+, K+, Mg2+, Ca2+) material measured in field and laboratory studies will be compared, and dominant processes that shape the airborne particle size distribution in the freeway environment will be discussed.

10B7

IDENTIFICATION OF SOURCES TO AIRBORNE PM2.5 AT THE ST. LOUIS MIDWEST SUPERSITE. JONG HOON LEE, Philip K. Hopke, Clarkson University, Potsdam, NY; Jay Turner, Washington University in St. Louis, St. Louis, MO; James Schauer, University of Wisconsin-Madison, Madison, WI

The metropolitan St. Louis area spanning metropolitan St. Louis City in Missouri and East St. Louis in Illinois was the location of the Midwest Supersite. The location is situated in a setting broadly representative of the urban Midwest. This area is affected by synoptic weather patterns and free of localized influences from the Great Lakes, oceans, the Gulf of Mexico, and mountains, and includes numerous local industries such as chemical manufacturing, non-ferrous metal smelting, and paint pigment manufacture. Daily integrated 24-hr average PM2.5 composition samples were collected at the St. Louis Midwest Supersite in Illinois from June 2001 to May 2003. These samples were analyzed for major ions, temperature-evolved organic and elemental carbon, and elements. The PM2.5 compositional data were used in receptor modeling to identify sources affecting to airborne PM2.5 in the St. Louis Midwest Supersite. For the identification of source profiles and contributions, positive matrix factorization was used, and conditional probability function was calculated to locate the identified PMF sources to local known sources in the area. The PMF coupled with wind direction analysis resolves local point sources such as a zinc smelter, copper production plant, lead smelter, and steel mills. The results also include the separate identification of spark- and compression-ignition emissions. Secondary aerosol factors were determined from the analysis, along with airborne soil that is likely attributed to the long-range transport of African dust.

10C1

AEROSOL PROPERTIES IN PUBLIC TRANSPORTATION SYSTEM IN HELSINKI.

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Exposure in traffic contributes considerably to the daily total human exposure to aerosol particles. The adult population in European cities spends on the average 8 % of their workday in traffic. The concentrations in traffic are typically high due to closeness of the emission sources. The public exposure can also be significant due to large number of passengers every day. However, little is known about the exposure levels in the traffic and especially inside the cabins. We studied the exposure to aerosol particles in the public transportation system in Helsinki. The aim of the study is to measure the concentrations and properties of fine and ultrafine particles inside the cabins of public transportation in which the drivers and other people work.

The main focus of the study was to use on-line instrumentation to monitor aerosol particle number concentrations, PM2.5 mass concentrations and black carbon. In addition, the composition of the aerosols was studied. The measurements were carried out in the subway system, in buses and in trams. In addition, temperature, relative humidity and other environment conditions are monitored. The data is synchronized and connected with GPS information. The results were compared with urban air concentrations in order to study the spatial and temporal characteristics of the exposure. The measurements were carried out during different seasons and in different environments.

The investigations in the subway system showed, that the average daytime PM2.5 concentrations were 47 (± 4) and 60 (± 18) µg m-3 at the two underground subway stations and 19 (± 6) and 21 (± 4) µg m-3 at a ground level station and in subway cars, respectively. For the same measurement period the corresponding PM2.5 concentrations at the urban background and street canyon monitoring sites were 10 (± 7) and 17 (± 10) µg m-3. The particle number concentrations and size distributions at the underground subway station were very similar to those measured at the urban background monitoring site indicating that the dominating source of particles of this size is street traffic. The average daytime particle number concentration was 31 000 (± 14 000) cm-3 compared to 27 000 (± 17 000) cm-3 at an urban background monitoring site.

ACKNOWLEDGEMENTS

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10C2

NIGHT TIME CONCENTRATION AND SIZE DISTRIBUTION OF ULTRAFINE PARTICLES NEAR A MAJOR HIGHWAY IN LOS ANGELES.

YIFANG ZHU, William C. Hinds, Paul Mayo, University of California at Los Angeles, Los Angeles, CA; Thomas Kuhn , University of Southern California, Los Angeles, CA

Increasing evidence suggests that ultrafine particles (diameter < 100nm) are causally involved in inflammatory responses and may contribute to observed health effects associated with fine particles. In an urban environment, motor vehicle emissions usually constitute the most significant source of ultrafine particles. We have conducted systematic measurements of the concentration and size distribution of ultrafine particles in the vicinity of major highways at daytime in Los Angeles. The present study compares these previous measurements with those made at night.

Particle number concentration and size distribution in the size range from 7 to 300 nm were measured by a condensation particle counter (CPC) and a scanning mobility particle sizer (SMPS), respectively. Measurements were taken at 30, 60, 90, 150, and 300 m upwind and downwind from the center of the I -405 freeway. Average traffic flow at night was about 20% of that observed during the day. Particle number concentration measured at 30 m downwind from the freeway was 80% of previous daytime measurements. This discrepancy between changes in traffic counts and particle number concentrations is apparently due to the decreased temperature and lower wind speed at night. The modal diameter increases as the aerosol moves downwind from the freeway. This is similar to what we observed during the daytime. But the particle size distributions do not change as dramatically as they did during the daytime. Particle number concentration decays exponentially downwind from the freeway similar to what was observed during the day, but at a slower rate. No particle number concentration gradient has been observed for the upwind side of the freeway. No PM2.5 and very week PM10 concentration gradients were observed downwind of the freeway at night. Ultrafine particle number concentration measured at 300 m downwind from the freeway was still distinguishably higher than upwind background concentration at night. These data may be used to help to estimate exposure to ultrafine particles in the vicinity of major highways for epidemiology studies.

10C3

FROM PERSONAL EXPOSURE TRACKS TO COMMUNITY EXPOSURE MAPS: INTEGRATION OF GPS TECHNOLOGY WITH REAL-TIME PM MEASUREMENTS. JOHN VOLCKENS, Kaila Benton-Vitz, Department of Environmental and Radiological Health Sciences, Colorado State University, Fort Collins, CO

Tracking human exposure to airborne particulate matter (PM) has become increasingly more sophisticated in recent decades. The use of real-time, personal-exposure monitors allows for the temporal resolution of an individual's exposure on a minute basis. The development of small, portable global-positioning systems (GPS) allows for the resolution of spatial location on a similar time scale. By integrating these two technologies we may generate a highly resolved exposure map for an individual through space and time. Such information could provide detailed information on human exposure-activity patters as well as establish when and where the most serious exposures to PM occur. This study demonstrates that real-time, personal PM monitors may be coupled with GPS tracking technology to generate spatial-temporal exposure maps on a personal level. In addition, regional PM concentration maps may be dervied from combined tracks of multiple individuals without the use of a cost-intensive sampling campaign; these maps can provide enhanced exposure data as an alternative to traditional, fixed-point monitors. Results from a local sampling campaign will be discussed, as well as calibration and limitations of the method.

10C4

ON-ROAD MEASUREMENT OF SIZE-RESOLVED AND VAPOR-PHASE PAH EMISSIONS FROM LIGHT- AND HEAVY-DUTY MOTOR VEHICLES. Arantza Eiguren-Fernandez, Bill L. Grant, Paul R. Mayo, and ANTONIO H. MIGUEL, University of California, Los Angeles, CA.; Thomas W. Kirchstetter, Lawrence Berkeley National Laboratory, Berkeley, CA.; Robert R. Harley, University of California, Berkeley, CA.

Motor vehicles are a significant source of toxic polycyclic aromatic hydrocarbon (PAH) emissions. Fuels reformulation and vehicle technologies advancement that occurred in the 1990s places exigent demands on the assessment of how these changes affected vehicular emissions. Vapor- and particle-phase concentrations of 15 US-EPA priority pollutant PAHs were measured in the Caldecott Tunnel (San Francisco Bay Area) during the summer of 2004 and the winter of 2005. Measurements were made for uphill traffic influenced by heavy-duty diesel (HDD) truck emissions (bore 1) separately from exclusive light-duty (LD) emissions traffic (bore 2). Target species concentrations were measured in the traffic tubes ~50 m before the tunnel exit and in the background air injected into the tunnel by the ventilation fans. Fine PM2.5 and vapor-phase samples were collected onto telflon-coated fiber filters using a model LS-TM-XAD sampler (L. Sheetz Enterprises, Reno, NV); size-resolved particles were collected on aluminum foil with a new 13 stage, non-rotating, Nano MOUDI Cascade Impactor with cutpoints at 10nm, 18, 32, 56, 100, 180, 320, 560, 1,000, 1,800, 3,200, 5,600, and 10,000nm @ 10 lpm (MSP Corp. Shoreview, MN). Concentration data were normalized to fuel consumption to compute emission factors using co-located measurements of CO and CO2. Except for increased partitioning of semi-volatile PAHs to the particle-phase observed during winter, small differences were found for the others. For instance, LD emission factors, in μ;g per kg of fuel burned, for total PAHs (Σvapor +particulate) observed during the winter and summer (in parenthesis) were: naphthalene 245 (332); fluoranthene 4.57 (2.99); chrysene 1.10 (0.85); benzo[a]pyrene 0.77 (0.60); benzo[ghi]perylene 1.42 (1.39); and indeno(1,2,3-cd) pyrene 0.58 (0.62). The observed emission factors are, on average, about ten fold lower than those reported in our previous study (Marr et al., 1999). Our size-resolved PAH emission factor estimates for LDs during winter show that, 20% and 50%, respectively, of the total emissions of benzo[a]pyrene and benzo[ghi]perylene are associated with particles in the Aiken size range (Dp < 56 nm). For HDDs, about half of the benzo[a]pyrene emissions, and nearly all of the benzo[ghi]perylene emissions are in the ~6 to 56 nm size range. Emission factors for vapor-phase, PM2.5 PAHs, for each vehicle class, and size-resolved particulate PAHs will be presented, along with toxicological concerns regarding these findings.

Marr L.C., Kirchstetter T.W., Harley R.A., Miguel A.H., Hering S.V., Hammond S.K. (1999) Environ. Sci. Technol. 33:3091-3099

10C5

AITKEN MODE MEASUREMENTS WITH A NEW COMMERCIAL NANO-DMA IN COMBINATION WITH A HIGHLY SENSITIVE ELECTROMETER. C. GERHART 1), T. Rettenmoser 1), M. Richter 2) and H. Grimm 1) 1) GRIMM AEROSOL Technik GmbH, Dorfstrasse 9, D-83404 Ainring, Germany. 2) G.I.P GmbH, Research Department, Mühlbecker Weg 38, 0671 Pouch, Germany.

In the recent years small particles and nucleation of new particles (Aitken mode) became more into the focus of atmospheric aerosol research. Therefore also the development of new techniques and instrumentation has been increased.

Up to now mainly sensitive Condensation Particle Counters (CPC) are used for the range down to a few nanometre. The main disadvantages of CPCs are:

1. limitation to a d50 cut-off as 2 to 5 nm
2. a relatively slow response time
3. due to the operation principle of nucleus condensation a defined temperature difference and a condensation liquid and supply is required

An alternative to the condensation particle counting is the direct counting of charged particles (or ions) by electrometers. Faraday Cup Electrometer (FCE), require no liquids and supply, no optical and laser parts and are theoretical not limited in the particle size. The only limitation is given by the number of charged particles and the necessity to combine it with a Differential Mobility Analyser (DMA) to cut out adequate charged particles.

The presented new GRIMM FCE 5.700 is highly sensitive to low concentration but on the other side robust enough to mechanical shocks and pressure fluctuations.

The FCE in combination with the GRIMM Nano S-DMA (a Vienna type DMA), which is able to measure even below 1 nm, is the proper solution for nucleation measurements. With this system it is possible to measure already bigger ion clusters around 0.8 nm and up to about 50 nm [1].

There are three important advantages of this system (fig 1):

1. The DMA has an active length of just 15 mm, short inlet distances and avoids electrical fields at the isolator section. This leads to comparatively low losses of fine particles.
2. The FCE has a sensitivity down to 0.1 fA (1 Hz, ~ 600 charged particles), an automatic zero point adjustment, changeable concentration ranges and sheath airflow to reduce the humidity.
3. The connection of both devices is very simple. The DMA outlet is directly connected with the FCE inlet. The DMA is directly screwed into the FCE inlet section, so that the classified particles are directly introduced to the FCE. The distance to the FCE filter is less than 20 mm, which also leads to a reduced particle loss.

The nano-DMA is a short version of the new Vienna Type DMA 5.500 of GRIMM, which allows flexible length combinations by an easy alteration [2].

Both units are controlled and supplied by a separate DMA-controller. This controller supplies the system with sheath air (5 to 20 l/min) and sample air (5 to 20 l/min), controls the high-voltage power supply for the DMA and has a data acquisition system and interface integrated.

LITERATURE

[1] J. M. Mäkelä, G. P. Reischl and J. Necid „Ion Spectra of Organic Vapours as a Mobility Reference for DMA Testing Purposes“ J. Aerosol Sci., Vol 28, Suppl. 1, pp S705 - S706, 1997

[2] Reischl, G. P., Mäkelä, J. M. and Necid, J. \Performance of Vienna Type DMA at 1.2 - 20 Nanometer\ Aerosol Sci. and Technol., Vol. 27, pp. 651 - 672 (1997).

10C6

ESTIMATING AEROSOL SURFACE AREA IN THE AUTOMOTIVE INDUSTRY. DOUGLAS E. EVANS, Andrew D. Mayard, National Institute for Occupational Safety and Health Division of Applied Research and Technology Cincinnati, OH, U.S.A. Thomas M. Peters and William A. Heitbrink The University of Iowa Department of Occupational and Environmental Health, Iowa City, IA, U.S.A.

An increasing number of studies have indicated that possible adverse health effects arising from inhaling low-solubility respirable particles may be more appropriately associated with particle surface area than with mass concentration. While exposure data from both the workplace and the ambient environment are needed to further investigate associations between aerosol surface area and health, the means of measuring exposure to aerosol surface area are not readily available.

One possible interim solution is to make initial estimates of particle surface area exposure from measurements of particle number and mass concentration, using readily available direct-reading instruments (Maynard; 2003). By assuming a lognormal aerosol size distribution with a specific geometric standard deviation, number and mass concentration measurements may be used to estimate the surface area concentration associated with the distribution.

The applicability of this approach is being experimentally evaluated in aerosol characterization studies within the automotive industry. Co-located measurements have recently been conducted with condensation nucleus counters, aerosol photometers and diffusion charger based instruments in workplaces within the automotive industry. Environments have included a foundry, an engine machining and assembly plant and within an air handling unit above the engine machining and assembly plant.

A preliminary comparison has been made between estimated surface area, from the method described above, and ‘active’ surface-area measurements made using a DC2000CE diffusion charger (EcoChem, USA). Analyses of the data show a clear linear correlation between estimated and measured aerosol surface area. However, there are indications that the gradient of the linear regression between the two is dependent on factors such as the aerosol source and the environment in which measurements are made. A full analysis of the data will be discussed.

References

Maynard A. D. Estimating Aerosol Surface Area from Number and Mass Concentration Measurements. Ann. Occup. Hyg., Vol. 47, No. 2 pp. 123-144, (2003).

10C7

REAL-WORLD AND REAL-TIME PM EMISSIONS FROM HEAVY-DUTY DIESEL VEHICLES. ANIKET A. SAWANT, David R. Cocker III, University of California, Riverside, CA

The quantitative impact of real-world emissions is a topic of great interest in academia, industry and government alike. Two factors now allow us to investigate this topic in greater depth than before. First, the advent of on-road laboratories such as the UCR/CE-CERT Mobile Emissions Laboratory (MEL) has allowed us to determine on-road emission factors as a function of engine operating mode. Second, advances in instrument technology have made possible measurements of PM in real time. These advances open up several avenues for research. For example, we can now compare conventional filter-based mass measurements with real-time PM measurements with a view towards developing a mechanistic model to account for differences between the two. Further, we can now directly compare and evaluate standardized test cycles relative to nonstandard real-world driving conditions, a task that would have been considered impossible a few years ago.

Towards this end, the MEL was used to sample emissions from an in-use Class 8 diesel tractor traveling on a historically heavily congested segment of freeway having a percentage of heavy-duty diesel vehicles three times the southern California average, and on the ARB 4-mode heavy heavy-duty diesel cycle. Two real-time PM instruments for measuring mass and mobility (Dekati DMM-230, and UCR/CE-CERT/Caltech f-SMPS, respectively) were used in conjunction with a 2007 CFR-compliant secondary dilution system for integrated PM measurement.

Our presentation will show that the two instruments track each other well, and that the DMM-230 shows very good correlation with the filter-based measurement. Additionally, we will demonstrate that a PM/NOx tradeoff occurs as the vehicle moves from lower to higher congestion conditions, and that significant increases in PM number concentrations occur during acceleration events. Further, these results are being used as inputs to emissions models such as the Comprehensive Modal Emissions Model (CMEM) and the U.S. EPA Motor Vehicle Emissions Simulator (MOVES), and we will discuss the implications of these results for the scientific community, regulatory agencies, and public policy.

10D1

AIRCRAFT EMISSIONS STUDY – NASA APEX PROJECT. CHOWEN CHOU WEY, ARL/NASA GRC, Cleveland, OH Changlie Wey, QSS/NASA GRC, Cleveland, OH

In recent years, fine particle emissions from aviation have become increasingly important since they were identified as a potentially strong contributor to global climate change as well as impacting local air quality. The international aviation community has shown interest in these potential effects, specifying measurement technology relevant to these concerns, and possible limitations and control. Regulatory agencies have likewise begun to examine methods for measuring particle emissions from aircraft gas turbine engines. There is a general consensus that current international regulations regarding visible smoke do not address and are not relevant to the measurement of particles responsible for health effects and environmental impacts.

The National Aeronautics and Space Administration (NASA) responded with an aircraft emissions study – the Aircraft Particle Emissions eXperiment (APEX) project. NASA led this collaborative research project by working closely with fellow federal government agencies, including the Environmental Protection Agency (EPA), the Department of Defense (DoD) and the Federal Aviation Administration (FAA), and by recruiting top-notch researchers in the aircraft emissions measurement field. Both gaseous and particulate emissions were acquired on multiple engine power settings from the CFM 56-2C1 engine of the NASA DC8 aircraft at 3 downstream locations and with 3 different fuels. Major gaseous species were acquired to provide foundational knowledge of engine operation conditions. Some trace gaseous species were also acquired. Both physical and chemical properties of particulate emissions were acquired by multiple instruments.

This paper will describe the detailed set-up and test procedures of the APEX project. Major gaseous species and some trace gases, including a few hydrocarbon species, will also be presented in this paper.

10D2

CONCENTRATIONS AND CHARACTERISTICS OF PARTICLES WITHIN COMMERCIAL AIRCRAFT EXHAUST PLUMES.

B. E. ANDERSON, C. H. Hudgins, K. L. Thornhill, and E. L. Winstead, NASA Langley Research Center, Hampton, VA; H. Boudries, S. Herndon, J. Jayne, R. C. Miake-Lye, T. B. Onasch, and D. Worsnop Aerodyne Research, Inc., Billerica, MA

To quantify and better understand the factors that control the generation of particles and pollutants by commercial aircraft during ground-based operation, NASA recently sponsored two collaborative field investigations: the January 2002 Experiment to Characterize Aircraft Volatile Aerosol and Trace Species Emissions (EXCAVATE), which sampled emissions from the Rolls Royce, RB-211-535-E4 engines on NASA Langley B-757 aircraft, and the May 2004, Aircraft Particle Emission Experiment (APEX), which sampled the General Electric, CFM56-2-C1 engines on NASA Dryden's DC-8. Objectives of both experiments included determining the concentration, composition, and microphysical properties of particles emitted by the aircraft as functions of engine power, fuel composition and plume age. To accomplish these goals, samples were drawn from exhaust plumes approximately 1, 10 and 30 m behind the engines as the engines burned low and high sulfur content fuels and operated at powers ranging from ground idle (4% of maximum rated thrust) to takeoff (100%). Samples were analyzed with a suite of instruments that included condensation particle counters (CPCs) and scanning mobility particle spectrometers (SMPS) equipped with thermal denuders to determine total and nonvolatile particle number densities and size distributions; soot photometers to measure elemental carbon; and an aerosol mass spectrometer to establish organic and sulfate aerosol concentrations as a function of aerodynamic diameter. Results indicate that at 1-m sampling location, black carbon (BC) dominated particle mass emissions from both aircraft. For the RB-211, BC emission indices (EI) ranged from ~20 mg/kg fuel burned at idle to ~150 mg/kg at approximately climb thrust. CFM-56 BC emissions were slightly lower, ranging from 2 mg/kg at idle to 100 mg/kg at 100% of maximum thrust. BC size distributions were mono-modal and exhibited geometric mean diameters (GMD) that increased from ~20 nm at idle to ~40 nm at high engine powers. Despite these similarities, RB-211 BC number EIs were significantly higher, ranging from 0.6 - 4 x 1015 kg-1 compared to 0.5 - 8 x 1014 kg-1 for the CFM56. For both engine types, total particle emission indices derived from 30-meter samples were typically a factor of 10 or more greater than 1-meter values, indicating that significant numbers of new particles form as the exhaust gases cool and dilute with ambient air. For the RB-211, organic aerosols derived from engine oil or unburned fuel contributed significantly to particle mass emissions, particularly after cold engine starts or power changes; EIs in some of these cases exceeded 1000 mg/kg. Organic aerosols were also detected within diluted CFM56 exhaust, but at much lower concentrations. For both engines, sulfate aerosol was primarily responsible for elevated number EIs as this species tended to undergo homogeneous nucleation to form new particles whereas the organics exhibited a greater tendency to condense onto the surface of existing soot particles. Sulfate aerosol mass (and number) EIs depended directly upon fuel sulfur concentrations and typically represented a 0.3-0.5% fraction of the total sulfur budget.

10D3

MEASUREMENT OF SPECIATED HYDROCARBONS FROM A COMMERCIAL AIRCRAFT DURING THE NASA APEX EXPERIMENT.

S. HERNDON, J. Jayne, I. Mortimer, P. Yelvington, T. Onasch, J. Wormhoudt, D. Worsnop, R.C. Miake-Lye, Aerodyne Research, Inc., Billerica, MA, USA B. Knighton, Montana State University, MT,USA

The exhaust from an in-use commercial aircraft engine was characterized in April 2004 as part of the Aircraft Particle Emissions eXperiment (APEX) at the NASA Dryden Research Center (Edwards Air Force Base, California, USA). The aircraft used for this test, a DC-8 equipped with four GE CFM56-2-C1 engines, was parked on a runway pad during all of the testing. The test matrix included seven different engine power levels (varying from ground idle to take-off), three fuels (typical Jet A, high sulfur fuel, high aromatic fuel), and three downstream distances (1, 10, 30 meters).

In addition to the wide array of aerosol measurements conducted at APEX, an effort was made to characterize trace gases emitted by the aircraft because of their environmental impact and role as aerosol precursors. This talk focuses on speciated hydrocarbon emissions, although emissions of oxides of nitrogen are also included. The instrumentation used in this study consisted of several Tunable Infrared Laser Differential Absorption Spectrometers (TILDAS), a Proton-Transfer Reaction Mass Spectrometer (PTR-MS), and a conventional Non-Dispersive Infrared (NDIR) CO2 analyzer. More than 20 hydrocarbon species were measured including alkenes, carbonyl compounds, alcohols, and aromatics. This is the first time that a comprehensive hydrocarbon speciation has been determined with fast time response instrumentation in an aircraft exhaust.

Hydrocarbon emissions were highest at idle (4-7% max. rated thrust) and decreased rapidly at higher engine powers. Formaldehyde and ethene were the most prevalent non-methane hydrocarbons in the aircraft exhaust. With the exception of a few species, the emissions indices for the heavier hydrocarbons showed a strong linear correlation with the formaldehyde emissions index. Evidence of a strong effect of downstream distance or aromatic/sulfur content of the fuel was not observed. However, chemical composition of the exhaust does seem to be affected by the conditions in the probe and sample line. Also, the highest hydrocarbon emission indices were observed during periods when the aircraft was transitioning between stable operating points. This new data will be compared to prior studies of the chemical composition of aircraft exhaust.

10D4

PM CHARACTERIZATION OF AIRCRAFT ENGINES – PROJECT APEX. PHILIP WHITEFIELD, Donald Hagen, Prem Lobo, University of Missouri-Rolla, Rolla, MO

The UMR approach for PM emission measurements of gas turbine aircraft engines, in the field, will be discussed. In particular, data taken in the exhaust nozzle exit plane and near field plume of a General Electric CFM56-2C1 engine will be presented. These data were acquired during Project APEX in April 2004. A new method for fast (0.1-1Hz) real-time analysis of the size distributions, shape parameters, number density, mass concentration and number- and mass-based emission indices of exhaust particulates from 5nm to 1000nm (1µm) was employed and this presentation will focus on these data. At the exit plane both geometric mean diameter and geometric standard deviation increase with thrust. Number-based emission indices demonstrate a minimum at mid-level thrusts. A similar but less pronounced trend is observed for mass-based emission indices. Similar measurements at two downstream locations in the near-field plume (10m and 30m) reveal evidence of gas to particle conversion. In particular new particle growth mode is observed especially at low thrust settings where plume residence times are greater and this new mode is observed to shift the distribution shape parameters to smaller mean values.

10D5

CHARACTERIZATION OF THE FINE PARTICLE EMISSIONS FROM A COMMERCIAL AIRCRAFT JET ENGINE DURING PROJECT APEX: PHYSICAL CHARACTERIZATION RESULTS. JOHN KINSEY, Lee Beck, and Michael Hays, U. S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC Craig Williams, Russell Logan, Tom Balicki, and Yuanji Dong, ARCADIS-Geraghty & Miller, Durham, NC

The fine particulate matter (PM) emissions from aircraft operations at large airports in PM-2.5 non-attainment areas are of increasing environmental concern. The International Civil Aviation Organization is also taking steps toward establishing a PM emission standard for the certification of new aircraft engines. To address the lack of substantive emissions data for modern engine designs, the U. S. Environmental Protection Agency's National Risk Management Research Laboratory (NRMRL) has initiated a major research program to characterize the fine PM emissions from commercial aircraft engines with respect to mass emissions, particle size distribution, and chemical composition. This paper provides results from a ground test conducted in April 2004 of a National Aeronautics and Space Administration-owned DC-8 aircraft equipped with CFM56-2-C1 turbofan engines located at their Dryden Flight Research Center during Project APEX (Aircraft Particle Emissions eXperiment). Sampling was conducted both at approximately 1 m behind the engine using NRMRL's dilution stack sampler and at approximately 30 m behind the engine using our Diesel Emissions Aerosol Laboratory configured for plume sampling. Available data on the PM emission factors and particle size distributions determined during APEX will be presented which incorporated an engine test cycle indicative of airport landing and take-off operations as well as a series of steady-state engine operating conditions.

10D6

CHARACTERIZATION OF THE FINE PARTICLE EMISSIONS FROM A COMMERCIAL AIRCRAFT JET ENGINE DURING PROJECT APEX: CHEMICAL CHARACTERIZATION RESULTS.

JOHN KINSEY, Lee Beck, and Michael Hays, U. S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC Craig Williams, Russell Logan, Tom Balicki, and Yuanji Dong, ARCADIS-Geraghty & Miller, Durham, NC

The fine particulate matter (PM) emissions from aircraft operations at large airports in PM-2.5 non-attainment areas are of increasing environmental concern. Of particular importance are the chemical characteristics of the PM emissions, which are needed for source apportionment studies used in the development of State Implementation Plans. To address the lack of substantive emissions data for modern engine designs, the U. S. Environmental Protection Agency's National Risk Management Research Laboratory (NRMRL) has initiated a major research program to characterize the fine PM emissions from commercial aircraft engines with respect to mass emissions, particle size distribution, and chemical composition. This paper provides results from a ground test conducted in April 2004 of a National Aeronautics and Space Administration-owned DC-8 aircraft equipped with CFM56-2-C1 turbofan engines located at their Dryden Flight Research Center during Project APEX (Aircraft Particle Emissions eXperiment). Sampling was conducted both at approximately 1 m behind the engine using NRMRL's dilution stack sampler and at approximately 30 m behind the engine using our Diesel Emissions Aerosol Laboratory configured for plume sampling. Available data on the chemical composition of the PM emissions determined during APEX will be presented which included an engine test cycle indicative of airport landing and take-off operations as well as a series of steady-state engine operating conditions. The chemical characterization results presented include water-soluble ions, elemental composition, speciated organic composition, and organic composition by particle size.

10D7

PARTICULATE EMISSIONS OF COMMERCIAL AIRCRAFT MEASURED IN THE NASA APEX EXPERIMENT.

T. B. ONASCH, J. Jayne, I. P. Mortimer, P. Yelvington, S. Herndon, D. Worsnop, R. C. Miake-Lye, Aerodyne Research, Inc., Billerica, MA, USA; B. Knighton, Montana State University, MT,USA; B. Anderson, NASA Langley Research Center, Hampton VA, USA; P. Whitefield, D. Hagen, University of Rolla, Missouri, MI, USA;

The exhaust emissions from an in-use commercial aircraft engine were characterized in April 2004 as part of Aircraft Particle Emissions eXperiment (APEX) at NASA Dryden Research Center (Edwards Air Force Base, CA). The Aerodyne Mobile Laboratory was deployed with an onboard suite of particle instruments: Aerosol Mass Spectrometer (AMS); Condensation Particle Counter (CPC); and Multi-Angle Aerosol Photometer (MAAP). The AMS measured the non-refractory PM1 chemically-speciated and size-resolved aerosol mass. The CPC provided a particle number emission index and the MAAP provided the black carbon content. Size distribution measurements were conducted with multiple Scanning Mobility Particle Sizers (SMPS) operated by NASA and UMR.

The test aircraft was a DC-8 equipped with four CFM56-2-C1 engines and was parked on a runway pad during all of the testing. The test matrix included seven different engine throttle levels (varying from ground idle to take-off, 4-93% of maximum rated thrust), three fuel compositions (nominal, high sulfur, and high aromatic), and three sampling distances behind the inboard, right side engine (1, 10, and 30 meters).

The black carbon emission indices increased with engine power, ranging from 2-100 mg/kg fuel. The organic aerosol component (lubricating oils and other hydrocarbon-based compounds) moderately increased with engine power and probe distance from 2-10 mg/kg fuel. Both of these emission components were minimized under nominal cruise throttle levels of 30-60%. The aromatic content (but not the hydrogen content) of the fuel was varied and resulted in no significant changes in the organic aerosol emissions. The sulfate emissions increased slightly with engine power and strongly with probe distance and fuel sulfur content (FSC). The exhaust emissions under idle conditions were dominated by the volatile fraction of the aerosol. The middle throttle settings had comparable volatile and black carbon compositions and the high power conditions were dominated by the black carbon component. The specific volatile-to-black carbon composition was strongly dependent upon the FSC.

The particle emissions were characterized by a bi-modal size distribution. The larger size mode consisted of black carbon with sulfate and organic coatings. The smaller mode was completely volatile and consisted of sulfate and organic components. The CPC and SMPS systems observed a dramatic increase in the number concentrations of the smaller size mode and the condensational growth of the soot mode as a function of probe distance (10-30 meters) behind the engine exit plane. The majority of the particulate sulfate is condensed in the nucleation mode.

10E1

ENHANCEMENT OF CULTURABLE AIRBORNE BIOLOGICAL AGENT COLLECTION THROUGH UTILIZATION OF THEIR NATURAL ELECTRICAL CHARGE.

MAOSHENG YAO, Gediminas Mainelis, Rutgers, The State University of New Jersey, New Brunswick, NJ

Bioaerosol exposure assessment and monitoring require effective airborne microorganism collection methods. Common microorganism sampling techniques, such as impaction and impingement, have been shown to decrease the culturability of microorganisms being sampled. Our earlier research indicated that airborne microorganisms carry certain electrical charges. Thus, we hypothesized that this phenomenon could be utilized for effective microorganisms collection by electrostatic means.

To test this hypothesis, we designed, built, and tested a new electrostatic sampling device (Electrosampler), in which the ambient airborne microorganisms were drawn in and deposited onto four square agar plates without any additional charging of incoming particles. The performance of the new sampler when collecting airborne culturable bacteria and fungi in indoor and outdoor environments was compared against a traditional microbial impactor that was operated in parallel. The Electrosampler was tested at three different collection flow rates (1.2, 5, and 10 L/min) and a fixed electrostatic field strength of 5 kV/cm inside the instrument's collection chamber. A traditional microbial impactor, BioStage, was operated at its standard sampling flow rate of 28.3L/min. The experiments in indoor and outdoor environments were performed during two independent time frames. For each set of experiments performed for both samplers, the microorganisms collected onto the agar media were incubated, and the concentrations of Colony Forming Units (CFUs) per air volume were calculated. In addition, the physical collection efficiencies of the Electrosampler when collecting airborne particles of different sizes both indoors and outdoors were also determined for all three tested sampling flow rates.

The obtained results have shown that the Electrosampler utilizing natural electrical charges on airborne microorganisms recovered substantially higher concentrations of culturable airborne microorganisms compared to the traditional impactor. This observation was true for bacteria and fungi in both test environments. In some cases, the observed difference was as large as 5-10 times. Results also indicated that the physical collection efficiency of the Electrosampler can exceed 90 % when collecting airborne particles outdoors at a flow rate of 1.2 L/min. Overall, the data obtained in this research indicate that utilization of natural microorganism charge and electrostatic collection technique may provide a bioaerosol sampling method that yields substantially higher recovery of culturable airborne microorganisms compared to inertia-based techniques.

10E2

RELEASE OF FINE RESPIRABLE CHINESE ELM POLLEN FRAGMENTS INTO THE OUTDOOR AIR: AN ASSOCIATION WITH METEOROLOGICAL FACTORS.

ANN MIGUEL, Philip Taylor, Richard Flagan, James House, California Institute of Technology, Pasadena, CA; Michael Glovsky, Huntington Medical Research Institute, Pasadena, CA

Various types of airborne pollen are important from a health perspective because they can elicit allergic responses in predisposed individuals. Whole pollen grains, 18 – 90 µm-sized particles which deposit in the nasopharyngeal region of the respiratory tract can trigger hay fever, but asthma is thought to be caused by smaller pollen fragments which are capable of reaching the small airways. Chinese elm is a prolific producer of wind-dispersed allergenic pollen. In order to understand the factors leading to pollen release and fragmentation we have examined the rupture of Chinese elm pollen, first under controlled laboratory conditions and then in the outdoor atmosphere. When freshly collected Chinese elm pollen grains were suspended in water, about 70% ruptured after a period of 30 minutes and cytoplasm was released. Chinese elm flowers, placed in the atmosphere of a controlled chamber, emitted pollen and pollen debris after a sequential treatment of high relative humidity followed by drying and a gentle disturbance. Immunologic assays were used to measure antigenic proteins specific to elm pollen present in the emitted particles. Fine particulate material ($d_p < 2$ µm) collected from the chamber contained elm pollen antigens. We then expanded our studies to the native (outdoor) environment during the Chinese elm flowering season in 2004. Peak periods of fine respirable elm antigen concentration (24 ng/m3) and pollen counts (551/m3) occurred at the beginning of the season when nocturnal relative humidity exceeded 90 %. However, later periods of hot dry weather led to much lower pollen counts which tailed off to zero. In contrast the Chinese elm pollen fragment concentration initially dropped, but displayed peaks later in the season during periods when the relative humidity and temperature were more moderate. That elm antigens were found in the ambient fine particle fraction raises the possibility for exposure of large urban populations to pollen allergens through pollen fragments.

10E3

A NEW PROTOCOL FOR MEASURING ASPERGILLUS, A MOLD COMMONLY FOUND IN THE INDOOR AIR.

MARIAN GOEBES, Lynn Hildemann, Stanford University, Stanford, CA.

Airborne mold particles are ubiquitous in the indoor environment, and can cause a variety of health problems, including allergic and asthmatic reactions. The Aspergillus genus of mold is of special interest, because its airborne concentrations in indoor environments have at times been reported to substantially exceed outdoor concentration levels. Several methods exist for the detection of Aspergillus, but none offers a sensitive, reliable, and specific estimate of its concentration. For example, culturing techniques generally underestimate concentrations and only quantify viable conidia (the asexual equivalent to spores), even though dead conidia and mature mold particles can still elicit an allergic reaction.

We have developed a sensitive, specific protocol for quantifying the concentration of airborne Aspergillus particles, regardless of viability. The protocol relies on a novel assay that uses quantitative Polymerase Chain Reaction (qPCR), a DNA-based method in which a sequence of DNA specific to the target organism is copied in cycles of temperature mediated steps. By using the number of cycles required to reach a certain threshold of concentration, the amount of DNA (and hence, the mold concentration) present in the original sample can be back-calculated. Thus, the qPCR method amplifies a previously undetectable level of mold into a detectable, quantifiable concentration.

Published qPCR assays are specific to either a single species within the Aspergillus genus, or they detect a large spectrum of molds, including those from the Penicillium genus. We will show the results of lab tests demonstrating that our assay has the unique specificity of detecting the entire Aspergillus genus, with minimal interference from non-Aspergillus organisms. We will also show that our assay has very good sensitivity: DNA representing one conidium has been reproducibly detected. Thus, we have developed an assay with very good sensitivity and specificity to Aspergillus. With this analytical technique, one could collect a series of aerosol samples with much finer time resolution, as well as separating Aspergillus particles into different size fractions (e.g., using multi-stage impactors).

The protocol is intended for use in indoor air quality testing, particularly when it is desired to focus on molds with an indoor origin but exclude as much as possible the confounding effects of molds infiltrating from the outdoors. Our goal is to use the protocol to investigate the temporal variation of Aspergillus particles indoors, in order to investigate what aspects of building design or operation may correlate with periods of elevated concentration levels.

10E4

POLLEN AND POLLEN-FRAGMENT RELEASE.

PHILIP TAYLOR, Gwenyth Card, Jennifer Fisher, James House, Michael Dickinson, and Richerd Flagan, California Institute of Technology, Pasadena, CA

Common descriptions of pollen release by anemophilous (wind-pollenated) plants suggest that pollen is actively dispersed upon anther dehiscence (opening), but most of the plants require wind or some other disturbance to release the pollen. Lacking such disturbances, most of the pollen remains on the anther for some time. A few plants do actively disperse the pollen, however, even with the most violent motions, much of the pollen remains on the anther until disturbed. Under certain meteorological conditions, some of that remaining pollen undergoes osmotic rupture, generating allergy-laden fragments that can later be released along with the pollen. We will report on observations of pollen and pollen fragment release from both types of plant. Wind tunnel studies provide reveal the wind speeds that are required to entrain pollen and pollen fragments from flowers, typically at velocities exceeding about 3m/s. Observations of bursts of pollen release at lower wind speeds provide evidence of energetic releases, while high speed movies reveal the remarkable dynamics of these events.

10E5

DEVELOPMENT AND APPLICATION OF REAL-TIME PCR TO QUANTIFY TOTAL BACTERIAL LOAD COLLECTED BY LIQUID AIR SAMPLERS.

HEYREOUN AN, Gediminas Mainelis, Lori A. White, Rutgers, The State University of New Jersey, New Brunswick, NJ

Rapid and sensitive detection methods are needed to quantify the presence of airborne microorganisms in air samples. Application of DNA-based methods offers a great potential for sensitive and rapid air sample analysis. In this study, we developed Real-Time PCR protocol for common test organisms and evaluated standard curves for optimal detection and quantification of bacterial particles collected by liquid air samplers.

Escherichia coli Catellani (ATCC 11775), one of the recommended organisms when testing bioaerosol samplers, was used in this study. PCR reactions with the universal primers to generate standard curves were performed using purified genomic DNA from pure cultured E. coli cells. The standard curves were generated from linear relationship between the threshold cycle (CT) from the above reactions and concentrations of viable bacteria (determined from Colony Forming Units) and total bacteria (determined by microscopy). Once the family of standard curves was generated, we aerosolized E. coli cells and collected them using a liquid air sampler, BioSampler. The amount of airborne bacteria from air samples was quantified using the standard curves. The obtained numbers were compared with microscopic counts and the number of bacteria entering the sampler as determined by an optical particle counter.

All standard curves generated with purified E. coli genomic DNA ranged between 50 fg DNA and 500 µg DNA, and a linear quantitative response between CT value and microorganism number over at least four log units was obtained. Our standard curves based on E. coli genomic DNA from pure culture demonstrated that we could detect between 10 cells (corresponding to 50 fg DNA) and 1x10^7 cells (corresponding to 50 µg DNA). The ratios of PCR-determined cell numbers in BioSampler's collection liquid with the number of airborne cells entering the sampler ranged from 30% to 60% depending on the repeat. There was no substantial difference in cell numbers determined using standard curves generated using either epifluorescence or light microscopy. Relatively low ratios (below 10%) were determined when CFUs were used to obtain standard curve. The ratios increased when higher microorganism concentrations were collected by the BioSampler.

The obtained data indicate that the Real-Time PCR method with universal primers for the amplification of 16S rDNA from the E. coli can be used not only to detect but also to quantitate total bacterial load in air samples. Further research is expected to improve the sensitivity and accuracy of the method.

10E6

ANTIMICROBIAL EFFICACY OF IODINATED FILTER MEDIA.

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A new technology has been developed that combines the use of filtration and iodine disinfection to provide—with a significantly lower associated pressure drop—protection against airborne pathogens equal to or better than that afforded by conventional high-efficiency filtration systems. Physical capture efficiency and biological disinfection of various types of filtration media were evaluated in this study. Capture efficiency as a function of particle size was determined along with the pressure drop associated with each filter type. During phase two the biological disinfection was evaluated using viable microorganisms.

A wide size range of ammonium fluorescein particles were generated by atomization and introduced into a filtration system for testing. Particles entering and penetrating the filters were classified by particle size using a six-stage Andersen impactor. Both iodine-treated and untreated media were compared to a control with no filter present upstream of the impactor, as well as to a standard glass fiber filter. Significant capture efficiency, greater than 97%, was observed for both the iodine-treated and untreated media tested. In many cases the efficiency was greater than 99%. There was no significant difference in capture efficiency between the iodine-treated and untreated filters. Efficiency decreased as particle size decreased. The pressure drop was initially around 3 in H2O—significantly less than that of glass fiber filters—and increased as particles were accumulated on the filter. The efficiency increased as filter thickness increased, as did pressure drop.
Suspensions of M. luteus or E. coli cells or B. subtilis spores in 25% Ringers solution were atomized and introduced into the testing system. Challenge and penetrating concentrations of microorganism were measured using two Andersen impactors in parallel with agar Petri dishes as the collection medium. After 24–36 hrs, colony forming units (cfu) on each stage were counted. A high efficiency of biological deactivation (>99.99%) was observed for M. luteus and E. coli. Viable penetration through the biocide filters was observed in 2 of 10 experiments. The collection efficiency for B. subtilis spores was over 98.68%. The higher biological removal efficiency compared to the physical capture efficiency is indicative of the presence of reactive iodine within the filtration system and/or downstream of the filter.

10E7

IDENTIFICATION OF BIO-AEROSOL ON-THE-FLY BY BIOLOGICAL ASSAY AND UV-LIF SPECTROSCOPY.

HERMES HUANG, Yong-Le Pan, Richard K. Chang
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We have built a real-time bio-aerosol deflecting [1] and collecting system cued by fluorescence spectroscopy. Suspect bio-aerosols, such as Bacillus subtilis (anthrax stimulant), were successfully deflected from the main mixed-aerosol flow, thus leading to enrichment and increased concentration that are needed for a second stage bio-aerosol identification via various laboratory methods that may take several minutes to days. However, faster on-the-fly identification systems are required. We now report a new continuously running system that can identify aerosols via biological assay of the deflected bio-aerosols.

In the present system, the aerosols are formed into a laminar air stream by an aerodynamic focusing nozzle. Each particle is illuminated by a single-shot pulsed UV-laser once it passes through a trigger volume, which is determined by the intersection of two CW diode lasers at different wavelengths. A droplet launcher instead of the air puffer [1] is triggered as soon as a flowing aerosol particle is determined by an onboard micro-processor to exhibit UV-LIF spectral signatures of pathogenic bacteria or viruses. If triggered, a nanoliter-volume droplet that contains labeled biorecognition elements will be ejected and subsequently will envelop the suspect bio-aerosol. In order to allow sufficient time for the biochemical reaction to occur, the aerosol-containing droplet is introduced into a capillary tube or microfluidics channel to allow longer time for the reaction, and the biological agent (BA) will be identified downstream.

As a proof-of-concept, we selected as the bio-recognition element avidin, labeled with a green fluorescent molecule, which is normally quenched via ligands that occupy the biotin binding sites. Biotin is used as the BA coating on micron-sized polystyrene spheres. The fluorescence increase upon binding of biotin to labeled avidin was first demonstrated in 1981 by Al-Hakiem et al. [2]. We find that within 50 ms after the collision of a large (several mm) avidin droplet with a smaller biocytin droplet, the fluorescence is detectable via excitation by an argon ion laser. Additionally, we have successfully launched 300 micron droplets into a 500 micron capillary tube. This allows us to identify suspect bio-aerosols that have been presorted by the UV-LIF from large abundance of various background aerosols.

References:
[1] Pan YL et al, “A puff of air sorts bioaerosols for pathogen identification”, Aerosol Sci. & Techn. 38, (2004) 598-602
[2] Al-Hakiem M, et al. “Fluorimetric Assays for Avidin and Biotin Based on Biotin-Induced Fluorescence Enhancement of Fluorescein-Labeled Avidin.” Analytical Biochemistry, 116, (1981) 264-267.

11A1

PROCESSING OF ORGANIC POLLUTANTS BY FOGS AND CLOUDS.

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In many environments, organic compounds account for a significant fraction of fine particle mass. Because the lifetimes of accumulation mode aerosol particles are governed largely by interactions with clouds, it is important to understand how organic aerosol particles are processed by clouds and fogs. Recently we have examined the organic composition of clouds and fogs in a variety of environments as well as how these fogs and clouds process organic aerosol particles and soluble organic trace gases.

Our results show that organic matter is a significant component of fog and cloud droplets. In polluted California radiation fogs, we observed concentrations of total organic carbon (TOC) ranging from 2 to 40 ppmC, with significantly lower concentrations measured in marine and continental clouds. An average of approximately 80% of organic matter was found in solution, while the remainder appears to be suspended material inside cloud and fog drops. Ultrafiltration measurements indicate that as much as half of the dissolved organic carbon is present in very large molecules with molecular weights in excess of 500 Daltons. Field measurements made using a two-stage cloud water collector reveal that organic matter tends to be enriched in smaller cloud or fog droplets. Consequently, removal of organic compounds by precipitating clouds or by direct cloud/fog drop deposition will be slowed due to the fact that small drops are incorporated less efficiently into precipitation and removed less efficiently by sedimentation or inertial impaction. Despite this trend, we have observed that sedimentation of droplets from long-lived radiation fogs provides a very effective mechanism for cleansing the atmosphere of carbonaceous aerosol particles, with organic carbon removed more efficiently than elemental carbon.

Efforts to characterize organic matter in clouds and fogs reveal that the most abundant species are typically low molecular weight carboxylic acids, small carbonyls and dicarbonyls, and sugar anhydrides. These species have been observed collectively to account for roughly 20-30% of the total organic carbon in some fogs and clouds. Dicarboxylic acids, frequently used as model compounds for organic CCN, typically account for only a few percent 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.

Although more than 100 organic species have been quantified in many samples, the majority of the organic carbon mass remains unspeciated by conventional approaches. Given the importance of high molecular weight material, recent efforts have focused on application of new separation and analytical approaches previously used for characterizing natural organic matter in surface waters. A particular target of this approach was characterization of \humic like substances.\

An overview of our findings concerning the amount and the speciation of organic carbon in fogs and clouds will be provided, along with information about fog scavenging of different carbonaceous particle types and contributions of fog deposition to removal of organic pollutants from the atmosphere.

11A2

ORGANIC AND INORGANIC COMPOSITION IN MARINE CLOUDS. LYNN RUSSELL, Scripps Institution of Oceanography, La Jolla, CA; Cynthia Twohy, Oregon State University, Corvallis, OR; Monica Rivera, SciTec Inc, Princeton, NJ

The interactions between aerosol chemistry and marine stratus clouds have been investigated through recent field measurements and process modeling. Ambient aerosol size distributions and chemical composition were measured during aircraft flights as part of DYCOMS II. Drizzling and non-drizzling stratus clouds were sampled with airborne measurements in the western Pacific in 2001. These data are used to assess the efficiency and chemical dependence of aerosol interactions with clouds. The particles in this study contain complex mixtures of organic and inorganic components, with many components being mixed within each individual particle. One consequence is that activation of particles in cloud reveals similar relationships for chemical constituents that have very different hygroscopic properties. Size-based differences in activation properties may account for distinctions in droplet and particle composition.

11A3

ARE ORGANIC SURFACTANTS UBIQUITOUS?. AKUA ASA-AWUKU, Athanasios Nenes, Amy Sullivan, Chris Hennigan, Rodney Weber, Georgia Institute of Technology, Atlanta,GA; Song Gao , Richard C. Flagan, John H. Seinfeld, California Institute of Technology Pasedna, CA

Quantifying the effect of water soluble organic compounds (WSOC) on cloud droplet activation constitutes a major source of uncertainty in aerosol-cloud climate interaction studies. This study focuses on characterizing the WSOC found in a diverse set of aerosol samples, such as rural biomass burning, urban Atlanta aerosol, and secondary organic aerosol samples obtained from the California Institute of Technology SOA chamber. We focus on properties most relevant for cloud droplet activation, which are surface tension depression, droplet growth kinetics and soluble mass. Surfactant properties are characterized by surface tension measurements with a KSV inc, pendant drop method tensiometer. Water soluble mass is characterized by a functional group analysis, by separation of the samples into hydrophilic, hydrophobic, and deionized components. Finally, the droplet growth kinetics and aggregate activation properties of all the samples are measured using a Droplet Measurement Technologies CCN counter.

11A4

SHIP-BASED MEASUREMENTS OF THE AEROSOL BELOW THE SOUTHEASTERN PACIFIC STRATOCUMULUS DECK.

JASON TOMLINSON, Runjun Li, Don Collins, Texas A&M University, College Station, TX

The extent and persistence of the marine stratocumulus deck over the southeastern Pacific Ocean impact both regional and global climate. Despite the importance of the cloud layer, few in-situ measurements of the aerosol population that may modulate the clouds have been made. The lack of data complicates establishing a link between the present day aerosol and cloud properties, which is a prerequisite to modeling the response of the cloud deck to future changes in aerosol emissions.

A suite of instruments including a differential mobility analyzer, a tandem differential mobility analyzer, and an aerodynamic particle sizer was operated on board the R/V Revelle in the late spring of 2003 and on board the R/V Ronald Brown in the late spring of 2004 during two similar cruises beneath the stratocumulus deck in the southeastern Pacific. Direct measurements of size-resolved hygroscopicity and volatility of the submicron aerosol, and of the size distribution of the sub- and supermicron aerosol, were used to infer size-resolved composition and CCN spectra. Hygroscopicity and volatility measurements suggest the submicron aerosol was dominated by sulfate with an ammonium to sulfate ratio of less than 1.0. The measured number size distribution was consistently bimodal, which permitted estimation of the CCN concentration and the peak supersaturation within the stratocumulus responsible for cloud processing of the aerosol. The relationship between CCN concentration and aerosol volume concentration for this region will be contrasted with that determined for other marine environments.

11A5

ON THE RELATIONSHIP BETWEEN F(RH) AND CLOUD CONDENSATION NUCLEI.

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We explore the relationship between the dependence of light scattering on relative humidity f(RH), and the number of cloud condensation nuclei (CCN) active at specified supersaturations. Data were acquired during the recent International Consortium for Atmospheric Research on Transport and Transformation (ICARTT, 2004) at the Chebogue Point ground station in Nova Scotia, Canada. A three wavelength humidified nephelometer operated by NOAA's CMDL laboratory measured the hygroscopic growth factor at a temporal resolution of 1-min. Aerosol size distributions were measured by a Differential Mobility Particle Sizer (DMPS) over the size range 3 nm - 893 nm at 10-min temporal resolution. CCN spectra were measured using a new commercially available CCN counter developed by Droplet Measurement Technologies (DMT, Boulder, Colorado). The instrument measures the number of nuclei activated at a single supersaturation. CCN spectra were acquired by cycling the instrument through 5 supersaturation points (nominally 0.1% – 0.5%) during the course of 30 min. A numerical model describing the uptake of water vapor by inorganic and/or organic particles is used to interpret the observed relationship between f (RH), size distribution, composition, and CCN. Results of this analysis will be presented, and sensitivities studies performed, to show conditions under which one can infer useful information on CCN from measured size distributions and f(RH).

11A6

CCN ACTIVITY OF MIXED INORGANIC/ORGANIC PARTICLES: LAB AND FIELD STUDIES. JONATHAN ABBATT, Keith Broekhuizen, University of Toronto, Toronto, ON; Richard Leaitch, Meteorological Service of Canada, Toronto, ON

We have studied the role that the organic component of mixed composition aerosols has on the particles' CCN abilities. In the lab, we have coated ammonium sulfate particles with a variety of organic materials, some soluble and some insoluble. In all cases, the activation properties are described well by a Kohler model that incorporates organic solubility and assumes that the vapor-pressure-lowering solute effects are additive. We see clear evidence for a size-effect from insoluble organics and no evidence for a surface-tension effect. In the field, we have conducted a CCN closure experiment on a busy urban street using parallel measurements of CCN numbers, AMS aerosol composition and particle size distributions. Using a Kohler model that incorporates the size-dependent particle compositions, we obtain full closure between modeled and measured numbers of CCN by assuming the organics are fully insoluble and that they do not lower the surface tension of the growing droplet below that of water. Together, these studies emphasize that the inorganic component of mixed composition particles is the primary driver of droplet activation.

11A7

PROPERTIES OF CLOUD CONDENSATION NUCLEI AND ICE NUCLEI IN WINTERTIME CLOUDS. CYNTHIA TWOHY, Kathryn Bearden, Oregon State University, Corvallis, OR; Sonia Lasher-Trapp, Purdue University, West Lafayette, IN; Jorgen Jensen, National Center for Atmospheric Research, Boulder, CO

In the Alliance Icing Research Study-II, wintertime clouds in the U. S. Great Lakes region and southern Canada were investigated. Cloud residual nuclei and ambient aerosol and giant nuclei were sampled using aircraft and analyzed using electron microscopy. Both droplets and particles were collected in two size ranges. Many different particle types were observed both in and out of clouds, including sulfates, salts, organics, crustal dust, and industrial metals. Sources of these particles and airmass back trajectories will be used to explore the role of anthropogenic pollution in modifying cloud microphysical properties. The preferential incorporation of various particle types into warm, supercooled, and mixed phase clouds will be discussed, using data from each of these cloud types.

Giant nuclei (larger than 1 micron) have the ability to form the largest droplets in a cloud. As a result, they are potentially very important in producing supercooled large drops (important for aircraft icing) and precipitation in supercooled and mixed phase clouds. Giant particles were sampled in clear air using an in-situ impaction device. Particles 10 to 20 microns in size were found to be abundant in this region. A variety of compositions of giant particles were observed, including organics, salts, and mixed particle types. Implications for formation of supercooled drops and precipitation, using microphysical data from the AIR-2 clouds, will be presented.

11B1

EVALUATION OF A MODEL FOR PREDICTING THE FOSSIL-FUEL AND BIOGENIC CONTRIBUTIONS TO FINE PARTICULATE CARBON.

PRAKASH BHAVE, Shaocai Yu, National Oceanic and Atmospheric Administration, Research Triangle Park, NC; Charles Lewis, U.S. Environmental Protection Agency, Research Triangle Park, NC

Radiocarbon (14C) is a robust tracer for "biogenic" sources of carbon because it retains its identity during atmospheric chemical transformations. To date, 14C data have received limited use in air quality model evaluations because most models do not distinguish between biogenic carbon and fossil-fuel carbon. For example, carbonaceous aerosol in the Community Multiscale Air Quality (CMAQ) model is tracked as elemental carbon (EC), primary organic aerosol (POA), anthropogenic secondary organic aerosol (SOA), and biogenic SOA. Of these model species, both EC and POA contain a mixture of biogenic and fossil-fuel carbon. Recently, a version of CMAQ was developed to track explicitly the EC and POA contributions from individual source categories [1]. These source-segregated model outputs may be combined with anthropogenic and biogenic SOA concentrations to obtain estimates of biogenic- and fossil-fuel-carbon concentrations. The resulting model estimates can be compared against radiocarbon-based measurements to assess our ability to simulate the source contributions to particulate carbon.

The CMAQ model was exercised for the summer 1999 season using the primary-carbon-tracking capability described above. Model results were speciated using organic-molecular source profiles and compared against molecular-tracer measurements collected at eight locations in the southeastern U.S. [2]. These comparisons indicated that the primary carbon contributions from biomass combustion and meat cooking are underestimated in the emission inventory, whereas the contributions from motor-vehicle exhaust are estimated adequately [1]. The modeled source contributions from biomass combustion and meat cooking were scaled up to match the molecular-tracer measurements, and these adjusted values were used to compute model estimates of biogenic- and fossil-fuel-carbon concentrations for evaluation against the 14C data.

Radiocarbon analyses were performed on fine-particle samples collected near Nashville, Tennessee from June 21 to July 13, 1999 [3]. These measurements showed high levels of biogenic carbon, ranging from 51% to 73% of the fine particulate carbon. The model estimates of biogenic carbon, in spite of scaling up the contributions from biomass combustion and meat cooking, are consistently lower than the measured values. Detailed comparisons will be presented and possible explanations for the differences will be discussed.

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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.

11B2

SOURCE CONTRIBUTIONS TO PRIMARY ORGANIC AEROSOL; COMPARISON OF THE RESULTS OF A SOURCE-RESOLVED MODEL AND THE CHEMICAL MASS BALANCE APPROACH.

TIMOTHY LANE, Robert Pinder, Manish Shrivastava, Allen L. Robinson, Spyros N. Pandis, Carnegie Mellon University, Pittsburgh, PA

A source-resolved model has been developed to predict the contribution of different sources to primary organic aerosol concentrations for the eastern United States during a seventeen day pollution episode starting on July 12, 2001. The inventory used in this study is based on the EPA National Emission Inventory. The performance of PMCAMx+, a three-dimensional chemical transport model, for total carbon, organic carbon (OC), and elemental carbon (EC) has been evaluated using data from the PM Supersites, AIRS and IMPROVE networks. Unlike the source-oriented model developed by Kleeman and Cass (2001), individual emission inventories developed for each source are separately tracked using PMCAMx+ to predict the primary OC and EC concentrations from each source. The source-resolved model is simple to implement and is faster than the source-oriented model because the primary OC and EC in the model did not have to be split into eight different species. This computational efficiency comes at the cost of a numerical error that is estimated to be less of the order of a few percent. Primary organic carbon and elemental carbon concentrations are tracked for eight different sources: gasoline vehicles, non-road and on-road diesel vehicles, biomass burning, wood burning, natural gas combustion, road dust, and other forms of combustion. The results of the source-resolved model are compared to the prediction of the chemical mass balance model (CMB) for Pittsburgh and Atlanta. Significant discrepancies exist between the source-resolved model predictions and the CMB model predictions for some of the sources. For example, the model predicts 28% of the primary OC in Pittsburgh is from natural gas combustion when the CMB model predicts none. Clearly the natural gas combustion emission inventory used in this study is greatly overpredicted and should be 50 times less. Other similarities and discrepancies between the source-resolved model and the chemical mass balance model for primary OC and EC are discussed along with problems in the current emission inventory for certain sources.

Reference: Kleeman, M.J. and Cass, G.R., 2001. A 3D Eulerian Source-Oriented Model For an Externally Mixed Aerosol. Environmental Science and Technology 35 (24), 4834–4848.

11B3

AN URBAN AIRPORT AS A SOURCE OF ULTRAFINE PARTICLES AND OTHER AIR POLLUTANTS FOR NEARBY COMMUNITIES.

DANE WESTERDAHL, Scott Fruin, California Air Resources Board, Sacramento, CA; Philip L. Fine, Costantinos Sioutas, University of Southern California, Los Angeles, CA

Air monitoring was performed in the vicinity of the Los Angeles International Airport (LAX). The purpose of this monitoring was to determine the nature and extent of impacts of airport operations on community air near the airport. A mobile air monitoring platform consisting of an electric RAV 4 Toyota Sub SUV, was instrumented to measure ultrafine particle number (UFP), size distributions and particle length, black carbon; oxides of nitrogen; particle-phase PAH; and carbon monoxide. Observations include background concentrations at a coastal site just upwind of the airport, community sites downwind of the airport, and a site adjacent to an active runway and taxi area. Pollutant levels were low at the coastal site with average UFP between 750 and 3800 counts/cm3, NOx between 4 to 22 ppb, black carbon between 0.2 to 0.6 ug/m3, PAH between 18 to 36 ng/m3, and particle length readings (reported by an electrical aerosol detector) between <0.01 to 0.2 mm/cm3. Markedly higher UFP values were observed 500 meters downwind of the airport with average counts of approximately 50,000/cm3 while black carbon, PAH, and NOx levels were similar at upwind and downwind locations. Particle length was approximately three times higher at the downwind site. Cyclic peaks of elevated UFP, with one observation of 1.5 million particles/cm3, were observed that corresponded to specific aircraft activity, but base levels also increased downwind of the airport. These events were found at distances as great as 800 meters from the ends of active runways, the maximum distance evaluated. An aircraft takeoff was observed from a surface street directly downwind of the runway that produced high UFP counts that reached 4.8 million particles/cm3. The UFP levels observed at downwind sites show a particle size distribution that resembles what has been measured on freeways with peak particle counts at approximately 20 nm. Upwind size distributions differ markedly with few particles smaller than 40 nm and a maximal count at approximately 90 nm. It appears that both dispersion of emissions from aircraft take-offs and landings, as well as from aircraft passing overhead on landing approaches are sources of the observed ground level UFP. These novel observations suggest that airport operations strongly impact UFP levels in areas immediately adjacent to the airport and that they extend extend farther into residential and commerce sites near the airport. This counters observations from studies performed downwind of freeway where UFP rapidly fall to near background levels within 200 meters of the freeway source.

11B4

PM 10 SOURCE APPORTIONMENT AT THREE URBAN BACK GROUND SITES IN THE WESTERN RUHR-AREA, GERMANY.

Thomas Kuhlbusch, Ulrich Quast, Klaus Schmidt, HEINZ FISSAN,IUTA e. V., Duisburg, Germany; Matthias Koch,ECOFYS,Cologne, Germany; Peter Bruckmann, Ulrich Pfeffer, State Environmental Protection Agency NRW, Germany

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). 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 with HiVol-samplers (DIGITEL DHA 80) or LowVol-samplers (LVS 3, Derenda). PM10 online data were also recorded . 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. Overall 24 different elements and chemical compounds were analysed.

The available data on PM10 and PM2.5 including the chemical composition were investigated with Positive Matrix Factorisation (PMF) 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. PMF resolved 8 factors for PM10. The data set comprised the chemical composition data of the three investigated sites. 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 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. PMF source apportionment results for PM10 and PM2.5 will be presented for the three urban background stations and the source factors discussed in more detail.

11B5

CHARACTERIZATION OF GALLIUM CONTAINING PARTICLES AND IDENTIFICATION OF THEIR SOURCES DURING THE PITTSBURGH SUPERSITE EXPERIMENT: SINGLE PARTICLE ANALYSIS, PARTICLE MASS MEASUREMENTS AND GAUSSIAN PLUME DISPERSION MODELING.

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RSMS-3, a single particle mass spectrometer, was deployed during the Pittsburgh Air Quality Study (PAQS), July 2001-September 2002, to obtain high-temporal-resolution measurements of single particle size and composition. Analysis of this data identified a class of particles composed primarily of silicon, potassium, iron, and gallium which was the single largest class of metal containing particles detected throughout the PAQS. On 10/27/01, an isolated plume of these particles impacted the measurement site for a period of seven hours from 06:00-13:00 EST. Approximately 80% of the particles detected on this day belonged to the Na/Si/K/Ca/Fe/Ga/Pb particle class and the observation of these particles was highly correlated with wind direction. As a result, it was possible to isolate the source of these particles as coal combustion within the H.J. Heinz Pittsburgh Factory. This was validated using a Gaussian Plume dispersion model and, using the same model, the particle number emission rates for this facility were determined to be as large as 1.8E16 particles/second during this event. Elemental mass distributions were constructed using the single particle data, in conjunction with concurrent SMPS measurements, for several of the metals detected in these particles, including calcium, iron, gallium and lead, and combined with MOUDI/ICP-MS distributions for the same metals to investigate some of the physical properties of the Na/Si/K/Ca/Fe/Ga/Pb particles detected on this day. The density and shape factor of these particles were estimated to be 3.9 +/- 0.8 g/cc and 1.3 +/- 0.1, respectively.

11B6

USING SINGLE PARTICLE MASS SPECTRAL SOURCE SIGNATURES TO APPORTION AMBIENT PARTICLES.

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Aerosols cause many adverse environmental effects, including deleteriously impacting health, inducing climate change, and reducing visibility. It is extremely important to better understand the relative contributions of different sources to ambient particles on both the regional and global scales. The size and chemical composition of particles emitted from a number of major atmospheric anthropogenic and natural sources, including vehicles (light duty gasoline and heavy duty diesel), coal combustion, biomass burning, and dust, have been characterized using aerosol time-of-flight mass spectrometry (ATOFMS). Single particle libraries were created which can be used for comparison with signatures acquired during ambient sampling. Several methods are used to apportion ambient aerosol particles sampled in California. The procedures used for scaling the ATOFMS data with an aerodynamic particle sizer to produce the number concentrations of particles produced from different sources will be described. The challenges encountered with this approach and potential for using ATOFMS source signatures to identify the origin of aged ambient particles will be discussed.

11B7

SELECTION OF SOURCE PROFILES FOR CHEMICAL MASS BALANCE MODELING USING ORGANIC MOLECULAR MARKERS.

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The Chemical Mass Balance (CMB) model has been used for source-apportionment of primary organic carbon (OC) and PM2.5 mass using individual organic species or molecular markers. CMB requires source profiles. A source profile is the relative emission rate of each compound from a given source class. These profiles must be representative of the set sources in the region of interest; however, profile development is often limited by the availability of resources. A common practice is to use published source profiles. From the perspective of CMB using molecular markers, source profiles have two key attributes: (1) the relative emission rate of the set compounds included in the CMB model; and (2) the molecular-marker-to-PM2.5 mass or marker-to-OC ratio of each source profile used to convert the solution onto an OC or PM2.5 mass basis.

In this talk we examine the suitability of using organic PM2.5 source profiles from the literature to estimate source contributions to fine particle concentrations in the Pittsburgh region using the CMB model. A powerful approach for comparing ambient data to source profiles is a ratio-ratio plot, which considers three compounds, two target species and a normalizing compound. Source profiles appear as points on a ratio-ratio plot, and mixing lines are drawn between different source profiles to visualize mixing scenarios. We apply this methodology to a large ambient data set of organic molecular markers measured as part of the Pittsburgh Air Quality Study. The analysis considers markers for motor vehicle emissions (hopanes and polycyclic aromatic hydrocarbons), biomass smoke (levoglucosan, resin acids, and syringols), and cooking emissions (cholesterol and alkenoic acids). The ambient PAH data are highly correlated and consistent with the coke production source profile. The ambient concentrations of cooking markers are reasonably well organized consistent with a single dominant source of these compounds, but the data are inconsistent with the available source profiles. The ambient concentrations of biomass smoke markers are not well correlated potentially reflecting the heterogeneous nature of biomass combustion. This heterogeneity complicates selection of source profiles. Ambient motor vehicle markers can be described using available source profiles, but differences in the marker-to-OC ratios of the different profiles has a significant impact on the predicted contribution of gasoline and diesel vehicle OC.

11C1

DUAL WAVELENGTH OPTICAL PARTICLE SPECTROMETER – PERFORMANCE AND ACCURACY OF A NEW APPROACH FOR OPTICAL PARTICLE MEASUREMENT.

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The optical design of a novell laser particle spectrometer (Dual Wavelength Optical Particle Spectrometer – DWOPS), which provides simultaneously and in real-time from every detected particle an information about the size and complex refractive index is investigated for its measuring feasibility and precision. We discuss the overall performance of the method for following range of parameters: particle size 0.1-10 um, real part of the refractive index 1.1 – 2.0 and imaginary part 0-1. The DWOPS is a technique based on the collection of scattered light fluxes in four angular ranges. It contains two monochromatic, focused light sources with different wavelengths illuminating aerosol particles passing through the sensing volume. Light scattered from single particles is then collected over two angular ranges in the forward and backward direction with respect to the incoming beam of each light source. The scattered light fluxes are consequently separated based on their wavelengths by means of dichroic beam splitters and collected on four scattered light sensors. This yields a quadruple set of independent scattered light pulses from each single particle, hence providing information from which optical properties and size of a particle can be obtained. The strength of this approach is its principal simplicity. In this work we characterize the performance and accuracy of the DWOPS system based on numerical modeling using stochastic method. For modeling purposes, as illumination wavelengths we selected 532 nm and 685 nm. The scattering angles were 10° - 30° and 150°-170° for both forward and backward directions with respect to the direction of propagation of both laser sources. The lasers were assumed to be unpolarized. To obtain realistic results a certain amount of noise was superimposed on the generated signals. Results are very satisfactory. We found that for the above specified range of parameters the overall particle sizing error of the technique stays always within ±7% with the reference to the ideal result. The errors in the determination of the real and imaginary part of the refractive index are typically less than ±10% and ±20%, respectively. Concluding we also present an actual optomechanical design of the DWOPS developed on the basis of this modelings efforts capable to perform optical particle measurement outlined above.

11C2

A NANO-PARTICLE, WATER-BASED CONDENSATION PARTICLE 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 20°C and 60°C respectively. Its lower cutpoint, defined as the particle size detected with an efficiency of 50% is below 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 12°C and 75°C respectively. Tests with ambient, tunnel and laboratory generated aerosols show that the effective cutpoint is below 3 nm. The time response is characterized by an exponential time constant of 0.2 sec. The relatively high aerosol sampling rate yields significantly better counting statistics, allowing much faster size distribution scans that previously possible. A dead time correction factor allows single particle counting to 100,000 cm-3. Comparison to traditional, butanol-based instruments under field conditions will be presented.

11C3

LASER INDUCED INCANDESCENCE APPLIED TO CARBON NANOTUBES AND NANOFIBERS.

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Many reacting flows are aerosols composed of multiple elements. Such is the case for catalyzed aerosols whose products will be chemically and physically different than the catalyst particle. One of the most sought aerosols are carbon nanotubes (CNTs). Aerosol synthesis of CNTs is currently the method of choice for both purity and yield of CNTs and offers the opportunity for both continuous processing and scalability. Currently, yield measurements and synthesis conditions are characterized by collecting samples for subsequent processing and electron microscope analysis, steps which do not provide real-time feedback. Clearly, process control and optimization of nanotube/nanofiber production could benefit from a real time, in situ diagnostic. One such potential diagnostic is laser-induced incandescence (LII).

It is likely, based on previous studies of LII applied to metal aerosols, that the catalyst particles contribute to the incandescence and/or plasma emission, the particular process depending upon the laser fluence. The super-elevated temperatures, derived from blackbody fits to spectrally resolved emission, observed using laser fluences of 0.8 J/cm2, suggest continuum emission from a laser generated plasma. The absence of atomic, molecular and cluster electronic emission upon the “blackbody” (plasma) radiation is surprising, but highlights the utility of 1064 nm excitation in order to avoid electronic excitation of plasma species.

Unlike previous observations, LII from the metal nanoparticles does not produce distinct spectral signatures. Thus, their relative contribution to the emission signal is not readily extracted from that arising from the carbon nanotubes or nanofibers. Additionally, it is not readily rejected, spectrally nor temporally. The short temporal existence of the emission signal from Fe-SWNT system and Ni-nanofiber system confirms that vaporization occurs at high laser fluences, e.g. 0.8 J/cm2. In this case there is no remaining solid incandescence. Fluence dependencies reveal the onset of laser induced vaporization as commensurate with that of pure carbonaceous material, approximately 0.6 J/cm2.

Two-pulse experiments highlight the differences observed in the temporal decay rates with a) dependence upon laser fluence, b) detection wavelength, c) size of laser heated nanostructure and d) laser induced material changes other than vaporization. An altered nanostructure would be consistent with the variation in LII peak intensity and different temporal decay rates produced by pulse 2, as compared to pulse 1. Apparently laser induced coalescence of the heated nanostructure occurs leading to different optical and thermal behavior. This appears to be the case for LII applied to SWNTs and nanofibers.

11C4

INTEGRATING NEPHELOMETER WITH LOW TRUNCATION ANGLE AND FAST TIME RESPONSE AND A NOVEL CALIBRATION SCHEME.

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A 4-degree-truncation angle reciprocal Integrating Nephelometer (IN) is described and demonstrated. An experimental setup for the measurement of the IN sensor cosine response is developed and described. At a correlation coefficient R2 of 0.9985, the IN sensor measured cosine response is within 1.5 % with that of the ideal cosine. To calibrate the IN, the sampling volume can be filled with an aerosol with negligible light absorption (e.g., ammonium sulfate) for which the scattering and extinction coefficients can be simultaneously monitored to verify calibration. The performance of the IN is evaluated, at 532 nm, through extensive comparison with a 1-degree-truncation angle Integrating Sphere Integrating Nephelometer (ISIN) that operates at the same wavelength. Linear regression analysis indicates that the IN measures an ammonium sulfate scattering coefficient 3 % lower than the ISIN does. Due to sensor cosine response non-ideality, the IN ambient air scattering coefficient is 8 % lower than that of the ISIN. The IN main advantages over the ISIN are its fast time response, relatively large signal-to-noise (S/N) ratio and design simplicity. In addition, the IN utilizes a novel white aerosols extinction-scattering calibration method.

11C5

MEASURING THE AEROSOL ASYMMETRY PARAMETER.

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In addition to aerosol scattering and absorption coefficients, the angular distribution of light scattered by aerosol particles is needed to determine the aerosol contribution to radiative forcing. This angular distribution is commonly parameterized into a single value, the asymmetry parameter (g), for use in large-scale radiative transfer models. The asymmetry parameter (g) is defined as the intensity-weighted average cosine of the scattering angle with values ranging from –1 for pure backscattering to +1 for pure forward scattering.

Despite the importance of g for radiative transfer and climate modeling, no instruments for the direct measurement of aerosol g in the atmosphere are available. Therefore values for g are commonly derived from other aerosol properties (Andrews et al., 2005). However, cloud integrating nephelometers (Gerber et al., 2000) and polar nephelometers (Gayet et al., 1997) have been used for the measurement of g for large particles including water drops and ice crystals and modifications to an integrating nephelometer to measure aerosol g directly (Heintzenberg and Charlson, 1996) have been proposed previously.

Here we describe a simple g sensor for use in reciprocal nephelometers or in conjunction with a laser beam. This sensor utilizes four individual light detectors to obtain a measurement of g. Possible implementations and limitations are discussed.

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11C6

PERFORMANCE EVALUATION OF A RECENTLY DEVELOPED WATER-BASED CONDENSATION PARTICLE COUNTER. SUBHASIS BISWAS, Philip M. Fine, Michael D. Geller, Constantinos Sioutas, University of Southern California, Department of Civil and Environmental Engineering, Los Angeles, California Susanne V. Hering, Aerosol Dynamics, Inc., Berkeley, California

This study provides an intercomparison of the performance of a newly developed water-based condensation particle counter (WCPC) and a more widely used butanol-based CPC (TSI 3022A). Four test aerosols (ammonium nitrate, ammonium sulfate, adipic acid, and glutaric acid) were generated and tested in the laboratory
before the instruments were deployed at four field locations (USC/downtown LA, I-710 Freeway, Pacific coast, and Los Angeles International Airport). Both instruments sampled the same incoming aerosol. Selected experiments utilized a differential mobility analyzer to select a particle size upstream of the CPCs. Evaluation of performance was based on the response of the instruments to varying particle composition, concentrations, and size. The results indicated good correlation between the two CPCs, with R2 values ranging from 0.74–0.99. Good agreement was found between the two instruments for particle concentrations between 0 and 40,000 particles/cm3, with W-CPC/TSI 3022A ratios between 0.8 and 1.2. 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 above 100,000 particles/cm3 to 1.0–1.1. Results of this evaluation show that the W-CPC is a reliable particle counting technology for particle concentrations encountered downstream of a DMA as well as in some ambient environments (<40,000 particles/cm3).

11C7

CERTIFICATION MEASUREMENTS FOR NEW 100 NM AND 60 NM NIST STANDARD REFERENCE MATERIALS. GEORGE W. MULHOLLAND, Michelle K. Donnelly, Charles Hagwood, Scott R. Kukuck, National Institute of Standards and Technology, Gaithersburg, MD

Accurate particle size calibration standards are needed for advances in aerosol science and to meet the needs of industry. In the semiconductor industry, for example, waver suppliers and integrated circuit manufacturers use scanning surface inspection systems (SSISs) to inspect bare front-end silicon wafers for particle contamination. Accurate calibration of the response, performed using certified reference particles that are typically deposited on a silicon wafer with a differential mobility analyzer followed by an electro-static deposition facility, is required in order to provide consistent compliance with wafer specifications. Certification of the size distribution for two new particle size standard reference materials has been completed based on differential mobility measurements calibrated to existing NIST SRM 1963, 100.7 nm mean particle size. The new standards are certified for the peak in the number distribution at values of 101.6 nm and 60.7 nm with expanded relative uncertainties (95 % confidence interval) of about 1.1 % of the peaks. One of these standards will replace SRM 1963, which has undergone significant agglomeration. Verification that the particles have not formed agglomerates, through the use of dynamic light scattering by suspensions of the new calibration particles in water, will be discussed. One novel feature of the study is the use the DMA transfer function together with an assumed size distribution to assess the accuracy of various methods for determining the peak size from the measured mobility distribution. The slip correction measurements by Kim et al. (NIST J. Res., 110,31-54, 2005), which is the first study on particle sizes of 100 nm and 20 nm and also the first to include a quantitative uncertainty analysis, were used in this study. An additional novel feature of the uncertainty analysis was accounting for the correlation between the slip correction uncertainty in the calibration measurement and the slip correction uncertainty in the unknown size measurement. The overall uncertainty decreases by almost a factor of two if this correlation is accounted for. The 60 nm spheres were generated using an electrospray aerosol generator to minimize the effect of nonvolatile impurities in the water enlarging the particles and to essentially eliminate doubly charged doublets. Key challenges in the use of electrospray were long term operation of three to four hours a day without clogging, elimination of CO2 to reduce the uncertainty in viscosity, and stable output with a drift of 5 % or less over a typical 15 minute scan.

11D1

COMPETING EFFECTS OF HYDROCARBON COMPOUNDS AND SULPHUR SPECIES ON THE CCN ACTIVATION OF COMBUSTION AEROSOL PARTICLES - RESULTS FROM THE PARTEMIS EXPERIMENT.

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During the European PartEmis project (Measurement and prediction of emissions of aerosols and gaseous precursors from gas turbine engines) which was focussed on the characterisation and quantification of exhaust emissions from a gas turbine engine, a comprehensive suite of aerosol, gas and chemi-ion measurements were conducted under different combustion conditions and fuel sulphur concentrations. Data sets on aerosol mass and number concentration, size distribution, mixing state, thermal stability of internally mixed particles, hygroscopicity, cloud condensation nuclei (CCN) activation potential and aerosol chemical composition were collected simultaneously from the exhaust of a gas turbine combustor. The composition of the carbonaceous particle fraction was determined using multi-step combustion methods for the determination of total carbon (TC) and elemental carbon (EC), and evolved gas analysis methods (EGA) for measuring thermograms of the thermal stability of carbonaceous compounds.
Targeted scientific objectives were aerosol microphysics and aerosol dynamics of combustion particles, formation of condensation particles from the gas phase, interaction of combustion particles with gaseous and particulate sulphuric acid, speciation of the organic fraction of combustion particles, hygroscopic particle growth factors at water-subsaturated conditions, and CCN activation at well-defined water-supersaturated conditions. Modelling of CCN activation of combustion particles was conducted using microphysical and chemical properties as measured in the experiment. Based on this unique data set, the importance of the chemical composition of the organic particle fraction and of the mass transfer of water-soluble compounds from the gas and particle phase to the combustion aerosol surface was investigated with respect to the resulting CCN activation potential of the emitted carbonaceous combustion aerosol particles.
Two major scientific questions are addressed in the presented study: 1/ Which role play volatile condensation particles forming in the cooling exhaust gas from sulphuric acid in the CCN activation of carbonaceous combustion particles? 2/ Which role plays the organic fraction of the carbonaceous combustion particles in the CCN activation process?
It was found that particles containing a large fraction of nonvolatile organic compounds grow significantly lower than particles with a lower content of nonvolatile OC. Also the effect of the nonvolatile OC fraction on the potential CCN activation is significant. While a coating of water-soluble sulphuric acid increases the potential CCN activation, or lowers the activation diameter, respectively, the organic compounds partially compensate this sulphuric acid-related improvement in CCN activation of carbonaceous combustion aerosol particles.

11D2

MICROPHYSICAL AND CHEMICAL PROPERTIES OF NANOPARTICLES EMITTED BY FLIGHT ENGINES.

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It is well known that combustion of kerosene or diesel can form soot nanoparticles. In this work it is shown, that gasoline powered piston engines can also emit nanoparticles.
Particle number concentration and particles size distribution are measured behind an aircraft gas turbine as well as behind two small aircraft piston engines. Fuel for the aircraft gas turbine was JET – A1. The two flight piston engines were both powered with AVGAS 100 LL and AVGAS 91/96 UL. AVGAS 100 LL is a leaded flight gasoline with a maximum of 0,56g lead per liter and the AVGAS 91/96 UL is special environmental friendly AVGAS (not a MOGAS!) without lead.
The both AVGAS types are produced according to the current standard specification for Aviation Gasolines, ASTM D910.
Measurements are done with a Scanning Mobility Particle Sizer system (SMPS).
Test points are the ICAO power settings Taxi, Approach, Climb and Take Off, as well as Cruise.

The measurements show that the particle mean diameter and number concentrations for the gas turbine and for the piston engines are similar! The comparison of leaded and unleaded AVGAS show a significant reduction in particle diameter and number concentration for the AVGAS 91/96 UL.
It is recommended from the piston engine manufacturer to run the piston engine under rich conditions in order to keep engine temperatures low. The fuel rich conditions give extremely high CO values. Under these conditions it is not surprising, that soot particles are formed. As an indicator for “cold and rich flames” we measured carbonyl compounds in the exhaust gases, too.

The gas turbine tests are done in the altitude test facility of Stuttgart University. The piston engine tests are done at the airport DLR Oberpfaffenhofen.

11D3

CHARACTERIZATION OF AIRCRAFT ENGINE SOOT: UNIQUE PROPERTIES AND CLOUD IMPACT. OLGA B. POPOVICHEVA, Natalia M.Persiantseva, Natalia K.Shonija, Moscow State University, Moscow, Russia;Benjamin Demirdjian, Daniel Ferry, Jean Suzanne, CRMC-N/CNRS, Marseille, France

Aircraft engine soot collected at the outlet of a D30KU combustor is comprehensively characterized by numerical experimental techniques: TEM, EDS, AFM, FTIR, GC-MS, ion and liquid chromatography and gravimetry. Physical properties (morphology, microstructure, particle size, surface area, porosity) and chemical properties (elemental composition, water soluble/insoluble organic and inorganic fraction, surface functional groups, and volatility) are examined. The water uptake by engine soot is analyzed in a wide range of the relative humidity from 0.01 to 100% and temperatures from 233K to 295K. Engine soot exhibits unique features and especially a high hydrophilicity (20ML of adsorbed water at 240K) and an heterogeneity of its composition. Comparison with laboratory–made kerosene flame soot indicates that engine soot particles separates into two fractions: an hydrophobic main fraction which contains a reduced amount of sulfur and an hydrophilic fraction of impurities with large amounts of iron, oxygen, sulfur and potassium. These results allows us to estimate the environmental conditions able to develop aircraft engine soot indirect effects with respect to ice nucleation modes proposed for contrail and cirrus formation. Our finding of two fractions in engine soot leads us to suggest that the main fraction of aircraft – generated soot may initiate a sulfur-independent heterogeneous nucleation mode in the UT while the fraction of impurities is responsible for contrail formation.

11D4

DETAILED CHEMICAL SPECIATION OF AIRCRAFT EXHAUST. DAVID R. COCKER III, Aniket A. Sawant, J. Wayne Miller, University of California, Riverside

Limited data exist on non-regulated emissions from aircraft engines. One of the goals of the Aircraft Particle Emissions Experiment (APEX), and UCR's role in this experiment, was the characterization of gas- and particle-phase non-regulated emissions from these engines.

In this work, we report PM mass, elemental and organic carbon (EC/OC), carbonyl, and C1-C12 gas-phase hydrocarbons for a CFM56 commercial turbofan engine on the APEX test aircraft operated on the International Civil Aviation Organization (ICAO) duty cycle. Emissions are compared on a per kg CO2 basis with other sources also tested by UCR, and estimates of the relative importance of local emissions inventories to local air quality are presented.

11D5

PERFORMANCE EVALUATION FOR A FAST SCAN MOBILITY BASED PARTICULATE SPECTROMETER BASED ON THE APEX DATA SET.

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There is a growing concern, internationally, on the environmental impact of jet engine exhaust emissions in the atmosphere. An accurate assessment requires that the number density and size of the aerosols within engine exhaust and aging plumes be understood and well characterized. Soot particles formed during fuel combustion and emitted metallic particles constitute the solid (nonvolatile) particle fraction present in exhaust plumes. UMR has developed a mobile facility capable of sampling jet and rocket engine exhaust emissions, including both particulate and gas phase species, and has deployed it in numerous ground test and airborne campaigns. Normally emissions measurements are taken with the engine in a stable operating condition. A fast scan particulate spectrometer, using multiple electrometer particle sensing rather than condensation nucleus counting has recently been added to our facility's instrument suite. It has a fast response, around 200 ms, and covers the size range from 5 to 1000 nm. This fast response allows for reduced engine run times, and therefore lower costs, during measurement campaigns, and for observation of emission transients during changes in engine operating conditions. Here we report on the fast spectrometer's performance in comparison to traditional particulate size and concentration measurement systems, i.e. scanning differential mobility analyzers and condensation nuclei counters. In particular a size parameter comparison revealed a -2% difference (number based geometric mean) when comparing the fast to the traditional system, and less than 1% difference for the mass based geometric mean. These are global averages taken over the entire APEX data set. The comparison is made under field conditions, i.e. during the emissions testing of a General Electric CFM56-2C1 gas turbine engine, with the engine on the wing of a NASA DC-8 aircraft. Extractive sampling was performed, under a wide range of power conditions, with emission samples taken between 1 and 30 m downstream of the engine exit plane.

11D6

MEASUREMENT OF TURBINE ENGINE PARTICULATE MASS EMISSIONS USING A TAPERED ELEMENT OSCILLATING MICROBALANCE (TEOM).

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Matthew DeWitt, David Ostdiek, Ben Mortimer, University of Dayton Research Institute, Dayton, OH

Performance assessment of a Tapered Element Oscillating Microbalance (TEOM) to measure particulate matter (PM) mass emissions from aircraft turbine engines is discussed. A Rupprecht & Patashnick TEOM Series 1105 Diesel Particulate Monitor was used to quantify PM mass from three aircraft turbine engines of different type to support several aircraft emissions related research programs. A CFM56 engine was tested on an aircraft wing (DC-8), while the other two engines, a TF33 and T63, were tested in engine facilities. The engine exhaust samples were extracted using a water-cooled sampling probe positioned near the engine exit, and transported to the instrument through conditioned sampling lines. The particle-laden samples were normally diluted with dry air or nitrogen near the sampling point to minimize particle loss via condensation, thermophoresis or others, and to extend the life of the TEOM filter. Test results show that the performance of the TEOM was strongly influenced by the type of engine, the engine power condition and the environment surrounding the instrument. Notably, problems with the TEOM operation specifically very unsteady and highly noisy data resulted due to the high vibration environment produced by the engine. For conditions where the engine vibration was isolated, steady data and excellent data reproducibility between runs were observed. Comparisons of TEOM and direct mass measurements using gravimetric (filter) and carbon-burnoff techniques as well as calculated PM mass using particle size distributions are also discussed.

11D7

GAS TURBINE SOOT MASS CONCENTRATION MEASUREMENTS BY LIGHT SCATTERING. DONALD HOLVE, Jessica Chapman, Process Metrix, LLC, San Ramon, CA

As part of the Aviation Particle Experiment (APEX) group, we performed mass concentration and size (below 1 micron) measurements of the particulate soot exiting 1 meter downstream of the exhaust of a GE CFM56-2 (approximately 28,000 lbs of thrust) engine. Undiluted samples were transported through a heat-traced (approximately 350F) 9.5mm diameter line for approximately 30m to the instrument. We obtained approximately 500 independent size/concentration measurements with approximately 2-3 second time response for each measurement.

The technique that we have developed (LAPS/TAR) is based on measuring the absolute scattered light at 90 and 30 degrees from the laser illumination beam. The average agglomerate particle size is measured by the ratio of the 90/30 degree detector signals, and the size is then used in determination of absolute mass concentration by using Rayleigh-Debye-Gans (RDG) and Particle Fractal Aggregate (PFA) theories. The LAPS/TAR method can be used as an in situ or sampling configuration.

Two methods of data interpretation for LAPS/TAR measurements are in good agreement, showing low levels of soot generation at low engine engine power levels (10 micrograms/m^3) increasing rapidly above 65% power to maximum concentrations < 1500 micrograms/m^3. These results are in good quantitative agreement with optical filter absorption measurements (Multi-Angle Absorption Photometry) obtained by other APEX researchers.

11E1

PARTICLE DEPOSITION MEASUREMENTS AND NUMERICAL SIMULATIONS IN FOUR PROXIMAL LUNG BIFURCATION MODELS WITH AN IDEALIZED MOUTH-THROAT. YU ZHANG, Warren H. Finlay Department of Mechanical Engineering Aerosol Research Laboratory of Alberta University of Alberta Edmonton, Alberta, Canada

Determination of particle deposition in the human respiratory tract is an important topic related to the effects of pollutant aerosols on human body and the delivery efficiency of pharmaceutical agents for treating respiratory system diseases.

In this study, particle deposition efficiencies in four idealized proximal lung bifurcation models were measured experimentally. An idealized mouth-throat geometry (the “Alberta geometry”) was used as the inlet of these bifurcation models. Solid walled models were manufactured using a FDM 800 rapid prototyper in acrylonitrile-butadiene-styrene (ABS) plastic. Monodisperse particles of DEHS with mass median diameters of 2.5 - 7.5 micron were employed at three steady flow rates of 30, 60 and 90 l/min. Particle deposition measurements were conducted by gravimetry.

The experimental results show that particles entering the mouth are mainly intercepted by the mouth-throat and trachea. Particle deposition efficiency increases with increasing either inertial parameter or Stokes number as expected since inertial impaction is the dominant deposition mechanism in these regions. The laryngeal jet plays a key role in dominating particle deposition within the trachea. In addition, slightly enhanced particle deposition in the trachea is observed with increasing Reynolds number. However, particle deposition fractions in downstream generations are influenced little by the upstream flow condition, and therefore the laryngeal jet does not influence deposition in downstream bifurcations.

CFD simulation results of local particle deposition patterns and local particle concentrations present further information for evaluating dosimetry and health risks of differently sized particle in different geometries of the proximal lung bifurcation.

11E2

DEPOSITION OF SPHERICAL AND FIBROUS PARTICLES IN TRACHEOBRONCHIAL REGION. YUE ZHOU, Wei-Chung Su, Yung-Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque, NM

Regional particle deposition efficiency and deposition patterns were studied experimentally in a human airway replica made from an adult cadaver. The replica includes the oral cavity, pharynx, larynx, trachea, and four generations of bronchi. This study reports deposition results in the tracheobronchial (TB) region. For spherical particles, nine different sizes of monodispersed, polystyrene latex fluorescent particles in the range of 0.93 to 30 µm were delivered into the lung cast with the flow rate of 15, 30, and 60 L min-1. For fibrous particles, carbon fibers with the length ranging from 10 to 400 µm and a monodispersed diameter of 3.66 µm were used in this study at the flow rate of 15, 43.5, and 60 L min-1. Deposition in the TB region appeared to increase with the increasing flow rate and particle size. The experimental data of this study were compared with theoretical models based on a simplified bend and bifurcation model. The deposition efficiency for both spherical and fibrous particles was found as a function of Stokes numbers, bifurcation angle, and the diameters of parent and daughter tubes. The empirical models were developed for spherical and fibrous particle deposition efficiency in the TB region based on the experimental data. They can be used to predict the spherical particle and fiber deposition for inertial effects with improved accuracy in the TB region.

11E3

DEPOSITION OF FIBER IN THE HUMAN NASAL AIRWAY. WEI-CHUNG SU, Yung Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque, NM

Inhalation is the main route for aerosol entering the human body. Many occupational lung diseases are associated with exposure to fiber aerosol in the workplace. However, very few studies to date have been conducted for investigating fiber deposition in the human airway. As a result, there is a notable lack of information on the nature of the fiber deposition pattern in the human respiratory tract. With this in mind, this research consisted of a large number of experimental works to investigate the effects of fiber dimension on the deposition pattern for a human nasal airway. Carbon fibers with uniform diameter (3.66 µm) and polydispersed length were adopted as the test material. Deposition studies were conducted by delivering aerosolized carbon fibers into a nasal airway replica (encompassing the nasal airway regions from vestibule to nasopharynx) at constant inspiratory flow rates of 7.5, 15, 30, and 43.5 l/min. Fibers deposited in each nasal airway region were washed out and the length distribution was determined by microscopic measurement. The results showed that impaction is the dominant deposition mechanism. Most of the fibers with high inertia deposited in the anterior region of the nasal airway (vestibule and nasal valve). In contrast, fibers with low inertia were found to pass through the entire nasal airway easily and collected on the filter assembly at the outlet. Comparing the deposition results between fibers and spherical particles, our data showed that the deposition efficiencies of fibers are significantly lower than that of spherical particles, which implies that the inhaled fibers could pass through the entire nasal airway comparatively easier than spherical particles. Thus, relatively more fibers would be able to enter the lower respiratory tract.

11E4

COMPUTER SIMULATION OF PARTICLE DEPOSITION IN HUMAN TRACHEOBRONCHIAL TREE WITH 3-D ASYMMETRIC BIFURCATION MODEL.

LIN TIAN, Goodarz Ahmadi, Philip K. Hopke, Clarkson University, Potsdam, NY; Yung-Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque, NM

Accurate predication of micro-scale particle behavior in human upper airway is one of the prerequisites for effective design of inhalation drug delivery devices. It also could provide insight into the deposition of contaminants in human respiratory tracks and the nature of personal exposure. In the past very few works employed 3-D asymmetric model to study the airflow through human lung, although natural tracheobronchial branching is generally asymmetric, and such an asymmetry has profound effect on the subsequent flow fields. Also limited work was devoted to the study of particle depositions in upper airways where the effect of turbulence on particle depositions is important. This work approaches three of the underlying components to provide a realistic computational model for lung deposition. The new study include: a realistic 3-D asymmetric bifurcation representation of human upper trachea-bronchial tree; simulation of airflow field characterizing the inspiratory flow conditions in these branches with turbulence Reynolds Stress Transport (RSM) model; and lastly a particle transport model for identifying particle deposition pattern as well as deposition mechanism in the upper tracheobronchial tree.

11E5

3D ANALYSIS OF FLOW AND NANO-SIZE PARTICLE TRANSPORT AND DEPOSITION IN A HUMAN NASAL CAVITY.

PARSA ZAMANKHAN, Goodarz Ahmadi, Department of Mechanical Engineering, Clarkson University, Philip K. Hopke, Department of Chemical Engineering, Clarkson University,Yung-Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque, NM

In this work a 3D computational model for studying the flow and nano-size particle transport and deposition in a human nasal passage was developed. The nasal cavity was constructed using a series of MRI pictures of coronal sections of a nose of a human subject. For several breathing rates associated with low or moderate activities, the steady state flows in the nasal passage were simulated numerically. The airflow simulation results were compared with the available experimental data for the nasal passages. Despite the anatomical differences of the human subjects used in the experiments and computer model, the simulation results were in qualitative agreement with the experimental data.

Deposition and transport of ultra fine 1 to 100 nm particles in the cavity for different breathing rates was also simulated using an Eulerian-Lagrangian approach. The simulation results for the nasal capture efficiency were found to be in reasonable agreement with the available experimental data for a number of human subjects despite anatomical differences. The computational results for the nasal capture efficiency for ultra fine and nano size particles of different sizes and various breathing rate in a laminar regime were found to correlate with the ratio of particle diffusivity to the breathing rate. Based on simulated results an empirical equation for capture efficiency based on a dimensionless parameter was suggested.

11E6

PNEUMONIC ALVEOLAR CAVITY TRANSPORT AND DEPOSITION DURING INHALATION.

IL SOO CHANG and Goodarz Ahmadi, Department of Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY

Inhalation deposition patterns of different particle sizes in alveolar cavities with different orientations were studied. FLUENT(TM) software package was used and a series of simulations were performed. Stokes drag, gravitation, and Brownian forces were included in the particle equation of motion. The results showed that for small particles (less than 0.1 micron meters), Brownian motion and the Cunningham correction factor played a major role in deposition, while for larger particles (greater than 0.5 micron meters), gravity and drag force contributed significantly to particle deposition patterns. Alveolar structure orientations also influenced the deposition pattern of particles of all sizes at different generations. For large particle diameters, the deposition rate showed greater variation with orientation angle.

11E7

COMPARISON OF PARTICLE TRACKING ALGORITHMS IN COMMERCIAL CFD PACKAGES.

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Computational fluid dynamic modeling software has enabled microdosimetry patterns of inhaled toxicants to be predicted and visualized. These predicted initial local deposition patterns represent the dose of inhaled toxicants and therefore, are of great interest in inhalation toxicology and risk assessment. These predicted microdosimetry patterns in airway structures are derived from predicted airflow patterns within these airways and particle tracking algorithms used in computational fluid dynamics (CFD) software packages. Although these commercial CFD codes have been well tested for flow accuracy, their particle tracking algorithm accuracy has not been well studied. In this study, three software packages: Fluent Discrete Phase Model (DPM), Fluent Fine Particle Model (FPM) (Fluent, Inc.), and CFX (Ansys, Inc.) were tested. Each deposition mechanism, including sedimentation, impaction and diffusion, was isolated and tested for accuracy. A range of breathing conditions (rest - 10 l/min; normal activity - 20 l/min and heavy exertion - 60 l/min) were tested over the range of Stokes numbers, and dimensionless diffusion and sedimentation parameters found in the Weibel 23-generation lung model. Three geometries were examined in each software package: a straight tube, a Y bifurcation, and an idealized symmetric double bifurcation model (Heistracher and Hofmann, 1995). Both the Y bifurcation and idealized symmetric double bifurcation model were compared to experimental data. The straight tube model was compared to Pich (1972) and Yu (1978) analytic sedimentation models for parabolic and uniform flow, respectively, and Ingham's (1975) diffusion models. Significant differences were found among the various CFD packages, especially for the diffusion mechanism.

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Acknowledgments:

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12A1

SIZE-SEGREGATED PHYSICAL-CHEMICAL CHARACTERIZATION OF PARTICLES IN THE URBAN BACKGROUND OF SAXONIAN LOW LANDS (GERMANY). GERALD SPINDLER, Erika Brüggemann, Thomas Gnauk, Achim Grüner, Hartmut Herrmann, Konrad Müller, Birgit Wehner, Leibniz-Institut für Troposphärenforschung e.V., Leipzig, Germany; Markus Wallasch, Umweltbundesamt, Dessau, Germany

Extensive size-segregated characterization of tropospheric aerosol was performed at the research station of the Leibniz-Institut für Troposphärenforschung (IfT) in Melpitz, an air chemistry and physics station situated in a flat terrain in Central Europe (12°56' E, 51°32' N, 86 m asl.), a measurement site in the air quality network of the UBA and an EMEP level 3 aerosol station. The PM concentration mainly depends on transport from different source regions. Under the dominating wind direction from the Atlantic ocean (70 % of time) maritime air masses (MA) with showers were transported to Melpitz. The second important wind direction is East (20 % of time). Here, during high-pressure conditions continental dry air masses (CA) are transported over long distances with moderate wind velocity. The main sources for CA are Russia, Poland, Belarus, Ukraine, and the North of Czech Republic. In these areas major sources of anthropogenic air pollution (e.g. outdated power and industrial plants, older cars) still exist.

Particles were sampled daily with high volume filter-samplers (for PM1, PM2.5, PM10) and during selected days with meteorological well-definite air mass origin with five stage BERNER-Impactors (cut-off sizes 10, 3.5, 1.2, 0.42, 0.14, and 0.05 µm, stages 5 to 1) and analyzed for mass, content of water-soluble ions, organic and black carbon, and selected organic species. The particle number size distribution were measured continously directly in the range 3 to 800 nm and using a thermodenuder for evaporation of volatile particle mass before measuring the number concentration with DTMPS.

In winter the PM concentration is higher as in summer and for MA the concentration is lower as for CA. The PM2.5/(PM10-PM2.5) ratio increased from summer 2004 (MA 1.9, CA 2.7) to winter 2004/05 (MA 6.2, CA 4.9). During summer more coarse particles exist from local sources. The (PM10-PM2.5) mass decreases in winter complimentary and particles < PM2.5 from long range transport dominate the PM10 particle mass. These particles were detected at stages 2 to 4 of the BERNER-Impactor with the highest mass concentration in CA.

Daily mean particle mass concentrations PM10 can reach levels near 50 µg/m³ and at some days in winter also above depending of season and air mass origin for the urban background. This is already the limiting value for urban areas in the EU and can be exceeded only 35 times a year. Major cities can not fulfil this limit at traffic road sites, especially.

12A2

PARTICULATE PAHS AT SEOUL: EMISSIONS, AMBIENT SIZE DISTRIBUTION, AND DRY DEPOSITION. JI YI LEE, Yong Pyo Kim, Ewha Womans University, Seoul, Korea, Chang Hee Kang, Cheju National University, Jeju, Korea

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous organic pollutants some of which are reported to be mutagenic and carcinogenic materials. PAHs are one of twelve Persistant Oganic Pollutants (POPs) designated in the Stockholm protocol. The atmosphere plays an important role in the loading of PAHs to the rural and/or background areas which are influenced by the emissions of urban and industrial areas. Thus, it is important to understand the behavior of particulate PAHs in urban atmosphere.

The atmospheric TSP concentrations, size distributions, and dry deposition fluxes of particulate PAHs were simultaneously measured at Seoul, a representative urban site in Korea between 2002 and 2003 to understand general characteristics (from emission to deposition) of particulate PAHs in urban atmosphere. TSP samples were collected on quartz fiber filters on every six days for 24 hours and a 9 stage cascade impactor was used to collect particles with Dp ≤ 10 mm. In order to measure the dry deposition of PAHs, samples were collected on Velcro surrogated plates. The samples were extracted by ultrasonication method and then analyzed by a GC/MSD/SIM for the analysis of 17 PAH compounds.

Factor analysis result shows three possible major sources of particulate PAHs; vehicular emission, coal combustion, and natural gas combustion. The size distributions of PAHs were bi-modal with a fine mode peak in the 0.43-0.65 mm diameter range in summer, 0.65-1.1 mm diameter range in winter, respectively. The measured dry deposition fluxes of PAHs were ranged from 5.4 to 8.9 mg m-2 day-1 in summer and from 13.2 to 21.6 mg m-2 day-1 in winter. The higher deposition fluxes of PAHs in winter were due to the higher particulate PAHs concentrations in winter.

12A3

RECONSTRUCTION OF ATMOSPHERIC PAH DEPOSITION TO PEATLANDS OF EASTERN CANADA.

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Peat cores of 15 ombrotrophic bogs along a transect across Eastern Canada were sectioned, dated, and analyzed for polycyclic aromatic hydrocarbons (PAH) in order to determine historic PAH deposition patterns over a larger region. Ombrotrophic peatlands are not influenced by advection of ground water, they have an autonomous water regime. Moreover, post-depositional mobility in the peat column is limited, so undisturbed ombrotrophic bogs are ideal archives for the reconstruction of atmospheric deposition of particle bound contaminants.

Three different long-term trends in PAH deposition could be distinguished among the analyzed peatlands: sites with two separated periods of maximum PAH deposition, sites with one period of maximum PAH deposition, and sites with no clearly separated period of maximum PAH deposition. The temporal trends of PAH deposition indicated that increases in the PAH deposition rates followed the industrial development in Canada; recent abatement efforts were reflected in decreasing PAH deposition rates. Detailed analyses of three bogs using the concentration rations of individual compounds suggested that combustion of coal and vehicle exhausts mainly contributed to the peat PAH burden. This was also supported by a moderate but significant correlation of total PAH deposition rates to sulphur deposition rates (R2 = 0.54, P<0.0001).

In the more populated regions along the St. Lawrence River, deposition rates in individual bogs peaked at 300-1430 µg m-2 yr -1 in the mid-20th century, whereas in the remote regions of northern Québec, northern Ontario, and Nova Scotia deposition rates remained below 150 µg m-2 yr-1. Phenanthrene, benzo[b +k]fluoranthene, fluoranthene and pyrene were the most abundant PAH. In the remote regions phenanthrene dominated (40-60 % of total), whereas along the St. Lawrence River benzo [b+k]fluoranthene were most abundant (25-40 %) and indeno [1,2,3-c,d]pyrene and benzo[g,h,i]perylene occurred in larger quantities. This pattern only emerged in the 20th century, whereas before deposition rates and composition were more uniform.

The study documents that within Eastern Canada regions of particular PAH deposition patterns exist and suggests that both local emissions and regional transport played a role in the formation of these patterns.

12A4

PROPERTIES OF SIBERIAN FOREST FIRE SMOKE OBSERVED AT THE SUMMIT OF MT. FUJI (3776M), JAPAN.

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The periodic fires in boreal forest have been recognized as one of the major emission sources of trace atmospheric constituents in high-latitude and even in mid-latitude zones of Northern Hemisphere. From the beginning of April 2003, extensive forest fires broke out in the eastern Siberia; the area burned is reportedly the largest-ever.

During the period, the smoke layer aloft covered the meteorological observatory at the summit of Mt. Fuji (3776 m msl), Japan. This study reports the chemical, microphysical, and optical properties of aerosols observed in the thick smoke layer that originated in Siberian forest fire. The aerosols were collected on quartz-fiber filters with a High-Volume Air Sampler. Inorganic ion composition of the aerosols was determined by ion chromatography. Organic carbon in the aerosols was determined by a thermal-combustion technique. Some organic species (high-molecular n-alkanes and PAHs including retene) were determined by GC-MS after the extraction into solvent. Continuous monitoring of black carbon (BC) concentration was conducted with an Aethalometer at 1-hr intervals. Particle number concentration classified into 5 size bins was monitored by a handy-type optical particle counter for a limited duration. Aerosol absorption coefficients in the wavelength range of 550-850 nm were measured from the quartz-fiber filters with Integrating Plate method.

Black carbon concentration by Aethalometer, which is less than 20 ng m-3 in normal conditions, showed a steep increase on May 21, 2003, and reached to the maximum value of 1900 ng m-3 by midnight. Organic carbon concentration also showed sudden increases (14 ug m-3 in maximum) synchronizing with BC peaks However, sulfate, which is typically observed in industrial pollution originated aerosols, did not increase when the OC concentrations were high. Concentrations of retene, which derived from combustion of pine wood resin, were also high in the smoke layer. It is noteworthy that high-molecular n-alkanes, which are a potential marker substance of biomass burnings, were also high in the smoke aerosols. Absorption coefficient of smoke aerosols exhibited strong wavelength dependence, i.e., high vale in the shorter wavelength, compared to that collected in other background areas in Japan. Optical particle counter data showed that smoke aerosols had stable size distribution that characterizes aged smoke.

12A5

SOURCE COMPARISONS OF PM2.5 MEASURED AT THE SPECIATION TRENDS NETWORK SITES ACROSS US.

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

The association between particulate matter (PM) and adverse health effects has been shown in many studies. Since the U.S. Environmental Protection Agency (EPA) promulgated new national ambient air quality standards (NAAQS) for airborne PM, many air quality and epidemiology studies have been undertaken. As part of such studies, advanced source apportionment methods for the airborne PM are required to understand the relationship between source emissions and human exposure. US EPA established Speciation Trends Networks (STN) to characterize PM2.5 (particulate matter less than 2.5 µm in aerodynamic diameter) composition in urban areas and to assist identifying areas out of attainment of the promulgated new NAAQS for airborne PM. The objectives of this project are to separate the contributions of PM2.5 from various combustion sources as well as to understand the origins of the secondary portion of the ambient aerosol using new multivariate receptor modeling by analysis of the data measured at the EPA STN sites as well as to provide source contributions for the studies of adverse health effect of PM2.5.

In the present study, PMF was applied to an ambient PM2.5 compositional data set of 24-hour integrated samples collected at STN monitoring sites across US and the results of a selected subset of sampling sites are reported. It appears that credible source apportionments could be derived from the STN data. PMF resolved source profiles were very similar across U.S. In most locations, it was possible to separate secondary sulfate aerosols, secondary nitrate aerosols, and several combustion sources including gasoline and diesel powered vehicle emissions and residual oil combustion.

12A6

GASEOUS AND PARTICULATE POLLUTANT TRANSPORT IN STREET CANYONS - A THREE-DIMENSIONAL MODELING STUDY.

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Gaseous and particulate pollutant transport and dispersion in street canyons were studied using a three-dimensional computer simulation methodology. Effects of building size, street width, and wind velocity on the pollutant transport in symmetric and asymmetric street canyons were examined. A three-dimensional model of a typical city was developed and the FLUENT™ code along with the Large Eddy Simulation (LES) turbulence model was used to simulate the airflow field, pollutant dispersion, and particle deposition in the street canyon. Effects of building size, street width, and wind velocity on the pollutant transport were examined. While the LES turbulence model was used in most of the analysis, predictions of the other turbulence models were also examined. Depending on wind speed, building height, and street width, it was found that large recirculation regions in canyons may form. Under certain conditions, vehicle emission pollutants may trap inside the street canyon. The simulation results are compared with the available wind tunnel experiments and good agreement was found. Particulate pollutant transport and deposition were also studied for different particle sizes and relaxation times. It was found that the wind velocity and direction, buildings height and their arrangement were important factors in controlling particulate transport and deposition. Significant amount of particulate deposition was found to occur on the roads for all wind velocities.

12B1

DETAILED ANALYSIS OF SECONDARY ORGANIC AEROSOL ORIGINATING FROM THE PHOTOOXIDATION OF D-LIMONENE IN THE PRESENCE OF NOX AND ARTIFICIAL LIGHT AND ITS IMPLICATION TO AMBIENT PM2.5.

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Biogenic organic compounds in particular monoterpene are known for their contribution to ambient secondary organic aerosol (SOA), mainly in summertime. Although the oxidation of monoterpenes mainly α- and ß-pinene has been widely studied, less attention has been given to d-limonene, one of the most common emitted monoterpene from vegetations, despite its high potential for aerosol formation. To date, there have been very limited studies on the chemical characteristic of gas or particulate reaction products formed from d-limonene oxidation, and only few reaction products have been reported.

In this study, a detailed analysis was carried out of the aerosol phase originated from the photooxidation of d-limonene in the presence of NOx and artificial light. Emphasis was placed on polar oxygenated organic compounds. The experiments were conducted in a 14.5-m3 indoor smog chamber operated in dynamic or static mode. The identification and quantification of SOA reaction products was based on a newly developed technique that characterizes each functional group contained in the compound: BF3-methanol derivatization was used for carboxylic groups, BSTFA for hydroxyl groups, and PFBHA for ketone and aldehyde groups. GC-MS analysis showed the occurrence of more than 50 polar oxygenated organic products in the filter extracts. The major components include: six tracer compounds previously identified by our group from a- and b-pinene/NOx system (e.g. 3-isopropyl pentanedioic acid, 3-carboxy heptanedioic acid…), C3-C6 linear di-acids, ketolimonaldehyde, limonic acid, limononic acid, etc. Temporal profiles as well as tentative reaction schemes leading to most of these compounds are presented.

In order to determine and understand the relative contributions of SOA products originated from d-limonene to ambient PM2.5, a detailed analysis was also carried out for ambient summertime samples (PM2.5) collected at three locations in the eastern United States in 2001 and 2003. GC-MS analysis shows the occurrence of more than 10 d-limonene SOA compounds, indicating the impact of d-limonene on the regional aerosol burden at least in the southeastern United States. Some of these compounds could serve as indicators for d-limonene into atmospheric particulate matter.

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12B2

INVESTIGATIONS OF HETEROGENEOUS REACTIONS OF UNSATURATED FATTY ACIDS AND OZONE USING RAMAN SPECTROSCOPY OF SINGLE LEVITATED PARTICLES.

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Heterogeneous reactions of organic aerosols with atmospheric oxidants, such as ozone and OH, are an important process in affecting their chemical composition and physical properties. Most recent researches focus on investigating the kinetics and the mechanism of various heterogeneous oxidations. Although the detailed reaction mechanisms are still uncertain, the oxidation products formed are likely to be more hygroscopic and more CCN active than their hydrophobic parent molecules.

In this study, an electrodynamic balance was used to investigate the heterogeneous oxidations of unsaturated fatty acids with ozone. Raman spectroscopy, well suited for functional group analysis of organics, was used to probe the changes of the organic compositions of the levitated particle as the reactions take place. We have studied the heterogeneous reactions of ozone with oleic acid particles. When the reaction took place, the intensity of the characteristic bands due to presence of C=C bonds of oleic acid at wavenumber 1269, 1658 and 3008 cm^(-1) decreased with ozone exposure. These spectral changes showed that the C=C bonds of oleic acid were attacked by ozone. These preliminary results of the Raman characterization also suggest that the reaction products formed by the reaction of ozone and oleic acid are more oxygenated than the pure oleic acid. Furthermore, the hygroscopicity of the levitated particles slightly increased after ozone exposure but the change was not significant.

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12B3

COMPUTATIONALLY EFFICIENT ACTIVITY COEFFICIENT ESTIMATION METHOD FOR USE IN LARGE-SCALE ATMOSPHERIC MODELING.

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The incorporation of increasing detail in the atmospheric chemistry employed large-scale, multi-day, 3-D air quality modeling is accompanied by tremendous increases in computational demand. This is especially true when modeling secondary organic aerosol (SOA) formation from the gas/particle condensation of numerous oxidation products from numerous parent hydrocarbons. In SOA gas/particle partitioning modeling, the dynamic phase equilibrium of each partitioning organic species is established by iteratively solving for values of the composition- and species-dependent gas/particle partitioning constant. These iterative calculations become especially computational demanding when considering the activity coefficient dependency of the gas/particle partitioning constant. The UNIFAC method is currently considered to be the state-of-the-art method for estimating activity coefficients in SOA formation models. UNIFAC is a group contribution method that requires numerous multi-step computations to estimate activity coefficients for the partitioning compounds. This work describes a compound-based approach that greatly reduces computational demand without significant loss of real predictive power. This compound-based approach predicts activity coefficients based on summing compound-compound interactions rather than group-group interactions. This approach is simple to implement for any hypothetical, partitioning SOA species. The method is illustrated using ten SOA surrogate structures discussed in the Pun et al. (2002) model. A comparison of the computational efficiencies and model accuracies as compared to analogous calculations executed with the UNIFAC method are presented.

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12B4

MODELING THE FORMATION OF HYDROPHILIC AND HYDROPHOBIC SECONDARY ORGANIC AEROSOLS FROM ANTHROPOGENIC AND BIOGENIC PRECURSORS.

BETTY PUN, Christian Seigneur, Atmospheric and Environmental Research, Inc., San Ramon, CA

A secondary organic aerosol (SOA) modeling framework that represents the equilibrium partitioning of hydrophilic and hydrophobic compounds (Pun et al., 2002, J. Geophys. Res., Vol. 104 pp.4333, doi: 10.1029/2001JD000542) has been extended for use with common anthropogenic and biogenic precursors. Anthropogenic precursors include a high SOA yield and a lower SOA yield aromatic compound. Biogenic precursors include monoterpenes and sesquiterpenes. The SOA module is designed to function with any gas-phase mechanism. SOA products are added to the reactions of existing precursors. New SOA precursors and surrogate SOA products are added to the existing mechanism using chemical reactions that involve the relevant oxidants but do not affect their concentrations.

A review was conducted to compile products of anthropogenic and biogenic precursors, including toluene and other aromatic compounds, alpha-pinene, beta-pinene, humulene, terpinene and other monoterpenes. From the mixture of SOA forming products from these precursors, hydrophilic and hydrophobic surrogate products are identified based on groups of products with similar octanol-water partitioning coefficients and vapor pressures. Their partitioning properties are compiled from the literature or estimated by group contribution methods for modeling absorption of hydrophobic compounds and hydrophilic compounds below deliquescence relative humidity (DRH) and for modeling aqueous dissolution of hydrophilic compounds above DRH. These properties include the saturation vapor pressure, temperature dependence, deliquescence relative humidity, Henry’s law constant, acid dissociation constant, and activity coefficient in the condensed phase of each condensing compound, where applicable.

Results of box model simulations will be presented for a few case studies using concentrations typical of smog chamber experiments. The SOA module will be incorporated next into the three-dimensional air quality model CHIMERE that is used by the French R&D organization INERIS for air quality forecasting.

12B5

CHEMICAL REACTIONS AND ORGANIC AEROSOL: A UNIFIED FRAMEWORK. NEIL M. DONAHUE, Allen L. Robinson, Kara E. Huff Hartz, Amy M. Sage, Emily A. Weitkamp, Carnegie Mellon University, Pittsburgh, PA

Organic aerosol is tied to chemical reactions in three major ways. First, oxidation of volatile precursors leads to semi- or non-volatile products to form secondary organic aerosol (SOA). Second, condensed-phase monomer species interact chemically to form larger oligomers, with much reduced volatility. Third, all of the semi- and non-volatile organic material, whatever its origin, is subject to heterogeneous oxidation by gas-phase oxidants such as OH radicals and ozone (and quite possibly photochemical oxidation induced by UV light absorbed by the aerosol itself). All of these phenomena can be described in a unified framework of chemical transformation; at a minimum one must represent the organic aerosol constituents with a succession of vapor pressures, based on ideal partitioning. In addition, oxidation clearly influences aerosol hydrophillicity, so accurate representation of organic aerosol requires a second dimension related to the degree of oxidation.

Organic aerosol can be represented by a basis set spanning these two dimensions, with six or more vapor pressures ranging from non-volatile (10 ng/m3 saturation) to volatile (1 mg/m3 saturation), with vapor pressures increasing by a factor of 10 in each bin. In addition, each volatility bin can carry a `fully reduced' and `fully oxidized' constituent, with oxidation progressively transforming the former to the latter. Hydrophillicity and cloud droplet activation can be tied to this oxidation coordinate. This provides a framework for fitting chamber data constraining SOA yields, but it can also readily describe the effects of oligomerization as well as oxidative aging of organic aerosol.

Using this framework, we shall discuss constraints on the volatility and degree of oxidation of organic aerosol based on chamber and ambient data.

12B6

MODELING OF SURFACE REACTIONS ON CARBONACEOUS ATMOSPHERIC PARTICLES DURING A WOOD SMOKE EPISODE IN HOUSTON, TEXAS. UARPORN NOPMONGCOL, David T. Allen, Department of Chemical Engineering, University of Texas at Austin, Austin, TX Birnur Buzcu, Zhiwei Yue, Matthew Fraser, Department of Civil and Environmental Engineering, Rice University, Houston, TX

There is an increasing body of evidence indicating that surface reaction processes are important in controlling chemical processes in the lower atmosphere. One of those surface reactions is the formation of sulfuric acid on carbonaceous surfaces. Observational data, collected during a wood smoke episode in Houston, Texas, indicated that this surface reaction pathway is significant. Direct emissions from biomass burning could not explain high sulfate concentrations observed during the episode. Modeling of gas-phase and aqueous reaction pathways, and chloride displacement reactions led to sulfate concentrations much lower than observations. In contrast, simulations including sulfate formation reactions on soot particles led to sulfate concentrations and spatial distributions of high sulfate concentrations that were in qualitative agreement with observations. This presentation will describe the results of regional photochemical modeling, incorporating SO2 oxidation pathways on carbonaceous surfaces. The sulfate formation due to these pathways was consistent with spatial and temporal distributions of sulfate observed during the episode. These analyses provide direct evidence of the potential importance of heterogeneous sulfate formation on carbonaceous surfaces.

12C1

INDOOR/OUTDOOR POLLUTION TRANSPORT AND INTERACTIONS – A LARGE EDDY SIMULATION.

KAMBIZ NAZRIDOUST, Goodarz Ahmadi, Department of Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY

The indoor air environment in a building is the result of the indoor contaminant sources (building materials and furnishings, processes and activities within the building, and the HVAC systems), building occupants and outdoor pollution levels. The interactions between the outdoor air and the indoor are also an important factor controlling the quality of the indoor air. In addition to indoor air quality, there has been considerable interest in ensuring health and comfort of building occupants. Providing thermal and humidity comfort of building occupants has been the key in HVAC design. It is important to understand the role of indoor sources and transports from outdoor source in order to prevent, and resolve indoor air quality problems.

In this study, the coupled outdoor and indoor environments and their interactions are studied. A three dimensional computer model of a house with multiple rooms in a typical urban environment is developed using FLUENT™ code. Large eddy simulation is used to model the air flow, turbulence and thermal conditions inside the building and the in the outdoor region in the vicinity of the building are evaluated. Multi-species flow model is used and the concentration of gaseous pollutants inside the house due to indoor and outdoor sources is evaluated. Particulate transport and deposition on walls and furniture are also studied. Different configurations of ventilation systems are also examined. Particular attention was given to particulate emissions due to walking of the inhabitant indoor and road emission outdoor and the particles re-deposition of processes.

12C2

EFFECT OF IONIC AIR CLEANERS ON INDOOR-TO-OUTDOOR PARTICLE RATIOS IN RESIDENTIAL ENVIRONMENTS.

DAVID BERRY, Gediminas Mainelis, Donna Fennell, Rutgers University, New Brunswick, NJ

This study examines the effectiveness of commercial ionic air cleaners in removing particulate matter in typical residential settings. An ionic air cleaner emits ions through corona discharge, which unipolarly charges airborne particles causing them either to repel each other or deposit on nearby surfaces due to image charge forces. For this study, we measured indoor-to-outdoor particle mass and number concentration ratios in several residential settings under ambient conditions and with the ionic cleaner turned on. The particle mass concentrations were measured using pDR-1000 passive aerosol monitors, while particle number concentrations were measured in eight size fractions between 0.3 and 3 µm using Grimm optical counters. Ozone and ion concentrations were also measured. In a typical environment, an ionic cleaner was operated continuously for 32 hours in the living room of a two bedroom apartment inhabited by two people. All inhabitants engaged in their regular activities during the tests. The living room area was approximately 200 ft^2 and the entire apartment area was approximately 600 ft^2. All measurements were repeated during several campaigns.

The average indoor-to-outdoor particle mass concentration (mg/m^3) ratio was 1.03 under ambient conditions and 0.68 when the device was operating, resulting in an average indoor-to-outdoor particle mass ratio reduction of 33%. Reduction levels of indoor-to-outdoor particle number concentration ratios varied for individual particle size fractions. On average, there was no reduction for particles smaller than 0.5 µm, but the ratios of particles between 0.5 and 3 µm were reduced by 19%. Similar results were obtained in several other residences.

The ambient ion levels when the ionic cleaner was not in operation averaged 300 ions/cm^3. The ion concentration increased in an approximately linear fashion during the air cleaner operation (R^2 = 0.86), reaching a concentration of 60,600 ions/cm^3 after 32 hours of continuous operation. The ozone concentration was approximately 0.00 ppm under ambient conditions and increased to an average 0.02 ppm when the ionic cleaner was operating. The ozone levels remained steady during the 32-hour measurement, and did not exceed 0.04 ppm.

The results indicate that ionic air cleaners may be somewhat effective in removing a fraction of airborne particulate matter, performing most effectively at removing particles between 0.5 and 3.0 µm in size. However, one has to be aware that an operating ionic cleaner produces a continuous and stable ozone output as a byproduct of the cleaner’s corona discharge.

12C3

IDENTIFICATION, CLASSIFICATION AND CORRELATION OF ULTRAFINE INDOOR AIRBORNE PARTICULATE MATTER WITH OUTDOOR VALUES.

NICK FACCIOLA, Iain Elliott, Darin Toohey, John Zhai, Shelly Miller, University of Colorado at Boulder

This study examines the infiltration of ultrafine particles into mechanically-ventilated indoor environments, including typical office buildings and schools. With the use of an Ultra High Sensitivity Aerosol Spectrometer and an Aerosol Mass Spectrometer, the size and chemical speciation of ultrafine particulate matter as a function of time is measured. Indoor and outdoor carbon dioxide concentrations are also measured. Measurements are made continuously over two week days and two weekend days, during four different seasons. These data are used to compare and correlate indoor and outdoor ultrafine particulate matter concentrations. This study provides information needed to understand the exposure and health risks associated with inhalation of ultrafine particulate matter in mechanically-ventilated buildings. In addition, the information provided by this study can improve understanding of filtration requirements in buildings. The correlation of particulate concentrations between indoors and outdoors can be used to evaluate the performance of heating, ventilation, and air conditioning systems in conditioning the outside air as well as re-circulated air.

12C4

FINE PARTICLE FORMATION RESULTING FROM CLEANING PRODUCTS AND AIR FRESHENERS IN THE PRESENCE OF OZONE.

Hugo Destaillats, Melissa Lunden, Brett Singer, Albert Hodgson, Lawrence Berkeley National Laboratory, Berkeley, CA; BEVERLY COLEMAN, William Nazaroff, University of California, Berkeley, CA; Charles Weschler, Rutgers University, NJ and Technical University of Denmark

The use of cleaning products and air fresheners indoors can result in exposure to toxic air contaminants. While such exposures can result from direct inhalation of the primary emissions, many products contain terpene hydrocarbons and terpeniods that can produce secondary pollutants through reactions with ozone. Ozone is commonly present indoors through its introduction along with ventilation air from outdoors. Indoor sources also exist, including some copy machines and “air purifiers.” We conducted an experimental investigation of the generation of gaseous and particulate air contaminants owing to reactions of household products with ozone. Gas-phase emissions from three different, commonly available cleaning products were introduced at a constant rate into a 198-L Teflon-lined reaction chamber. Ozone was also introduced at a constant rate via a second air supply line. The primary airflow was adjusted to control the residence time within the chamber. The experiment explored two different reaction times, achieved by adjusting the ventilation rate, and two different inlet ozone concentrations. Gas-phase species concentrations were sampled using sorbent tubes. Particle concentrations were measured using a scanning mobility particle scanner and an optical particle counter. The results show a large number of nuclei-mode particles formed immediately upon ozone addition. Remarkably, the observed experimental production of ultrafine aerosol particles is strikingly similar to the fine-particle formation events reported from atmospheric sampling programs. A small concentration of ultrafine particles was present in the primary airflow; these particles provided additional condensation surface, leading to interesting changes in the growth dynamics of the particle size distribution as a function of ozone concentration and residence time. The presentation will focus on relationships among initial terpene and ozone concentrations, reactor residence times, and observed particle formation. Aerosol yields will be presented, and the role of OH in particle formation will be discussed.

12C5

PARTICLE DEPOSITION ON HVAC HEAT EXCHANGERS.

JEFFREY SIEGEL, Department of Civil, Environmental, and Architectural Engineering, The University of Texas at Austin, Austin, TX

Deposition of indoor aerosols on heating and cooling heat exchangers can lead to decreased equipment performance and indoor air quality problems related to microbiological growth. In order to understand the mechanisms that lead to particle deposition on heat exchangers, we conducted laboratory experiments to directly measure the penetration of particles through a typical air conditioner evaporator coil. We also conducted experiments that consider the impact of cold and condensing heat exchanger surfaces, and the relationship between coil pressure drop and mass of particles deposited. These experiments are used to predict deposition for the range of particle sizes and concentrations typically found in indoor environments. Particle deposition results are used in a model of particle deposition in residential systems. The results of our model suggest that a typical cooling coil in a residential system will foul such that its pressure drop is doubled in 4-6 years. This fouling time can be greatly extended with high efficiency filtration or by eliminating bypass around the filter. Larger commercial HVAC systems exhibit a wide variety of fouling times, and fouling times show a strong dependence on filtration efficiency and installation. Predicted energy and performance consequences of particle deposition on HVAC heat exchangers are small and are mostly related to the increased pressure drop, rather than the decreased heat transfer associated with a fouled cooling coil.

12C6

FORMATION OF NANOPARTICLES IN INDOOR AIR AT AN INCREASED OZONE LEVEL.

SERGEY A. GRINSHPUN, Mika Toivola, Shu-Ann Lee, Tiina Reponen, University of Cincinnati, Cincinnati, OH

Although nanotechnology is expected to have extraordinary societal benefits in future decades, there are concerns about major health effects that may be associated with nanoparticles aerosolized in indoor air environments. We investigated the influence of ozone generation on the evolution of the size distribution and concentration of aerosol particles in a 24.3 m3 indoor test chamber. The background (ambient) aerosol was measured in the chamber in real time using a Wide-Range Particle Spectrometer (WPS, model 1000 XP, Configuration A, MSP Corp., USA). By combining the capabilities of a differential mobility analyzer, a condensation particle counter, and a laser particle spectrometer, the WPS allows recording the data in 120 channels in the particle size range of 10 to 10,000 nm. In this study, the primary interest was devoted to the particles between 10 and 500 nm. The ozone level was gradually increased in the test chamber from 0.010 ppm (initial) to about 0.200 ppm (after 90 min). Once the indoor ozone level reached approximately 0.040-0.060 ppm (this occurred after 20-40 min of the continuous ozone generation, depending on the generator's output), we clearly observed the formation of nano-sized particles in the range of 10-40 nm. The aerosol concentration of these particles increased 10- to 100-fold in an hour as the ozone level increased to 0.078-0.127 ppm. The discovered phenomenon is attributed to the products of chemical reactions between ozone molecules and specific air components (e.g., organic compounds and trace elements). Theoretical basis is presently being developed to quantify the experimentally observed effect of formation of nanoparticles. The findings of this study are very important since some air cleaners utilize ozone generators to enhance indoor air purification. Our data suggest that the nanoparticle formation may take place at ozone levels that are close to (or even below) the EPA standard of 0.050 ppm.

12D1

CHEMICAL VAPOR DEPOSITION OF GROUP IV OXIDES ON AEROSOLIZED SILICON NANOPARTICLES. Amanda Nienow, Ying-Chih Liao, JEFFREY ROBERTS, Department of Chemistry, University of Minnesota, Minneapolis, MN

We describe a new method for chemically depositing metal oxide layers onto the surfaces of aerosolized nanoparticles. Chemical vapor deposition was used to deposit group IV metal oxide materials, including zirconium dioxide, onto silicon. The film precursors were anhydrous metal nitrates. Layers were deposited onto silicon particles of initial mobility diameter between 10 and 20 nm. Layers as thick as 1 nm could be deposited under relatively mild conditions. The results are important because they describe a new approach for manipulating and controlling interfacial properties in nanoparticles that have materials applications. More generally, the results are among the first kinetic and mechanistic studies of aerosolized silicon nanoparticle reactivity.

The kinetics and mechanisms of deposition were investigated using tandem differential mobility analysis (T-DMA) and transmission electron microscopy (TEM). Free-flowing streams of silicon particles were extracted from a low-temperature, low-pressure plasma synthesis chamber into an atmospheric pressure flow tube reactor. Using nitrogen as the carrier gas, the particle streams were sent through a furnace for thermal activation, through a bipolar diffusion charger to establish a known charge distribution on the particles, and then through a differential mobility analyzer (DMA-1). DMA-1 was used to create a stream of monodisperse particles; selected mobility diameters were in the 10-20 nm range The monodisperse particle streams were swept into a reaction zone, which was a heated copper tube with a valve for the precursor introduction. The reaction zone was designed for maximal flexibility, with variable temperature (25-200 ºC), particle residence time (1-10 s), and gas-phase composition. Particles that exited the reaction zone were analyzed in two ways: (1) for size changes, with a second DMA capable of measuring diameter changes as small as 1%, and (2) for nano-structural and nano-morphological changes that are induced by deposition, using transmission electron microscopy (TEM).

Results will be presented on the deposition of zirconium oxide onto silicon from zirconium nitrate. The growth rates were studied as functions of thermal pre-activation temperature, precursor flow rate, and deposition temperature. Growth rates, expressed in unites of mobility diameter change with respect to time, vary linearly with precursor flow rate, and they increase with deposition temperature. Growth rates also depend on the thermal pre-activation temperature. Film growth becomes more rapid if particles are pre-treated at temperatures of 500 ºC or more, which is close to the temperature at which hydrogen desorbs from silicon wafers.

12D2

GENERATION OF TAILORED MICROPARTICLES BY PHOTOPOLYMERIZATION OF MONODISPERSE DROPLETS. Zhiqiang Gao, ASIT K. RAY, Department of Chemical Engineering, University of Kentucky, Lexington, KY

We present a technique for generation of tailored microspheres of polymeric materials by in-situ photopolymerization of droplets containing monomers and additives. Highly monodisperse droplets, with size fluctuations of less than 0.01%, were generated by a vibrating orifice aerosol generator (VOAG) and dispersed in air to prevent agglomeration. The droplets were photopolymerized by exposing them to ultra-violet light. The droplet size was controlled by the volumetric flow rate of monomer solution through the orifice, and the vibrating frequency of the orifice.

A number of factors play critical role on the morphology of the final solid polymer particles. These factors include pressure used to generate monodisperse droplets through a vibrating orifice aerosol generator (VOAG), vibration frequency of the orifice, and the surrounding gas temperature, and dispersion air. The results of our experiments show that tailored microspheres (e.g., multicomponent, layered, and with nanoparticle inclusions) of highly reproducible size and physical characteristics can be produced, and the morphology of the final solid polymer particles can controlled by the initial droplet size and composition as well as through the reaction conditions. The results suggest possibility of preparing microparticles of various compounds with reproducible physical properties and functions through adding desired components, such as salt, additives and drugs et al. It is also possible to produce monodisperse multicomponent particles, spherical microcapsules, and micro-resonators.

12D3

FUNDAMENTAL APPROACH TO CORRECT THE HOMOGENEOUS NUCLEATION THEORY.

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The classical nucleation theory, in its current form, fails to quantitatively describe the experiment. It predicts the nucleation rates orders of magnitude higher than the experimental values with the disagreement between theory and experiment strongly depended on the process temperature. Also, the close inspection of the experimental data shows that the nucleation theory underestimates the molecular content of the critical cluster.

The important fundamental of the classical nucleation theory is based on an assumption that the clusters formed during the process are isothermal. Our recent findings [1] show that non-isothermality could significantly affect the cluster evolution. Particularly, a significant accumulation of the supercritical clusters in the system generating nanoparticles via the vapor condensation, we discovered, was explained with taking non-isothermality into account.

The phenomenological introducing non-isothermality in the nucleation theory leads to coupled effects – the reduction of the nucleation rate and the increase of the number of molecules in the critical cluster compared to that predicted for the isothermal system. This result is in agreement with the experimental data.

In order to describe non-isothermality in the consistent way, the detail kinetics of the clusters (which temperature fluctuates around that of the environment [2]) is developed. The deviation of the cluster temperature distribution from that under equilibrium fluctuations is considered as a degree of non-isothermality. Being introduced in the phenomenological model, the evaluated degree of non-isothetrmality can remove discrepancy between the theory and experiment.

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12D4

ION-INDUCED NUCLEATION: DIPOLE-CHARGE ORIENTATION, SIGN PREFERENCE AND CHEMISTRY EFFECT.

ALEXEY NADYKTO, Fangqun Yu, Atmospheric Sciences Research Center, State University of New York at Albany, Albany, USA

Gas-to-particle conversion via ion nucleation and subsequent growth plays an important role in the formation of atmospheric aerosols associated directly with the Earth climate and air quality. Recently we pointed out [1,2] that the effect of the dipole-charge interaction on the ion-induced nucleation rates and clustering thermodynamics is very important. Here we investigate the effects of the dipole-charge orientation, chemical composition of the seed ion and sign preference on the ion-induced nucleation rates, clustering thermodynamics and uptake efficiency. We analyze uptake of common precursors by ion clusters using seven different approaches and found that the enhancement factor due to the dipole-charge interaction predicted by different uptake/capture models can deviate by a factor of more than 5 [3]. We found that models, which are derived using different capture/uptake conditions and similar dipole orientation models, are in quite a good agreement in most cases, while the models obtained using identical capture/uptake conditions and different orientation models deviate dramatically. Present analysis shows that uncertainties in the enhancement factor are largely arise from the difference in how the relative dipole orientation of the polar molecule in an ion field is expressed. In order to study effect of the dipole orientation on the ion clustering we also performed comparison the experimental data on the mean ion mobility ion-induced nucleation rates and the Gibbs free energies of cluster-polar molecule reactions, including hydration, with our model predictions. The comparison shows that models of strong dipole-charge interaction (locked dipole and Langevin dipole orientation model) are in good agreement with the experimental data. We also analysized the effect of the chemical composition and ion sign on the clustering thermodynamics. We found that the effect of the charge sign and chemical composition of the core ion is essential for small ions only. This suggests that sign preference observed in a number of experiments relate is a special case of the chemistry [4] effect and it can be incorporated into nucleation theory through accounting for the difference in the Gibbs free energy between caution and anion at early stages of the cluster growth.

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12D5

EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM VAPOR PRESSURE CURVE OF ARGON BELOW THE TRIPLE POINT.

AMEWU MENSAH, Jan Wedekind, Reinhard Strey, Judith Wölk, Universität zu Köln, Cologne, Germany

We have measured the onset of heterogeneous nucleation of argon below the triple point in the temperature range $52 < T/K < 72$. From these measurements we obtain for the first time a comparatively reliable estimate for the equilibrium vapor pressure curve of liquid argon below the triple point. The experimental equilibrium vapor pressures differ from the best fits found in literature (based on extrapolations from above the triple point) by a factor of 1.2 to 2.5 in the indicated temperature range. The dramatic consequences for calculations of homogeneous nucleation rates for argon according to nucleation theories and comparison with experiments on homogeneous nucleation of argon will be discussed.

12D6

THERMAL PLASMA SYNTHESIS OF ALUMINUM NANOPARTICLES.

BIN ZHANG, Bo Liu, Steven L. Girshick, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN

Because of their highly pyrophoric nature and light weight, aluminum nanoparticles, if they can be properly sur-face-passivated, are of interest for applications such as solid fuel propulsion. This paper reports a new thermal plasma process for synthesizing aluminum nanoparticles, and parametric studies of particle formation. An ar-gon-hydrogen plasma is generated by a DC arc at near-atmospheric pressure, and is expanded in subsonic flow through a ceramic nozzle to ~50 kPa pressure. AlCl3 vapor, generated by subliming AlCl3 powder in a heated packed bed, is injected into the plasma at the upstream end of the nozzle. Al particles nucleate near or shortly downstream of the nozzle exit. A cold argon counterflow opposes the plasma jet exiting the nozzle. The pur-pose of the counterflow is to provide dilution and cooling, so as to reduce both particle coagulation and particle-particle coalescence, thereby maintaining small primary particle sizes. For on-line size distribution measurements a capillary sampling probe is inserted into the reactor upstream of the counterflow tube. The sample passes to a two-stage nitrogen ejector, with a typical dilution factor of approximately 6000. The diluted sample then passes to a scanning mobility particle sizer. Measurements of particle size distributions were obtained for various sets of operating conditions. Conditions that varied included the hydrogen flow rate, the flow rate of the argon carrier gas containing the AlCl3 vapor, and whether the argon counterflow was on or off. For the range of conditions tested the number-mean particle diameter lay in the range 10-20 nm. Higher AlCl3 feed rates tended to produce higher particle concentrations and larger values of number-mean particle diameter. The use of coun-terflow was found to reduce particle concentrations at the measurement location, and also to reduce the mean particle size. The hydrogen flow rate was found to have little effect on particle size distributions, at least within the range tested. Particles were also deposited onto transmission electron microscope (TEM) grids for off-line analysis by TEM and by energy dispersive X-ray spectroscopy (EDS). These studies indicate that the particles are spherical and nonagglomerated, with a crystalline aluminum core and a thin surface oxide layer.

12E1

FE(II) IN PARTICULATE MATTER: ITS ENVIRONMENTAL HEALTH IMPLICATION AND AN ORIGIN IN COMBUSTION. BING GUO, Ian M. Kennedy, University of California, Davis, CA

As the most abundant transition metal found in airborne ultrafine particles, the speciation of iron has implications in the toxicity of ambient particles. We have previously shown in rat inhalation studies that oxidative stress was indicated only when soot and iron were present together in an aerosol. We hypothesized that the carbon reduced Fe(III) to Fe(II) that was able to participate in a Fenton reaction to yield OH. In a separate study, we found significant OH generation by flame soot in buffer solution that simulated lung fluid. In this work, we study environmental particulate matter (PM) and laboratory flame aerosols to determine the iron speciation in these samples, and the factors that affect iron speciation in the laboratory samples, using Electron Microscopy/Spectroscopy, X-Ray Diffraction and a spectrophotometric method with acid digestion. We found significant concentrations of Fe(II) in a standard Diesel exhaust sample (NIST SRM 2975) and an urban PM sample (NIST SRM 1948). There was a significant fraction of Fe(II) in the iron in soot/Fe aerosols generated from a C2H4 diffusion flame seeded with Fe(CO)5. The Fe(II)/FeTotal ratio was found to increase with decreasing iron concentration in the soot/Fe mixture. It is hypothesized that the FeO vapor in the flame condenses on the soot surface to form Fe(II). The detailed mechanism is under investigation, which may provide insight into the toxicity of PM.

12E2

TOTAL DEPOSITION OF INHALED PARTICLES IN THE RESPIRATORY TRACT OF HEALTHY ADULTS: A UNIFYING EMPIRICAL RELATIONSHIP WITH PARTICLE SIZE AND BREATHING PATTERN. CHONG S. KIM, National Health and Environmental Effects Research Laboratory, US EPA, Research Triangle Park, NC; Shu-Chieh Hu, IIT Research Institute, Chicago, IL; Peter Jaques, Clarkson University, Potsdam, NY

Particulate matter in the air is known for causing adverse health effects and yet mechanisms by which such effects are exerted are not fully understood. Because health effects are essentially related to the dose at the site of action in the body, it is important to know how much of inhaled particles is actually deposited in the lung under various exposure conditions. We measured total deposition fraction (TDF) of monodisperse aerosols in the size range of 0.04 - 5 micron in diameter in nineteen healthy adults at various breathing patterns representing sleep, resting and mild exercise conditions. The tidal volume (Vt) was varied from 350 ml to 1500 ml, respiratory flow rate (Q) from 150 - 1000 ml/s and the breathing frequency from 7.5 to 30 breaths per min. Subjects inhaled test aerosols via the mouthpiece for 10-20 breaths following prescribed breathing patterns displayed on a computer monitor screen. During inhalation, aerosol concentrations were monitored continuously by a laser aerosol photometer for micron size aerosols and a ultrafine condensation particle counter for submicron aerosols. TDF was assessed for each breath and the average of 10-20 breaths was obtained for each of twelve breathing patterns used. TDF was then analyzed for effects of particle size and breathing pattern parameters including tidal volume, respiratory flow rate and respiratory time (or breathing frequency). We found that TDF was uniquely correlated with a single composite parameter Ω1 (=(D.Tm)^0.5xVt^k) for submicron aerosols (r2 = 0.97) and Ω2 (= da^m Q^n Vt^p) for micron size aerosols (r2 = 0.98) in the functional form of TDF = 1-1/(1+a Ω). Here, D and Tm are the diffusion coefficient of particles and mean respiratory time, respectively and da is the aerodynamic particle diameter. For the entire particle size range, TDF = 1-1/(1+aΩ1 + b Ω2) was a good functional form to consolidate the entire TDF data (a and b are constants). In conclusion, a unifying empirical equation for total lung deposition was obtained based on comprehensive human experimental data. The equation will be very useful for assessing deposition dose of orally inhaled particles under various inhalation conditions. This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.

12E3

3-D CFD STUDY OF THE DYNAMICS OF A MEDICAL-AEROSOL HOOD INHALER.

Tal Shakked, David Katoshevski, Department of Biotechnology and Environmental Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel; David M. Broday, Faculty of Civil and Environmental Engineering Technion – Israel Institute of Technology, Haifa, Israel; Israel Amirav, Pediatric Department, Sieff Hospital, Safed, Israel

Aerosol delivery to infants using a face mask is known to have several drawbacks in terms of patient's tolerance and efficient handling by non-professionals. The major drawback is the difficulty of achieving a good mask-face seal that arises as a result of screaming and crying of the infant. The low acceptance of the infant toward the mask interface is especially since nebulizer treatments takes about 15 minutes, much longer than most infants tolerate. The impatient behaviour of the infant also reduces the efficiency of drug delivery to the lungs. It was found recently that aerosol therapy to wheezy infants with the hood interface is as efficient as using a mask. The preferment of the parent and the better toleration of the infant toward the administration using the hood were also observed. This has led to the recently developed hood-shaped inhaler.

In the present study we study a complete 3-D configuration of the hood and the infant including, head, chin, shoulders, mouth, nose and nostrils. The infant's complete 3-D configuration is based on the dimensions of a real 5-month-old infant, thus the geometry dimensions and structure compromise a real physical computational geometry. The 3-D configuration includes most common scenarios: the funnel is perpendicular to the infant face, the head is tilt relating to the funnel and the funnel is tilt relating to infant head.

A full transient solution was implemented in the current study including continuous injection of aerosol. At the entrance to respiratory system (nose) many physical breathing patterns were implemented. This breathing patterns includes regular tidal breathing with inspiratory duty cycle of 0.5 and 0.4, and periodic breathing with crescendo-decrescendo, decrescendo and flat patterns. A combination of breathing from mouth and nose was also investigate

The 3-D equations were solved with FLUENT 6.1 finite volume CFD (computational fluid dynamics) code. The complex computational geometry was generated with the GAMBIT software package. The results of the present study agree well with experimental ones. The results indicates that the amount of aerosol penetrating to the respiratory system through the nose when the funnel is perpendicular to the infant face in regular tidal breathing with inspiratory duty cycle of 0.5 and 0.4 is 27% and 22% respectively. Results were also obtained for various tilt angles of the funnel when the head is strait and when the head is also tilt, that is, very realistic case were both the funnel and the head are tilt.

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12E4

INFLAMMATORY RESPONSE OF HUMAN AORTIC ENDOTHELIAL CELLS INDUCED BY METAL OXIDE NANOPARTICLES.

BING GUO, Ian M. Kennedy, Andrea Gojova, Abdul Barakat, University of California, Davis, CA

The role of composition in determining the toxicity of ultrafine metal particles is currently uncertain. We hypothesize that the reaction of metal oxide nanoparticles in cells depends on the electronegativity of the metal – hence the composition of the oxide particles will determine the response that the particles elicit from cells. The metals of interest in our current study range from yttrium that can be made luminescent for real time uptake studies, to iron and zinc: the latter metals are among the most abundant metals found in diesel exhaust particulate matter. Our flame synthesis method allows us to generate metal oxide nanoparticles with well-controlled composition and morphology. The particles are delivered to a culture of human endothelial aortic cells. The dose of particles to the cells is determined with inductively coupled plasma mass spectrometry (ICPMS). Uptake is studied with electron microscopy and confocal microscopy with the luminescent nanoparticles. Following exposure, the cells are subjected to cytokine analysis to determine inflammatory response. Specifically, levels of ICAM, IL8 and MCP-1 were measured. We found a dose dependent response for these markers to yttrium and zinc, with zinc showing the most dramatic effect – on the other hand, iron did not elicit a response. TEM images showed that all three types of particles were sequestered in cell vesicles that have yet to be identified positively. It is likely that the structures are lysosomes that present an acidic environment to the particles. We have checked the solubility of our nanoparticles under relevant pH conditions and found that the cell response can be correlated with the solubility and reactivity in acids. Yttrium is slightly alkaline and reactive, iron oxide is unreactive, while zinc oxide is amphoteric and quite reactive. Dissolution of the particles is indicated in the TEM images of yttrium and zinc; the iron oxide particles maintained their faceted crystal appearance inside the cell and were apparently unaffected. The results provide an indication of the role of composition in determining the health effects that may ensue from exposure to metal oxide nanoparticles, especially if these particles translocate to the heart following inhalation.

12E5

RESPONSES OF SELECTED BIOLOGICAL MODELS TO MANUFACTURED NANOPARTICLES. M.-D. Cheng, D. K. Thompson, B. H. Voy, D. K. Johnson, and B. Malone, Oak Ridge National Laboratory, POBox 2008, MS 6038, Oak Ridge, TN

Manufactured nanoparticles (e.g., diameter ≤ 100 nm) represent a new class of materials to be introduced into the environment and work places. As a class, little is known about the biological responses to the engineered nanomaterials. Adverse health risks due to exposure to complex atmospheric particles, occupational dusts, and coal fly ash particles are well documented. However, the later class of nanoparticles is by no means the same as (or similar to) manufactured nanoparticles except in their geometrical sizes, and should not be treated as they are when studying their impacts (positive or adverse) on the environmental and health. These precisely controlled nanostructures have properties fundamentally distinct from incidentally produced waste particles that are typically the concern in pulmonary toxicology. Specifically, it is unclear how cells and/or animals will respond when they are exposed to manufactured nanoparticles, where nanoparticles would translocate once they enter the biological system, and how to measure the nanoparticles and the biological responses, properly. A group of scientists at the Department of Energy Oak Ridge National Laboratory in Oak Ridge, Tennessee, is conducting systematic and fundamental investigations on various fronts related to the biological effects of selected nanoparticles using selected biological models. These models include selected cell lines and microbes commonly found in the environment. Experimental techniques required to conduct precision exposure experiments and to characterize particles as well as biological responses at cellular and molecular levels have been explored, we will report our recent findings from exposure experiments.

12E6

GENERATION OF DIESEL EXHAUST FOR HUMAN EXPOSURE. DAVID R. COCKER III, Aniket A. Sawant, J. Wayne Miller, Tony Taliaferro, University of California, Riverside, CA; David Diaz-Sanchez, University of California, Los Angeles, CA; Henry Gong Jr., William S. Linn, Kenneth W. Clark, Los Amigos Research and Education Institute, Downey, CA

A test facility for exposure of human subjects to diesel exhaust (DE) has been developed and thoroughly characterized. DE is generated from a 1999 medium-duty pickup truck equipped with a 250-hp 7.27L V-8 engine operating on ultra-low-sulfur diesel fuel. DE from the vehicle tailpipe is diluted and transferred to a 9.7 m3 exposure chamber to produce a stable diesel exhaust particulate (DEP) concentration of 100 mg/m3. This paper reports on the characterization of the DE suspended within the chamber with emphasis on generation of reproducible, stable, and representative DE samples for future human exposure studies. The vehicle emissions are shown to be typical of a modern, light-duty diesel vehicle when tested following the Federal Test Procedure (FTP-75) driving cycle. The chemical speciation and physical characteristics of the dilute DE inside of the chamber is verified to be similar to DE tailpipe emissions. Run-to-run and day-to-day experimental reproducibility and chamber homogeneity are verified. Finally, the concentrations of regulated emissions and detailed gas-phase, semi-volatile, and particulate matter are reported for the chamber as it operates at a 100 mg/m3 DEP loading.

13A1

DETERMINATION OF PARTICLE EFFECTIVE DENSITY IN URBAN ENVIRONMENTS WITH AN ELECTRICAL LOW PRESSURE IMPACTOR AND SCANNING MOBILITY PARTICLE SIZER.

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While ambient particulate matter has been associated with adverse health effects, the specific properties of particles eliciting these responses have not been discovered. It is known that particles vary from perfect spheres to almost linear chains, which can be described by their fractal dimensions. A fractal chain agglomerate has a low effective density and high surface area due to the nature of its structure. These properties will affect adsorption of vapors as well as where it deposits in the respiratory tract. This study focuses on the determination of effective density of various ambient aerosols using an Electrical Low Pressure Impactor (ELPI) in comparison with a Scanning Mobility Particle Sizer (SMPS). Since the ELPI sizes particles based on aerodynamic diameter and the SMPS by mobility diameter, the effective density is calculated by comparing the number and volume distributions of both instruments. A MOUDI and Aerodynamic Particle Sizer (APS) also sampled during this study as an alternate means of calculating the aerosol density. The ELPI was first evaluated with lab aerosols with known densities, such as PSL particles, ammonium sulfate and glutaric acid. Their measured effective densities were 1.0, 1.7 -1.8, and 1.2, respectively, which are nearly identical to the book values of PSL and ammonium sulfate and within 20% of the book value for glutaric acid. The field sites include I-710 freeway (35% heavy duty diesel vehicles), CA-110 freeway (a gasoline freeway), Riverside (receptor site with secondary particle formation), and USC (urban location). Sampling occurred at USC for an extended period in order to determine diurnal changes in effective density. A curve-fitting algorithm indicates that effective density decreases with particle size at both I-110 and I-710, with lower calculated effective densities of super-100 nm particles at I-710. Sub-100 nm particles have effective densities greater than unity while super-100 nm particles have effective densities lower than unity. Effective density is variable at USC, and at times it is constant across all particle diameters.

13A2

URBAN-SCALE DIFFERENCES IN AEROSOL CONCENTRATION IN HAIFA, ISRAEL.

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In regions like Haifa, where industries, traffic and residential areas blend, urban air quality is of vital concern. This research examines the spatial differences in airborne particulate matter and elemental carbon concentrations between similar (with respect to altitude, socio-economic status, private vehicle ownership, etc.) residential neighborhoods that are located in close proximity to one another. Air sampling was conducted at several paired sites in Haifa during different seasons. The measurements were carried out in local parks and open spaces within the neighborhoods, at a distance of ~20-50 m from the nearest road. Additionally, a semi-urban location in the Carmel Park was chosen for urban-background measurements. The vegetation cover, estimated using aerial photographs, varies considerably among the paired neighborhoods. Continuously monitored data collected by the Haifa District Municipalities Association for the Environment and the Israel Electric Company were used as reference throughout the sampling periods.

Particulate matter concentrations and size distribution were measured using a portable multi-size channel (0.23-20μm) mini aerosol spectrometer (Grimm Inc., Germany). The concentration of optically absorbing black (elemental) carbon in the aerosol phase was measured using an Aethalometer (Magee Scientific, USA). Meteorological data were collected by a portable meteorological station and, in addition, meteorological data from monitoring stations in close proximity to the sampling sites were used. Intensive sampling campaigns were conducted during summer 2003, spring 2004, and summer 2004 throughout the weekdays.

Seasonal differences in concentrations are clearly observed and often the daily concentration variation is notably greater than the spatial variation between the neighbourhoods. Nonetheless, inter-neighborhood differences in concentrations do exist. Local scale emission variability and site-specific meteorological conditions are possible explanations for some of these differences. However the ability of trees to capture gaseous and particulate phase pollutants cannot be ruled out. Preliminary indications suggest that mainly during the morning, the levels of different particulate matter fractions in the densely-vegetated neighborhoods are lower than in the poorly-vegetated neighborhoods.

13A3

IMPLEMENTATION OF A BAYESIAN INVERSE METHOD TO INORGANIC AEROSOL MODELING: MEXICO CITY METROPOLITAN AREA CASE STUDY. FEDERICO M SAN MARTINI, Jose M. Ortega, Gregory J. McRae, Luisa T. Molina, Mario J. Molina, Massachusetts Institute of Technology, Cambridge, MA Edward Dunlea, Katja Dzepina, Jose-Luis Jimenez , University of Colorado - Boulder, Boulder, CO Joanne H. Shorter, Manjula R. Canagaratna, Scott C. Herndon, Timothy B. Onasch, John T. Jayne, Mark S. Zahniser, Douglas R. Worsnop, Charles E. Kolb, Aerodyne Research, Inc., Billerica, MA Dara Salcedo, Universidad Autónoma del Estado de Morelos, Cuernavaca, México Nancy A. Marley and Jeffrey S. Gaffney, Argonne National Laboratory, Argonne, IL Michel Grutter, National Autonomous University of Mexico, Mexico City, Mexico

Significant effort has been devoted to collecting data on urban particulate matter (PM) concentrations, and advances in particle measurement technologies have allowed for an increasingly sophisticated picture to be developed. Relative to this, the dataset for the gas phase precursors to the inorganic PM is sparse, despite the necessity of these observations in determining effective control strategies. A Bayesian method has been implemented to exploit the asymmetry between the rich aerosol dataset and the relatively poor dataset on gas-phase precursors. A Markov Chain Monte Carlo algorithm was combined with the equilibrium inorganic aerosol model ISORROPIA to produce a powerful tool to analyze aerosol data and predict gas phase concentrations where these are unavailable. The method directly incorporates measurement uncertainty, prior knowledge, and provides for a formal framework to combine measurements of different quality. The method was used to discriminate between diverging long-path and point source observations of gas phase precursors taken during the 2003 Mexico City Metropolitan Area (MCMA-2003) field campaign. The role of aerosol chloride and water in determining aerosol behavior is investigated. Probabilistic estimates of gas phase nitric and hydrochloric acid are presented, and the diurnal variation and likely sources of these pollutants are discussed. We conclude with a discussion of the policy implications of these findings.

13A4

THE ORIGIN OF WATER SOLUBLE PARTICULATE IRON IN THE ASIAN ATMOSPHERIC OUTFLOW. P. Y. CHUANG, University of California Santa Cruz, Santa Cruz, CA; R. M. Duvall, M. M. Shafer, J. J. Schauer, University of Wisconsin-Madison, Madison, WI

Iron, and in particular water soluble iron, is an important trace nutrient in the surface ocean, and therefore an important component in the global carbon cycle. Deposition of Asian aerosol is thought to be a primary source of water soluble iron in the northern Pacific. Analysis of aerosol samples obtained during the Aerosol Characterization Experiment (ACE)–Asia field campaign from Jeju Island, Korea, which intercepts the outflow from the Asian continent, shows that water soluble iron is not dominated by airborne dust sources even during large dust storms. Instead, our analysis shows that particulate soluble iron and elemental carbon concentrations are correlated. This leads to the conclusion that soluble iron in this region is primarily associated with anthropogenic activity rather than mineral dust.

13A5

SOURCE APPORTIONMENT OF ALPHA–PINENE PHOTOOXIDATION PRODUCTS IN DUKE FOREST, NORTH CAROLINA. Matthew P. Fraser, SHAGUN BHAT, Civil and Environmental Engineering Department, Rice University, Houston, TX

Fine particulate samples were collected in Blackwood division of Duke Forest, North Carolina. The samples were collected daily as part of the CELTIC study in 2003, between July 10 and 23. The major types of vegetation in the forest consist mainly of pine and pine-hardwood. The most common species of pine found within the forest are loblolly, shortleaf and Virginia pine. Particulate samples were collected on quartz filters using high volume air sampling equipment. Organic compounds (polar and non polar) were quantified, including α-pinene oxidation products, namely pinic acid and pinonic acid. Gas Chromatography (GC) coupled with Mass Spectroscopy (MS) was used to identify and quantify individual organic species. Polar compounds were derivatized using a two-step derivatization technique involving the use of O- (2,3,4,5,6-pentafluorobenzyl) hydroxyl amine (PFBHA) and N, O-bis (trimethylsilyl)-trifluoro acetamide (BSFTA). The results indicate that both biogenic sources contribute significantly to ambient aerosols. Biogenic contribution to n-alkanes ranged from 17.5% to 61.5%. Oxidation products of α-pinene, namely pinic acid and pinonic acid, were detected in all samples. Pinic acid, being a dicarboxylic acid has a low vapor pressure of the order of 10-8 Torr and is expected to contribute significantly to secondary organic aerosol (SOA) formation. Source contribution estimates from primary organic aerosol emissions were computed using the polar and non-polar organic species concentrations in the chemical mass balance (CMB-8) model. The unapportioned organic carbon (OC) was determined as the difference between measured and apportioned OC levels. This unapportioned OC was then correlated with pinic and pinonic acid to get a better understanding of the potential of monoterpene oxidation products to form secondary organic aerosols. A reasonably good fit between pinic acid concentrations and unapportioned OC levels, is indicative of the contribution of α – pinene oxidation products to secondary organic aerosol formation in ambient atmosphere. The results are significant considering the fact that monoterpenes contribute about 80% to global emissions of primary organic carbon out of which a significant 35% are α-pinene emissions (Griffin et al., 1999).

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13A6

TEMPORAL VARIATIONS OF ELEMENTAL CARBON IN TOKYO. YUTAKA KONDO, Yuichi Komazaki, Yuzo Miyazaki, Nobuhiro Moteki, Michimori Nogami, Nobuyuki Takegawa, Seiji Deguchi, Masato Fukuda, Takuma Miyakawa, Yu Morino, Daisuke Kodama, Research Center for Advanced Science and Technology, University of Tokyo, Tokyo, Japan

Mass concentrations of elemental carbon (EC) and mixing ratios of carbon monoxide (CO) were measured at the University of Tokyo campus in Tokyo in different seasons in 2003-2005. Measurements of EC were made using a semi-continuous thermal-optical analyzer. The correlation of EC and CO was generally compact throughout the measurement period due to the similarity in sources. The slope of the EC-CO correlation (EC/ CO) is therefore a useful parameter in validating EC emission inventories. CO2 can also be a good tracer for EC because of observed tight CO-CO2 correlation. The EC concentration and EC/ CO showed distinct diurnal variation. On weekdays, EC and EC/ CO reached maximum values of about 3 µg m-3 and 9 ng m-3/parts per billion by volume (ppbv), respectively, in the early morning (0400-0800 LT), when the traffic density of heavy-duty trucks with diesel engines was highest. In addition, these values were lower by a factor of 2 on Sundays. The heavy truck traffic showed similar diurnal and weekday/weekend variations, indicating that exhaust from diesel engines is an important source of EC. The EC/ CO values on rainy days showed no detectable difference from the average value. Monthly mean EC/ CO values showed a seasonal variation reaching maximum in spring-autumn and minimum in winter caused by the corresponding seasonal variation in temperature . More stringent regulation of emissions of EC from diesel cars started in the Tokyo metropolitan area in October 2003, and the present analysis is used to estimate this effect. Current estimates of the EC emission rate averaged over Japan are assessed by comparison with the observed EC/ CO and EC/ CO2 in Tokyo and Nagoya. The EC/ CO values obtained in Japan are compared with those obtained in other cities outside Japan.

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13B1

BUILDUP OF AEROSOL LOADING OVER THE INDIA OCEAN DURING THE MONSOON TRANSITION.. CRAIG CORRIGAN, V. Ramanathan, Scripps Institution of Oceanography, La Jolla, CA J. Schauer, University of Wisconsin, Madison, WI G. Carmichael, University of Iowa, Iowa City, IA

In recent years, black carbon has been recognized to significantly affect radiative forcing and global climate change. The Atmospheric Brown Cloud project (ABC-Asia) has focused on measuring the anthropogenic influence of aerosols, including black carbon, to determine the extent of sunlight dimming and radiative forcing over the Asian region. The first station in the ABC network is located in the Republic of Maldives, which is located in the Indian Ocean near the southern tip of India. The presence of black carbon over the Indian Ocean varies with the cyclic nature of the Asian-Australian Monsoon. Every 6 months, the winds change directions. From May to October, the wet season brings clean air into the region from the southern hemisphere. Conversely, the dry season brings polluted air from the Indian subcontinent and South East Asia from November thru April. As a result, the region becomes charged with black carbon and other anthropogenic pollutants during the dry season. During 2004, the transition between the clean and polluted seasons resulted in nearly a 10 fold increase of scattering and absorbing aerosols. The change occurred very abruptly over a period of a few days as air from India and South East Asia arrived in the Maldives at the surface level. The new, polluted aerosol was characteristically darker since the black carbon increased more substantially than the overall aerosol scattering. As a result, the single scatter albedo was reduced from an average of 0.98 to 0.92. Observed results have been compared to the CFORS regional model and show good agreement for trends and irregular agreement for numerical values.

13B2

IN-SITU MEASUREMENTS OF AEROSOLS FROM MOTOR VEHICLES IN THE CALDECOTT TUNNEL. A.G. Hallar, A. W. Strawa, , K. Bokarius, NASA AMES Research Center; T.W. Kirchstetter,Lawrence Berkeley National Laboratory; R. A. Harley, University of California Berkeley

Carbonaceous species (BC and OC) are responsible for most of the absorption associated with aerosol particles. The amount of radiant energy an aerosol absorbs has profound effects on climate and air quality. It is ironic that the aerosol absorption coefficient is one of the most difficult aerosol properties to measure.

A study was conducted during the summer of 2004 in the Caldecott Tunnel, a heavily-used tunnel located east of San Francisco, CA. The aerosol sampled in this study was characterized by fresh automobile and diesel exhaust. Roadway tunnel studies have some strong advantages over traditional dynamometer studies. For instance this study captured the aggregate emissions of a fleet of vehicles (4000 cars/hr in the center bore) operating under real-world, in-use conditions. This experiment involved two separate test-beds, one week of measurements within a light duty (gasoline) vehicle bore and one week within a mixed light duty (gasoline cars)/ heavy duty (diesel trucks) vehicle bore. Furthermore, within the framework of this study, the relative humidity was adjusted within the sample line to test the possible hydroscopic nature of the emissions.

A new cavity ring-down (CRD) instrument, called Cadenza (NASA-ARC), measures the aerosol extinction coefficient for 675 nm and 1550 nm light, and simultaneously measures the scattering coefficient at 675 nm. The absorption coefficient is obtained from the difference of measured extinction and scattering within the instrument.

Measurements from Cadenza, a standard aethalometer, and a Scanning Mobility Particle Sizer (SMPS, TSI Inc.) are presented. The aethalometer is a filter-based photometer and the near infrared channel is calibrated to produce a measure of BC mass loading. The SMPS system measures submicrometer aerosols in the range from 3 to 1000 nanometers in diameter. It employs an electrostatic classifier to determine the particle size, and a Condensation Particle Counter (CPC) to determine particle concentrations.

13B3

OPTICAL SATURATION EFFECTS ON AETHALOMETER RESPONSE. Bradley Goodwin, JAY TURNER, Washington University, St. Louis, MO

The Magee Scientific Aethalometer ™ provides a semi-continuous measure of aerosol black carbon. Aerosol is continuously deposited onto a quartz fiber filter tape and light transmittance through this aerosol-laden filter is measured at a user-defined frequency. The change in light attenuation through the aerosol-laden filter upon sampling a given volume of air is corrected for attenuation due to the filter alone (in the absence of particles). Aerosol black carbon is calculated from the aerosol-induced attenuation using an effective mass absorption efficiency (often called an absorption cross-section). Recently published works by Weingartner et al. (2003) and Arnott et al. (2005) describe a decrease in the effective mass absorption efficiency with increased loading of light-absorbing particles onto the filter. Presumably the accumulation of light-absorbing aerosol dampens the absorption enhancement caused by the massively scattering environment of the filter.

In this work, we adopted the empirical equation of Weingartner et al. (2003) to investigate the impact of this "optical saturation" phenomenon on aethalometer black carbon measurements conducted at the St. Louis – Midwest Supersite core monitoring location in East St. Louis (IL). A methodology was developed to account for both instrument bias and the optical saturation effect in reconciling collocated aethalometer data; a methodology was also developed for extracting the optical saturation parameter – a fitting parameter in the empirical equation of Weingartner et al. (2003) – from a time series of data for one aethalometer. Excellent agreement was obtained between these two methods for estimating the optical saturation parameter. A four-year time series for the optical saturation parameter exhibits a seasonal trend, with the light-absorbing aerosol appearing more chemically aged in the summertime compared to the wintertime.

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13B4

HOW BIOGENIC EMISSIONS AFFECT AEROSOL CONCENTRATIONS AND RADIATIVE FORCING IN THE MEDITERRANEAN AREA. RAFAELLA - ELENI P. SOTIROPOULOU, Efthimios Tagaris, Chris Pilinis, University of the Aegean, Dept. of Environment, Mytilene, Greece

The role of biogenic emissions in the aerosol budget and in the radiative forcing in two representative Mediterranean areas, Athens, Greece and Marseilles, France is examined with the help of the UAM-AERO model. These areas were selected as they are characterized by important biogenic emissions and sufficient degree of meteorological and land use diversity. Comparison of the results of the model with and without the inclusion of biogenic emissions reveals the significant role biogenic emissions play in modulating both ozone and aerosol concentrations. The emissions of gases of biogenic origin affect the concentrations not only of the organic aerosol constituents, but also the inorganic ones, like sulfates and nitrates. Biogenic emissions are predicted to affect the concentrations of organic aerosol constituents through the reactions of terpenes with O3, OH and NO3. In addition, the ozonolysis of terpenes is predicted to cause an increase in OH radical concentrations compared to the predictions without biogenic emissions. The reactions of this extra hydroxyl radical with SO2 and NOx increase the concentrations of sulfates and nitrates in the particulate phase. Using the aerosol concentrations, as they have been estimated by the UAM-AERO model, the scattering coefficient and the upscatter fraction are determined as a function of wavelength, for 960 wavelength bins in the range of 0.2 to 5.0 μm. The results for the two areas of interest indicate that, in both areas, biogenic emissions increase the radiative forcing (in absolute values) substantially, due to the extra aerosol formed by the biogenic gas-to-particle conversion. Thus, biogenic emissions are predicted to play an important role on the energy balance in both areas, as they contribute to the cooling effect.

13B5

OPTICAL PROPERTIES OF ASIAN OUTFLOW AEROSOLS MEASURED ON AN ISLAND (CHICHI-JIMA) IN THE WESTERN PART OF NORTH PACIFIC OCEAN. NAOKI KANEYASU, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; Masataka Shiobara, National Institute of Polar Research, Japan; Toshiyuki Murayama, Tokyo University of Marine Science and Technology, Tokyo, Japan

To evaluate the potential impact of air pollutants originated in Asia on the atmospheric constituents over the North Pacific Ocean, monitorings have been continued on a mountain (240 m m.s.l.) in Chichi-jima (Bonin) Island, Japan (27o 04' N, 142o 13' E), located 1000 km south of the mainland Japan and about 1800 km east of the Asian coast. The ground-based monitoring instruments at Chichi-jima include an Aethalometer for black carbon (BC) concentration, an Integrating Nephelometer for aerosol scattering coefficient, and an optical particle counter for aerosol size distribution. Aerosol optical depths are measured with a 6-wavelength sun-photometer. We also collected aerosols with a 12-stage low-pressure cascade impactor. Aerosol absorption coefficients were measured with a Particle/Soot Absorption photometer (PSAP) when intensive measurement campaigns were conducted.

BC concentration in the Marine Boundary Layer showed a clear seasonal variation; it was high (> 150 ng/m3) from December to early May when the continental airmass covers the area, and low (< 40 ng/m3) during the rest of the months when the airmass from the North Pacific Anticyclone system dominate the area. It is noteworthy that the appearance of high BC concentration is intermittent, i.e., a high BC concentration occurs roughly once a week and continues for about one day. This intermittent transport of pollutants is generally accompanied by the passage of a cold front.

From February 9 to 20, 2004, an intensive field measurement was conducted to study the properties of aerosols transported behind the cold front, were analyzed in detail. When the Asian outflow aerosols arrived at the island on February 15, 1994, aerosol absorption coefficient and scattering coefficient increased sharply. The single scattering albedo of the aerosols was calculated from these values. Using the size distribution obtained by the low-pressure cascade impactor and single scattering albedo, the imaginary part of the refractive index of aerosols was calculated with a fixed value of the real part of refractive index (= 1.55). The resultant imaginary part of refractive indices (from -0.010 to -0.013) lied between the values of "continental (-0.01)" and "urban/industrial (-0.017)" types in the WMO WCP-55 model. With vertical distributions of aerosols and relative humidity in the lower troposphere obtained by a Ceilometer and Radio Sonde, respectively, a column closure study was conducted for the aerosol optical properties in this episode.

13B6

ANNUAL APPLICATION OF REGIONAL PARTICULATE MATTER PHOTOCHEMICAL GRID MODELS TO THE CENTRAL US TO SUPPORT THE REQUIREMENTS OF THE REGIONAL HAZE RULE. RALPH MORRIS, Bonyoung Koo, Gerard Mansell and Greg Yarwood, ENVIRON International Corporation, Novato, CA; Gail Tonnesen, Chao-Jung Chien and Mohammed Omary, University of California at Riverside, Riverside, CA

The Central Regional Air Planning Association (CENRAP) consists of states, tribes, federal agencies and other interested parties and is one of five regional planning organizations (RPOs) in the United States (US) charged with implementing the requirements of the Regional Haze Rule (RHR). CENRAP includes the states and tribal areas of Nebraska, Kansas, Oklahoma, Texas, Minnesota, Iowa, Missouri, Arkansas and Louisiana. CENRAP is applying the Community Multi-scale Air Quality (CMAQ) and the Comprehensive Air-quality Model with extensions (CAMx) modeling systems for the 2002 annual period to project visibility at Class I areas in the CENRAP region. This paper discusses the application of the two models for the 2002 base period and the comparison of model performance using the IMPROVE, STN and CASTNet particulate matter (PM) monitoring networks. Emission and meteorological inputs were generated using the SMOKE emissions and MM5 meteorological models, respectively. Differences in CMAQ and CAMx model performance is related to differences in model formulation and inputs. The formulation and application of the CAMx PM Source Apportionment Technology (PSAT) used to identify the geographic source regions and major source category contribution to fine particle concentrations is also described. Areas for improvements in model inputs and formulation are identified and discussed.

13C1

REAL-TIME MEASUREMENT OF THE MASS AND COMPOSITION OF PARTICLES. KENNETH C. WRIGHT, Peter T. A. Reilly, and William B. Whitten. Oak Ridge National Laboratory, Oak Ridge, TN

Over the past decade, aerosol science has strived to characterize smaller and smaller particles while the field of mass spectrometry has strived to characterize larger and larger molecules. We will discuss how to merge the two disciplines using a quadrupole mass spectrometer with an essentially infinite mass range.

The mass limit of most mass spectrometers is currently under 100kDa. In terms of aerosols, this mass limit corresponds to particles less than 7nm in diameter. To move quadrupole MS beyond this limit three main problems must be overcome. (1) Particles acquire an enormous amount of kinetic energy, when transferred into vacuum, that must be reduced before trapping or mass analysis can be preformed. (2) A technique to detect such massive ions must be developed. (3) The quadrupole's frequency must be rapidly switched or scanned in order to effectively cover the entire mass range of particles/ions from 0.1nm to 10µm. We have solved these problems and are developing a mass spectrometer that will open new frontiers in mass spectrometry and be capable of real-time particle mass analysis.

The problems outlined above are being solved using the following methods: (1) A reverse jet of gas is being used to reduce the kinetic energy of a collimated particle beam. The same forces that first accelerated the particles are used by the reverse jet to slow them down again thus effectively slowing all masses simultaneously. (2) The quadrupoles used for mass analysis are driven with square waves (digitally) using pulse generators whose frequency can be rapidly switched or scanned to generate an optimal well-depth for any mass range. (3) Detection of the charged species is accomplished by pyrolytic vaporization and electron impact ionization of the evolving vapor with subsequent detection with a channeltron electron multiplier.

After experimentally confirming that the reverse jet slows incoming charged particles, the pyrolytic detector system was tested and optimized. Currently, single 41nm latex beads are easily detected. Of course, when used with a quadruple trap many charged species will be pulsed to the detector at once so this detector will be sensitive to much smaller particles. Recently, a linear quadrupole was used to control the transmission of particles. With this enabling technology in place, a complete mass spectrometer is currently being evaluated and its performance will be presented.

13C2

LIBS FOR QUANTITATIVE ANALYSIS OF AEROSOLS. DAVID W. HAHN, Vince Hohreiter, University of Florida, Gainesville, FL

Laser-induced breakdown spectroscopy (LIBS) has been developed in recent years for quantitative analysis of the size and elemental mass composition of individual micron to submicron-sized aerosol particles, including strong interest in recent years in analysis of bioaerosols. To date, detection limits approach several hundred nanometers for many metal-containing aerosols, with corresponding absolute detectable mass on the order of tens of femtograms to a few femtograms. This paper will focus on the status of LIBS as a novel means to address critical needs in the real-time monitoring and characterization of single aerosol particles. Issues include the upper particle size limit for quantitative analysis, aerosol sampling statistics, shot-to-shot fluctuations, and data precision. Results from the analysis of individual bioaerosols, and the LIBS-based real-time measurement of the temporal fluctuations of ambient aerosols and comparisons with light scattering data will be presented.

13C3

AEROSOL MALDI MASS SPECTROMETRY FOR ANALYSIS OF BIOAEROSOL.

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A.L. van Wuijckhuijse, Ch.E. Kientz, O. Kievit, TNO Prins Maurits Laboratory

We are developing a system designed to analyze proteins and other biologically based material present in single aerosol particles (van Wuijckhuijse et al. (2005)). Matrix-assisted laser desorption/ionization mass spectrometry (MALDI) has become a standard tool in bulk analysis of this type of material, but presents a variety of challenges distinct from either standard MALDI analysis or from standard single particle mass spectrometry. In the standard MALDI procedure, biomaterial is co-crystallized with an excess of photon-absorbing matrix. This solid mixture is irradiated with short laser pulses leading to a phase change. It is in this rarefying and reactive plume where proton-transfer reactions take place, resulting in the formation of the characteristic ions.

In our system, aerosols originating at ambient pressure form a beam of particles in the vacuum chamber of a time-of-flight mass spectrometer. The velocity of single particles is determined by measuring the transit time between two laser beams. This, in turn, allows accurate timing of an Excimer laser pulse that initiates ion formation. One of the two particle detection laser beams is of (continuous) 266 nm light and provides the ability to pre-select particles based on fluorescence excited by this light. This allows the system to preferentially respond to particles containing bacteria, either vegetative cells or spores, which emit light in the wavelength range of approximately 290 nm to 400 nm.

The primary goal of our effort is the development of a rapid, on-line detector for bacteria. However, we also see applications in a variety of other areas, including proteomics and rapid cell characterisation. In this paper, we will present recent progress in developing and applying the aerosol MALDI technique.

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13C4

MASS SPECTROMETRY OF INDIVIDUAL SUB-10 NM DIAMETER PARTICLES AND MOLECULES.

Shenyi Wang and MURRAY JOHNSTON, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE

A Nanoparticle Mass Spectrometer (NAMS) has been developed for analysis of individual airborne particles below 10 nm in diameter. In the current version, particles are charged with a radioactive neutralizer and sampled through a modified aerodynamic inlet. Once inside the mass spectrometer, particles are focused and translationally cooled in a quadrupole ion lens and then captured in a quadrupole ion trap. The trapped particles are irradiated with a high energy laser pulse (100 J/cm2). The laser pulse creates a plasma that disintegrates the particle, quantitatively converting it into positively charged atomic ions. These ions are characterized by time-of-flight mass analysis to give the elemental composition of the particle.

Using this setup, we have acquired mass spectra of test particles consisting of inorganic salts (sodium chloride with and without ammonium acetate; ammonium sulfate), sucrose, and single bovine serum albumin molecules. In each case, the relative signal intensities of the atomic ions produced by the plasma give a quantitative measure of the particle composition. Under standard operating conditions, singly charged particles between 7 and 10 nm in diameter are trapped. These conditions will be modified in the future to trap and analyze other size ranges. The detection efficiency, defined as the fraction of particles entering the inlet that are trapped, ablated and detected, is about 10-6. Studies of new particle formation using this instrument are underway and will be reported in this presentation.

13C5

REAL-TIME MEASUREMENT OF ELEMENTAL COMPOSITION OF AEROSOLS – BEYOND LIBS. M.-D. Cheng and R. W. Smithwick, III, Oak Ridge National Laboratory, PO Box 2008, MS 6038, Oak Ridge, TN

The best warning of human exposure to elevated toxic aerosol particles is a monitor that can provide a near-real-time alarm function. Use of surrogate indices such as particle-number concentration, mass concentration, and/or other flow-diagnostics variables is ineffective and could be costly when false positives do arise. We have developed a field- portable system specifically for monitoring beryllium particles in the air in near real-time. The prototype monitor is housed on a two-shelf handcart that can be used in workplaces involving beryllium extraction, machining, and parts fabrication. The measurement involves no sample preparation and generates no analytical waste. The operating principle of the monitor is laser-induced electrical-plasma spectrometry assisted with aerosol-focusing technology. Performance data of the monitor indicates a dynamic range spanning over four orders-of- magnitude, and the monitor is capable of detecting an airborne beryllium concentration of 0.05 µ;g m-3. In reference, the Department of Energy standard for beryllium is 0.2 µ;g m-3 within an 8-hour average, while the Occupational Safety and Health Administration standard for beryllium is 2 µ;g m-3. In addition, the monitor is capable of simultaneous detection of multiple elements using an Echellette spectrometer. The capability of simultaneous detection provides a convenient means for positive identification, and possible quantification of multiple elements in near-real time. We will present the beryllium results and show applications of the technology to simultaneous detection of several elements embedded in aerosol particles.

13C6

CHARACTERIZING THE ORGANIC COMPONENT OF ULTRAFINE AEROSOL USING TEMPERATURE-PROGRAMMED THERMAL DESORPTION CHEMICAL IONIZATION MASS SPECTROMETRY. MATTHEW J. DUNN, University of Colorado and National Center for Atmospheric Research, Boulder, CO; James N. Smith, Katharine F. Moore, Hans R. Friedli, Fred L. Eisele, National Center for Atmospheric Research, Boulder, CO; Peter H. McMurry, University of Minnesota, Minneapolis, MN; Jose-Luis Jimenez, University of Colorado, Boulder, CO

Previous attempts to characterize organic compounds in ambient nanoparticles using the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) were hindered by a poor understanding of the conditions required to properly desorb and ionize organic compounds from particles. This has led to the development of the Temperature Programmed TDCIMS (TP-TDCIMS). With the TP-TDCIMS, particles are collected by electrostatic deposition onto a metal filament, then the filament is moved into a chemical ionization source where it is heated gradually over the range of 30 – 500 degrees C. This gradual desorption improves sensitivity and minimizes compound fragmentation as compared to the instantaneous heating used in the former instrument.

In developing the TP-TDCIMS we have taken a 2-step approach. First, we examined the proton transfer chemistry that converts neutral organic species into ions to be analyzed by our triple quadrupole mass spectrometer. This was done by introducing model trace gases (e.g., acetone, octyl aldehyde) directly into the ion source. Results show that water clusters play a crucial role in the ionization chemistry. These tests also allowed us to study the characteristic tandem mass spectra associated with various organics, which will aid compound identification for ambient sampling. The next phase of our investigations focused on the thermal desorption process itself. For these tests we collected both laboratory-generated single and multi-component aerosol, or we applied dilute solutions (e.g., of succinic acid or oleic acid) directly onto the filament to observe the performance of temperature-programmed desorption for compound detection. Results show that ion fragmentation is greatly reduced using TP-TDCIMS and is characteristic of chemical family. This along with the additional information of volatilization temperatures greatly simplifies compound identification.

The successful application of this technique for ambient atmospheric aerosol shall be verified by directly measuring 4 – 50 nm diameter aerosol composition at the NCAR Marshall Field site outside Boulder, CO. These measurements are conducted for the purpose of identifying which compounds participate in new particle formation, and so TP-TDCIMS data are supplemented by particle size distributions in the 0.003-2 micron diameter range, the distribution and polarity of charged particles smaller than 6 nm, key trace gases (e.g., SO2, NO), and local

13D1

DEFINITION, QUANTIFICATION AND IMPLICATIONS OF SOOT NANOSTRUCTURE. RANDY L. VANDER WAL, The National Center for Space Exploration Research, (NCSER) c/o NASA-Glenn, Cleveland OH

Soot is ordinarily considered as a carbonaceous material with environmental and health consequences highly dependent upon particle size. Though to-date unexplored, the nanostructure of the soot, i.e. the degree of atomic level order in carbon lamella comprising the soot primary particle can have profound consequences for soot reactivity and associated environmental and health effects. The talk will define soot nanostructure, describe its quantification by image analysis of high resolution transmission electron microscopy images and illustrate its impact on oxidation rate.

Differences in soot nanostructure based upon formation and growth conditions will be presented first. Fuel structure effects can be masked or accentuated depending upon both temperature and rate of increase. Low temperature yields an amorphous soot for all fuels studied here, regardless of flow rate. High temperature yields different results depending upon the rate of increase. A rapid increase in temperature, as realized by a high flow rate, emphasizes pyrolysis kinetics that favor polyaromatic hydrocarbons (PAHs) with 5-membered rings leading to soots with many shells and capsules; a highly curved nanostructure. Slower rates result in a different pyrolysis chemistry leading to graphitic soot, as characterized by long graphitic segments, oriented parallel to each other.

To quantify these differences in nanostructure, a lattice fringe analysis program has been developed to quantify the data conveyed by HRTEM images. The robustness of this program is demonstrated by using a series of carbon blacks possessing different levels of graphitic structure, prepared at different heat treatment temperatures. Its credibility is benchmarked against a traditional measure of graphitic structure, as provided by Raman analysis. Lattice fringe length is found to be monotonic with the level of graphitic structure as provided by the ratio of the integrated intensities of the G/D spectral peaks in the Raman spectra.

We further explore the relationship between soot nanostructure and reactivity towards oxidation by measuring the oxidation rates of laboratory synthesized soots with “model” nanostructures as governed by the synthesis conditions of temperature, time and initial fuel identity. Structural variations in the graphene layer plane dimensions necessarily alters the ratio of basal plane versus edge site carbon atoms. A corresponding variation in the overall reactivity, reflecting an average of the different reactivities associated with these specific atomic sites arises. This variation is illustrated here between a disordered soot derived from benzene and a graphitic soot derived from acetylene. Their oxidation rates differ by nearly 5-fold. Curvature of layer planes, as observed for an ethanol derived soot, is found to substantially increase oxidative reactivity. Relative to fringe length as a manifestation of graphitic structure, curvature more effectively increases reactivity towards oxidation. Larger variations in oxidation behavior may be expected, depending upon the soot synthesis conditions. Other physical properties may similarly be affected. Related implications due to differences in nanostructure will be discussed.

13D2

RELATIVE EMISSIONS IMPACTS OF IN-USE AND EXPERIMENTAL DIESEL FUELS. ANIKET A. SAWANT, Abhilash Nigam, Thomas D. Durbin, J. Wayne Miller, David R. Cocker III, University of California, Riverside, CA

Engine-out emissions from modern heavy-duty diesel engines, in terms of both quantity and composition, are strongly dependent upon combustion characteristics. It is therefore expected that fuel properties would play a major role in determining emissions characteristics, and several studies have shown the beneficial impacts of lower sulfur fuels on emissions. Over the years, diesel fuels with varying specifications have become available in the United States. More recently, several vendors have developed alternative fuels with stated claims of reducing dependence on petroleum feedstock as well as providing emissions benefits.

The present work seeks to test the accuracy of these claims from an emissions/air quality perspective, by comparing them with in-use and experimental fuels. We investigate the impact of the fuels on emissions through a test matrix involving conventional 49-state and ultra-low-sulfur diesel fuel, Fischer-Tropsch fuel, JP-8, and various neat and blended biodiesels, an ethanol-diesel blend, and a water-diesel emulsion. We describe tests performed on two generators (60 kW and 350 kW), two on-highway class 8 diesel tractors, and a light-duty diesel vehicle for military applications. Further, we present results for a full speciation for particle-, semi-volatile, and gas-phase organics as well as regulated emissions and show their relationships with key fuel properties such as cetane number and aromatics content. Finally, we discuss the impacts of these fuels in terms of contribution to the regulated emissions inventory as well as to the Mobile Source Air Toxics (MSATs) inventory.

13D3

POLYCYCLIC AROMATIC HYDROCARBONS IN DIESEL PARTICULATE MATTER. DABRINA D DUTCHER, David B Kittelson, Peter H McMurry– Mechanical Engineering, University of Minnesota, Minneapolis MN

Polycyclic aromatic hydrocarbons (PAHs) are known human carcinogens. There is also strong evidence that PAHs induce reproductive toxicity. One significant source of PAHs to the atmosphere is diesel engines, in which PAHs can be produced through incomplete combustion. In this study the emission of PAHs by a modern diesel engine was studied using an Aerosol Time of Flight Mass Spectrometer (TSI 3800) equipped with a custom aerodynamic lens. Particle phase PAHs have traditionally been analyzed by collection on a filter substrate, extraction and wet chemical analysis. More recently some particle phase PAH analysis has been done using single particle mass spectrometry (SPMS) methods. While the traditional analysis has the advantage of being able to identify specific PAH isomers, the SPMS methods have the advantage of having no positive or negative filter artifacts and the ability to identify the size and associated chemical constituents of the PAH containing particles. It was found that a cold engine produced larger molecular weight PAHs than a warm stable engine. It was also found that while soot and sulfates tended to be associated in particles, PAHs were not as strongly associated with either soot or sulfate. It was also found that in the size range in which this instrument operates (~50-500 nm) PAHs were detected more frequently in particles with larger aerodynamic sizes. Understanding the information available from SPMS methods and combining it with information available from more traditional types of analysis may lead to an increased understanding of what engine conditions, lubricating oils, and fuels lead to lower emissions of hazardous PAH species.

13D4

COMPARISON BETWEEN SULFATE AND HYDROCARBON DRIVEN NANOPARTICLE FORMATION PROCESSES IN DIESEL EXHAUST. JYRKI MÄKELÄ, Kati Vaaraslahti, Topi Rönkkö, Mikko Lemmetty, Jyrki Ristimäki, Annele Virtanen and Jorma Keskinen, Tampere University of Technology, Tampere, Finland

Based on an empirical data-set, formation of nucleation mode particles in diesel exhaust gas is considered. In the data-set, a variety of several diesel engines were used varying the engine torque, fuel and lubricant sulfur concentration, dilution ratio and dilution air temperature. Experimental device consisted of number size distribution measurements by SMPS, plus e.g. thermodenuders. Furthermore, data obtained by using catalysts and particle filters are included to emphasise certain characteristic trends in the data.

As an overall result, a clear distinction between sulfur compound driven and hydrocarbon driven particle formation mechanisms could be made based mostly on particle data generated with variable sulfur content of the fuel and lubricant. Here, both torque dependencies of the data and effect of catalyst were taken into account. Most of the cases where particle formation was observed, can be, however, interpreted as particle growth from the true nanometer scale into the smallest particle size of the measuring instrument, which was, even in the lowest case as large as 3 nanometers. Thus, the division of sulfur/non-sulfur characteristic obtained above is concluded to apply for the particle growth in the size range of 1-15 nm. With no real physico-chemical analysis of the initial molecule clusters or critical embryos, the compounds involved in the actual nucleation process remain hidden. With the present results, one cannot avoid comparison of the situation with the recent excessive research on microphysical particle formation mechanisms performed for the atmospheric nucleation mode particles in natural ambient conditions.

13D5

EFFECTS OF PERFORATED TUBE DILUTION IN COMBUSTION AEROSOL STUDIES.

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The importance of controlled and well-defined dilution parameters in combustion particle studies has been shown in numerous articles and studies. In addition to dilution parameters, the structure of the diluter has been shown to have significant effects on the sample transformations during dilution. Effects of various diluter structures have however been consistently studied through experimental methods which do not necessarily produce enough information to reliably trace the causes behind the observed sample transformations. In this study, the performance of a perforated tube diluter in combustion studies is evaluated through both extensive modelling and experimental results from a dilution characterization project (HILA Part 2 TEKES FINE 40210/04).

The modelling results include time-resolved temperature, flow and pressure maps from within the perforated tube at different operating conditions as well as calculations of spatial nucleation rates during dilution of different heavy hydrocarbons with varying dilution ratios and temperatures.

The experiments were carried out using a sophisticated dilution & measurement setup, which enabled careful control and monitoring of flows, temperatures and concentrations of inert particles and heavy hydrocarbons. The experimental results include Electrical Low Pressure Impactor (ELPI, Dekati Ltd.) and Scanning Mobility Particle Spectrometer (SMPS, TSI inc.) measurements of aerodynamical particle distributions in real-time and electrical mobility particle distributions from dilution of various heavy hydrocarbons and a mix of heavy hydrocarbons and inert particles.

The calculations showed well-defined areas within the perforated tube with high nucleation rates and a strong dependence of the nucleation rates on the dilution ratio and temperature. In the experiments, nucleation was studied in repeated measurements with and without inert particles, and the effect of dilution parameters was clearly observed. In addition, growth of the inert particles through condensation was observed. Experimental and modelling results also revealed a pressure damping effect caused by the jet pattern within the perforated tube, which is beneficiary when sampling from a source such as a piston engine that causes high frequency pressure pulsation. Modelling and experimental results indicate that the used perforated tube diluter is a suitable and stable tool for various nucleation and condensation studies as well as a basic dilution device.

13D6

MEASUREMENT OF SOOT PARTICLE SIZE DISTRIBUTIONS FROM A WELL STIRRED REACTOR-PLUG FLOW REACTOR.

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It has been recognized that a well stirred reactor (WSR) coupled with a plug flow reactor (PFR) has many advantages for soot inception studies compared to laminar flames [1]. The advantages of sampling particles from the PFR section, as compared to laminar flames, are: (1) the gas velocity is large, so axial diffusion of species is negligible (2) the total residence time is spread over the entire length, so excellent spatial resolution is possible (3) disturbance due to sampling probes is minimal, as a PFR does not have flame stability issues, and (4) nearly isothermal conditions exist in the PFR [1].

To elucidate the soot inception process and to validate soot formation models requires detailed measurements of soot particle size distributions under conditions of incipient particle formation. The goal of this study was to measure soot particle size distributions in a WSR/PFR using both a diluter coupled with a nano-differential mobility analyzer (Nano-DMA) and a thermophoretic rapid insertion probe for transmission electron microscopy (TEM) analysis. The dilution probe, based upon the design of Zhao et al. [2], was used to minimize both coagulation growth of the particles and thermophoretic deposition on the sampling tube. Results are presented on the: (1) effect on the equivalence ratio of the soot size distributions obtained from the Nano-DMA for fixed dilution ratio (2) effect of dilution ratio on the soot size distributions obtained from the Nano-DMA for fixed equivalence ratio, and (3) comparison of soot size distributions obtained from the rapid insertion/TEM analysis and the Nano-DMA. In addition to particle sizing measurements, gas samples were sent to a gas chromatograph to determine the concentration of gaseous species in the PFR thought to be important in soot formation.

The particle sizing results from the Nano-DMA and the rapid insertion/TEM analyses suggested that condensation of low vapor pressure species was occurring during the dilution process. The Nano-DMA results differed significantly from the laminar premixed flame results of Maricq [3], which showed a bimodal size distribution with a significant nucleation mode. Our size distribution measurements demonstrate that the mixing conditions in the flame zone affect whether or not a nucleation mode was detected in the size distribution.

1. Lam, F., et al. , Proc. Comb. Inst. 22:323-332 (1988).
2. Zhao, B., et al., Aerosol Sci. Tech. 37:611-620 (2003).
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13E1

INTRA-COMMUNITY SPATIAL VARIATION OF SIZE-FRACTIONATED PM MASS, OC, EC AND ELEMENTS IN LONG BEACH, CA.

MARGARET KRUDYSZ, John Froines, University of California, Los Angeles, CA; Constantinos Sioutas, Philip M. Fine, University of Southern California, Los Angeles, CA

Ambient particulate matter (PM) from different sources and in different size fractions have been associated with varying degrees of health impacts. High concentrations of ultrafine particles have been found near freeways, with significantly lower concentrations further from the pollution source. This implies that local traffic patterns and proximity to complex pollution sources such as freeways, power plants, refineries, airports and seaports are important in assessing particulate matter exposure in urban communities. Understanding the effects on human health requires evaluation of particle sources, formation mechanisms, and the community-scale spatial variability. Among some of the heaviest residential traffic locations in southern California are communities in Long Beach. Single central site PM monitoring may not accurately reflect population exposure due to the presence and variability of local pollution sources. Furthermore, the partitioning of organic and metal compounds between the ultrafine, accumulation, and coarse modes helps to identify the types of sources present on local and regional scales. This research investigates the intra-community spatial variation in ultrafine, accumulation, and coarse PM mass as well as their organic carbon, elemental carbon, and elemental content.

Outdoor PM samples were collected from January to March 2005 at 4 sites in Long Beach. Sites are located 2-6 miles apart and are impacted by different pollution sources. A pair of Personal Cascade Impactor Samplers operating at 9 l/min and separating particles into ultrafine (<0.25 mm), accumulation (0.25-2.5 mm), and coarse (>2.5mm) fractions, were deployed at each site for 6 - 7 continuous days. Impactors were loaded with quartz filters for elemental and organic carbon analysis, and with Teflon filters for particle mass and elemental analysis by ICP-MS.

Average mass concentrations for ultrafine, accumulation, and coarse particles were 6.05 mg/m3, 6.84 mg/m3, and 6.31 mg/m3, respectively. Ultrafine mass concentrations correlated well with coarse particle concentrations across all sites. Inter-site comparisons revealed high spatial correlation for all size fractions. Average organic carbon concentrations ranged from 2.69 mg/m3 for ultrafine, 1.68 mg/m3 for accumulation, and 0.66 mg/m3 for coarse PM. Very high correlations were observed for organic carbon concentrations between all sites and size-fractions. The size-fractionation and spatial variability of the elemental composition is also presented. Results from these analyses are discussed in the context of the complex and varied PM sources found in the Long Beach community.

13E2

CLOSURE BETWEEN SEMI-CONTINUOUS MEASUREMENT OF PM2.5 MASS AND COMPOSITION.

DELBERT J. EATOUGH, Brett D. Grover, Justin Cannon and Norman L. Eatough, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT

EPA is promoting the development and application of sampling techniques for the continuous determination of PM2.5 mass and chemical composition. Such data will significantly improve our understanding of the primary sources, chemical conversion processes and meteorological atmospheric processes which lead to observed PM2.5 concentrations and will aid in the understanding of the etiology of PM2.5 related health effects. A major challenge in this effort is the development of techniques which accurately measure both the nonvolatile and semi-volatile (nitrate and organic material) fraction of PM2.5. The closure between semi-continuous measurement of PM2.5 mass and the estimation of PM2.5 mass from the semi-continuous measurement of fine particulate constituents has been evaluated in studies in Lindon, UT in March 2005 and will be repeated in Riverside, CA in July-August 2005. Emphasis is on the use of instruments which should determine the semi-volatile organic material and ammonium nitrate in fine particles. Results indicate that the R&P FDMS TEOM monitor (to measure PM2.5 mass, including the semi-volatile nitrate and organic material) coupled with a newly developed dual oven Sunset Laboratory ambient carbon monitor (to measure EC and both nonvolatile and semi-volatile carbonaceous material), an Aethalometer (to measure BC) and a Dionex GP-IC (to measure ions such as ammonium, nitrate and sulfate) will meet this sampling goal. Data obtained with the various instruments have been further validated by comparison with 3-h average PC-BOSS integrated sample results. The agreement between measured and constructed PM2.5 mass using these instruments in the two field studies will be presented.

13E3

MEASUREMENT EQUIVALENCE AND COMPARABILITY BETWEEN FILTER-BASED DATA AND SEMI-CONTINUOUS PM2.5 SPECIATION MONITORS FOR CARBON, SULFATE, AND NITRATE. Paul Roberts, Hilary Hafner, David Vaughn; Sonoma Technology, Inc, Petaluma, CA

An EPA pilot study was conducted to determine the suitability of semi-continuous PM2.5 speciation monitors to replace the 24-hour filter-based measurements currently made at Speciation Trends Network (STN) sites. Monitors included the R&P 5400C, 8400N, and 8400S carbon, nitrate and sulfate monitors, and the Sunset Labs carbon monitor. Measurement equivalence between the semi-continuous method and the Federal Equivalent Method (FEM) would allow direct substitution of these instruments for routine compliance monitoring. Benefits would include faster data acquisition, with higher temporal resolution and corresponding prompt public information; elimination of transportation and laboratory analysis costs for filter-based measurements; and potentially lower maintenance costs. Demonstrated comparability between the methods, though less demanding than that required for compliance monitoring, would be sufficient for determining spatial and temporal differences in air quality and could provide important information for PM forecasting. Graphical analyses and statistical evaluations were undertaken for several of the semi-continuous speciation study sites to determine equivalence and comparability. Preliminary results indicate that all three R&P semi-continuous speciation monitors have significant problems that must be addressed before they can be considered acceptable replacements for the STN filter-based compliance measurements. R&P 8400N and 8400S data, calibrated with aqueous standards, showed low precision and significant bias compared to filter-based measurements. The R&P 5400 total carbon showed similarly low precision and significant bias, while the total carbon concentrations from the Sunset Labs carbon monitor exhibited good precision and was comparable to the filter-based data.

13E4

COLLECTION AND CHARACTERIZATION OF COARSE, FINE, AND ULTRAFINE PARTICULATE MATTER USING AN INNOVATIVE PASSIVE AIR SAMPLER. DAVID LEITH, University of North Carolina, Chapel Hill, NC; Jeff Wagner, California Department of Health, Berkeley, CA; Tom Peters, University of Iowa, Iowa CIty, IA; Gary Casuccio,RJ Lee Group, Pittsburg,PA; Tom Merrifield, BGI Instruments, Waltham,MA

There is increased interest in the utilization of particulate samplers not constrained by issues related to space, sound, electricity, etc. Such a sampling device will be used in numerous industrial hygiene and environmental applications and promote the collection of particulate matter in a cost effective manner; especially in areas that lack electrical power.

A miniature passive particulate sampler recently developed by Wagner and Leith offers the potential to reliably estimate particulate concentrations and size distributions over periods that can be varied from minutes to weeks. The Wagner and Leith Passive Aerosol Sampler consists of a 1.5 cm wide scanning electron microscope (SEM) stub, a tacky collection substrate, and a protective micro-screen inlet cap. The sampler does not require power and due to its small size, does not interfere with human activity.

Upon exposure to the environment, particles are transported by gravity, diffusion and inertia through 157 μm diameter openings in the micro-screen inlet cap and deposit on the tacky surface of the SEM stub. After sampling, the inlet cap is removed to expose the substrate with collected particles for analysis. The sample can then be placed directly in to an SEM or optical microscope for individual particle analysis for size and elemental composition. An estimation of the mass distribution can be derived from this information.

This presentation provide an overview of the Wagner and Leith passive aerosol sampler, summarize results from field and laboratory studies, and discuss the implications of the sampling and analysis technologies as a tool for providing information on particulate coarse, fine and ultrafine particles.

13E5

IMPROVED DETECTION OF ORGANIC COMPOUNDS WITH THE USE OF PTV-GC-MS.

MICHAEL P HANNIGAN, Steven J Dutton, Catherine A Vos, University of Colorado, Boulder, CO; Gregory K Brown, Larry B Barber, United States Geological Survey, Boulder, CO

Quantitative determination of the origin of ambient PM2.5 is a critical step in the development of air quality abatement strategies; after all, how can we reduce the urban ambient PM2.5 levels without a thorough understanding of where the PM2.5 is coming from? The need to reduce urban ambient PM2.5 levels stems from the knowledge that these particles are linked with adverse human health. The observed adverse effects are numerous and likely due to various types of PM2.5 exposure. Acute exposures are a primary focus, as noted by the possibility of a future reduction in the PM2.5 24-hr NAAQS. As such, quantitative determination of the origin of the ambient PM2.5--termed source apportionment--needs to be undertaken on a long, continuous time series of short-duration PM2.5 filter samples.

Effective source apportionment of ambient PM2.5 relies on the use of chemical components that are uniquely emitted by a specific source type (or emitted in a unique ratio). These unique compounds, termed tracers, can be trace metals or specific organic molecules. Organic tracers are very effective for apportioning combustion sources, as the combustion of a unique organic fuel creates unique organic molecules in the emissions. Due to limitations of the method detection limit and the resources needed for the analysis, organic tracers have not been used for source apportionment of a long time series of acute PM2.5 exposures. We are overcoming these method and resource limitations via two research tracks: (1) improvement of organic compound detection limit with the use of the Programmable Temperature Vaporization (PTV) inlet on the GC-MS, and (2) simplification of the filter extraction procedures. This presentation will focus on PTV-GC-MS.

In prior organic analyses of PM2.5 filter samples, researchers have been limited by the ability to introduce only a fraction (1-2% at best) of a sample extract into the GC-MS. In theory, an increase in the mass of compounds introduced will increase the MS response, and thus reduce the detection limit. The use of the PTV inlet enables the introduction of the entire sample extract, up to more than 100 uL of the extract. So, in theory, we should be able to reduce the detection limits by 1-2 orders of magnitude. We will present results demonstrating detection limit improvements and document quantification uncertainties. For some organic compounds improvements of an order of magnitude were realized, while for other compounds no improvements were observed. For the latter compounds, GC-MS detection limit was not the limiting factor. The implications of these improvements for source apportionment will be discussed. In addition, pitfalls of the PTV inlet will be presented.

13E6

A VIRTUAL CYCLONE CONCENTRATOR FOR DIFFERENTIAL AEROSOL PASSBAND SAMPLING.

DAVID ALBURTY, Pamela Murowchick, Jason Downing, James Balarashti, Midwest Research Institute, Kansas City, MO

The design, optimization, and testing of a virtual cyclone concentrator (VCC) for use in a bioaerosol sampler is described. The VCC is used to create a differential bias of a target size passband of aerosols between the major and minor flows using different flowrate ratios. Critical design features of four VCCs were varied to determine their impact on efficiency and the shape of the passband. The VCCs were challenged using dry monodisperse particles (polystyrene latex microspheres and ammonium fluorescein) and droplets (fluorescent oleic acid). The major flow and minor flow of the VCCs were sampled using filters, wetted wall cyclones, TSI APS, and a TSI UV-APS. The sampling results include differential passbands for particles ranging from 0.85 to 10 microns aerodynamic diameter. Future work will include bioaerosol testing.