**5E.01**
The effects of atmospheric heterogeneous oxidation on the redox activity of soot aerosols. ROBERT MCWHINNEY, Jay Slowik, Jonathan Abbatt, *University of Toronto*

Inhalation of airborne particulate matter can result in a myriad of adverse health effects. While the mechanism of toxicity of PM is still incompletely understood, its ability to participate in redox cycling reactions generating reactive oxygen species (ROS) and to generate radical species is strongly implicated in toxicological studies. Chemical assays have been used to study the ability of PM to generate ROS through redox cycling (1) and by hydroxyl radical generation (2). Quinone species are particularly active in ROS generation and are produced in the heterogeneous oxidation of polycyclic aromatic hydrocarbons (PAH) (3). Therefore, atmospheric oxidation may lead to an increase in ROS generation by PM, particularly in PAH-rich soot particles.

To investigate the possible effect of atmospheric heterogeneous processing, engine and flame soot aerosols are oxidised in a flow tube with gas-phase ozone. ROS generation is measured prior to and after oxidation using a dithiothreitol assay to measure redox cycling activity and by quantifying hydroxyl radical generation. Aerosol composition is determined using time of flight aerosol mass spectrometry (ToF-AMS) to study the chemical changes may lead to the observed changes in PM redox activity.


**5E.02**
Effect of Aerosol Mixing State on Optical and CCN Activation Properties in an Evolving Urban Plume. RAHUL ZAVERI (1), Richard Easter (1), James Barnard (1), Nicole Riemer (2), Matt West (2), (1) Pacific Northwest National Laboratory, Richland, (2) University of Illinois, Urbana Champaign

Atmospheric aerosols are composed of a variety of primary (urban organic particles, sea-salt, dust, biomass burning, etc.) and secondary (organic, ammonium, sulfate, nitrate, etc.) aerosols. The primary particles are externally-mixed when emitted, but undergo chemical and microphysical transformations due to coagulation and condensation of many different semi-volatile gases (organic and inorganic), and therefore aerosols. The primary particles are externally-mixed when emitted but undergo chemical and microphysical transformations due to coagulation and condensation of many different semi-volatile gases (organic and inorganic), and produce numerous size and mixing-state distributions with widely different optical and CCN activation properties as a result. However, accurately tracking the mixing state in conventional aerosol models requires treating a multidimensional size distribution, which is computationally prohibitive. Therefore most current models typically consider one particle size distribution which is spread over discrete size sections (bins) or modes. Species within a given bin/mode are assumed to be internally-mixed while different bins/modes are treated as externally-mixed. The uncertainties in the predicted optical properties and CCN activation spectra associated with this assumption, which artificially and unrealistically ages all the particles to the same extent instantly, are not well quantified.

In this study, we use the stochastic particle-resolved aerosol chemistry and dynamics model PartMC-MOSAIC, which explicitly resolves the composition of individual particles in a given aerosol population of different types, and accurately tracks their evolution due to emission, dilution, condensation and coagulation. PartMC-MOSAIC is applied to an idealized urban plume case to simulate the evolution of urban aerosols of four different types (diesel soot, gasoline soot, meat-cooking aerosols, and road dust) due to condensation of various inorganic and organic trace gases and due to coagulation. We quantify the individual processes that contribute to the aging of the aerosol distribution as a function of time, and analyze the effect of aerosol mixing state on optical and CCN activation properties in such an evolving urban plume. Errors introduced in these two properties due to the internal-mixing assumption will be presented.
5E.03
Deliquescence, Growth and Recrystallization Characteristics of Mixed Aerosol Particles. Harry H. Hunter and Asit K. Ray, University of Kentucky

We present results on deliquescence, growth and recrystallization characteristics of mixed aerosol particles. An electrodynamic balance was used to suspend single charged particles, and a suspended particle was then exposed to an air stream whose relative humidity was adjusted in a controlled manner. The mass of the particle was determined from the d.c. voltage required to maintain the particle at the centre of the balance. The deliquescence and recrystallization points were measured from the jump in the balancing d.c. voltage as well as from the light scattering signals. For examining salt particles coated with water insoluble layers, a droplet generated from a homogeneous solution, for example, of NaCl, DOP, water and ethanol, containing known amounts of NaCl and DOP, was suspended in the balance. The droplet was exposed to a dry air stream for about 20 minutes, and during this period the water and ethanol evaporated leaving a particle containing known proportion of solid NaCl and liquid DOP. After drying, the relative humidity of the air stream was altered in steps. For generating soot particles coated with inorganic salts, we dispersed a known amount of soot particles in a given amount of an aqueous solution that was saturated with a salt. We obtained a particle of soot aggregates coated with salt when a droplet generated from this mixture was dried. The results from the coated particle show that the particle gradually absorbs water as the relative humidity is increased from 0 to 24%, where the water content reaches about 36.5 wt% on a DOP-free basis. Then the water content remains constant up to 75% humidity, where the water content rises sharply similar to the deliquescence of a pure NaCl particle. For soot particles coated with inorganic salts we observed that deliquescence relative humidities increase slightly, but the water content after the deliquescence is similar to pure salt particles.

5E.04
Homogeneous Ice Nucleation from Aqueous Aerosol Particles Containing Organic Surrogates of Biomass Burning. DANIEL A. KNOPF, Miguel D. Lopez, Bing Bing Wang, Stony Brook University

Aerosol particles in the atmosphere can act as cloud condensation nuclei (CCN) and ice nuclei (IN). These processes can lead to the formation of new clouds and to the modification of the radiative properties of existing clouds with subsequent consequences for the global radiative budget. The formation of ice clouds and corresponding effects on the global radiative budget are one of the least understood atmospheric processes. In addition, ice particles significantly affect the water vapor budget of the upper troposphere/lower stratosphere which has important consequences for the radiative budget and stratospheric chemistry. Here, we study the formation of ice by homogeneous nucleation from aqueous particles containing organic surrogates of biomass burning. It has been shown that aerosol particles from biomass burning plumes, originating e.g. from forest fires, can reach atmospheric altitudes at which temperatures promote the freezing of ice. We study the effect of typical biomass burning compounds, such as levoglucosan, on homogeneous ice nucleation. The freezing of ice from micrometer sized droplets deposited on a hydrophobically coated substrate is observed using optical microscopy. A new preparation method allows to expose the particles to controlled relative humidities which defines the particle's composition before observation of the freezing of ice. For experimental validation purposes we determine homogeneous ice nucleation from aqueous (NH4)2SO4 particles. We present the freezing of ice from aqueous levoglucosan particles and aqueous (NH4)2SO4-levoglucosan particles. The freezing temperatures are discussed with regard to the previously suggested water-activity based theory of homogeneous ice nucleation. The determined freezing temperatures, particle diameters, and the time the particles remained liquid are used to derive homogeneous ice nucleation rate coefficients. These ice nucleation rate coefficients are applied to estimate atmospheric ice particle production rates as a result of biomass burning plumes.
5E.05
Modeling Atmospheric Heterogeneous Chemistry Using a Dynamic Uptake Coefficient Treatment. Nicole Riemer (1), DANIEL KNOPF (2), (1) University of Illinois at Urbana-Champaign, (2) Stony Brook University, Stony Brook

Chemical reactions between the gas phase and at the surface and/or in the bulk of solid and liquid aerosol particles, termed heterogeneous reactions, can significantly change the chemical composition of the particles and their atmospheric environment. This is important for assessing aerosol and cloud effects on the environment and on public health. In recent years laboratory studies have indicated the importance of heterogeneous processes in the atmosphere, however, most modeling studies do not explicitly treat heterogeneous chemistry. For this reason, our understanding of these processes and our ability to predict them is still limited.

The efficiency of heterogeneous reactions is usually quantified by the reactive uptake coefficient gamma, which indicates the ratio of the net flux of a gas phase species to the condensed phase leading to reaction and the gas kinetic flux of the gas colliding with the surface. Modeling studies often assume a fixed gamma value. However, it is well documented by laboratory studies that gamma can vary with the particle age and with the environmental conditions such as the concentration of the reactive gas phase species. In addition, the reactive uptake can follow more complex reaction pathways such as Langmuir-Hinshelwood mechanisms.

In this study we couple a mechanistic approach for modeling atmospheric heterogeneous chemistry, the PRA (Poesschl-Rudich-Ammann) framework, to the well-established chemical gas phase solver RADM2. The PRA approach provides an explicit mechanistic description of concentration and time dependencies of reactive and non-reactive gas uptake and particle surface aging and enables us to calculate the temporal evolution of surface composition and uptake coefficients, which then feed back to the RADM2 gas phase chemistry.

Using this approach we systematically investigate a number of model systems including a Langmuir-Hinshelwood type reactive uptake of O3 by soot coated with Benz[a]pyrene and NO2 uptake by soot to quantify the impact of a dynamic uptake coefficient treatment on atmospheric photochemistry.

5E.06
Measurements of the Hygroscopic and Deliquescence Properties of Organic Compounds of Different Solubilities in Water and Their Relationship with Cloud Condensation Nuclei Activities. Man Nin CHAN (1, 2), Sonia M. Kreidenweis (3), Chak K. CHAN (1), (1) Department of Chemical Engineering, Hong Kong University of Science and Technology, Hong Kong (2) Current affiliation: Division of Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA (3) Department of Atmospheric Science, Colorado State University, Ft. Collins, Colorado

The initial phase (solid or aqueous droplet) of aerosol particles prior to activation is among the critical factors in determining their cloud condensation nuclei (CCN) activity. Single-particle levitation in an electrodynamic balance (EDB) was used to measure the phase transitions and hygroscopic properties of aerosol particles of 11 organic compounds with different solubilities (10^{-3} to 10^{2} g solute/100 g water). We use these data and other literature data to relate the CCN activity and hygroscopicity of organic compounds with different solubilities. The EDB data show that glyoxylic acid, 4-methylphthalic acid, monosaccharides (fructose and mannose), and disaccharides (maltose and lactose) did not crystallize and existed as metastable droplets at low relative humidity (RH). Hygroscopic data from this work and in the literature support earlier studies showing that the CCN activities of compounds with solubilities down to the order of 10^{-1} g solute/100 g water can be predicted by Standard Kohler theory with the assumption of complete dissolution of the solute at activation. We also demonstrate the use of evaporation data (or efflorescence data), which provides information on the water contents of metastable solutions below the compound deliquescence RH that can be extrapolated to higher dilutions, to predict the CCN activity of organic particles, particularly for sparingly soluble organic compounds that do not deliquesce at RH achievable in the EDB and in the hygroscopic tandem differential mobility analyzer.

Acknowledgments
This work was funded by an Earmarked Grant (610805) from the Research Grants Council of the Hong Kong Special Administrative Region, China. S.M.K. gratefully acknowledges support for this work from NOAA grant NA17RJ1228#80.
Partial Crystallization and Deliquescence of Particles Containing Ammonium Sulfate and Dicarboxylic Acids. Tsz Yan Ling (1,2), Chak K. Chan (1), (1) Department of Chemical Engineering, Hong Kong University of Science and Technology (2) Current affiliation: Particle Technology Laboratory, Department of Mechanical Engineering, University of Minnesota

Atmospheric particles play an important role in radiative forcing and global climate change. Changes in the phase and water content of atmospheric particles affect their physical and optical properties, as well as their reactivity. The partial crystallization and deliquescence of ammonium sulfate (AS) particles internally mixed with malonic acid (MA), glutaric acid (GA) and succinic acid (SA) were studied. Hygroscopic properties, elastic light scattering and Raman spectra were measured during water uptake and evaporation of single particles suspended in an electrodynamic balance.

AS/MA particles remained partially crystallized at RHs as low as 16%, while AS/GA and AS/SA particles became completely dry at about 30-36% RH and below. Partial deliquescence was observed at intermediate RHs of <10% to 79%, 70% to 80% and 80% to >90% for the AS/MA, AS/GA and AS/SA particles, respectively. Solid inclusions in various amounts were in equilibrium with the aqueous solutions. The Raman spectra show solid inclusions of both AS and MA in AS/MA particles, suggesting the heterogeneous crystallization of MA on solid AS. AS was found to deliquesce first at 76% RH in the AS/GA system, followed by GA at 78% RH. In the SA/AS system, AS was observed to dissolve at 80% RH, while SA remained as solid for RH as high as 90%. Comparisons to the thermodynamic model demonstrated the necessity to correctly predict the solid phase during partial deliquescence for accurate water content estimation.

The Raman spectra also revealed the formation of metastable forms of organic acids upon crystallization from supersaturated droplets of AS/GA and AS/SA. Transformation of metastable solids to stable forms was observed before water uptake in the AS/GA particles, while the SA in AS/SA particles transformed in the presence of water.

Accretion Reactions of Octanal Catalyzed by Sulfuric Acid: Product Identification, Reaction Pathways and Atmospheric Implications. Yong Jie LI (1), Alex K.Y. LEE (2), Arthur P.S. LAU (3) and Chak K. CHAN (2), (1) Environmental Engineering Program, Hong Kong University of Science and Technology, Hong Kong (2) Department of Chemical Engineering, Hong Kong University of Science and Technology, Hong Kong (3) Institute for the Environment, Hong Kong University of Science and Technology, Hong Kong

Organic aerosols have attracted much attention because of their impacts on visibility and human health, as well as their direct and indirect effects on the climatic system (1). Accurate model prediction of those impacts is impeded by inadequate understanding of the nature of organic aerosols, which are very complex in composition and change continuously over their atmospheric lifetime. Heterogeneous interactions between gases and aerosols will dramatically alter the physical/chemical properties of atmospheric aerosols during their suspension. Recently, reactive uptake of volatile organics, e.g. carboxyls, onto acidic particles is proposed to be an important route of organic aerosol formation. Several reaction mechanisms, including aldol condensation, acetate/hemicetal formation (in the presence of alcohols) and polymerization, have been proposed as accretion reactions of aldehydes that would lead to an increase in the organic aerosol mass (2). However, from recent laboratory, theoretical and kinetic studies, uncertainties and inconsistencies still exist about whether or not acid-catalyzed aldehyde reactions significantly increase the organic burden of aerosols (3, 4).

We examined sulfuric acid catalyzed accretion reactions of octanal (C8 aldehyde) in bulk liquid-liquid and gas-particle experiments, aiming at determining how acid catalyses aldehyde reactions and implicating whether those reactions will occur in atmospheric conditions. In bulk studies, trioxane, alpha, beta-unsaturated aldehyde and tri-alkyl benzene were identified as major reaction products with increasing sulfuric acid concentrations (0-86 wt%). From these observations of product formation, we proposed several acidity-dependent reaction pathways, including cyclotrimerization, one-step aldol condensation and multiple-step aldol condensation. Those reaction pathways, except cyclotrimerization, were also observed in gas-particle experiments performed in high octanal concentration (~20 ppm) and low RH conditions (<1% and 10%, sulfuric concentration >80 wt% and ~64 wt%, respectively). No such reaction products were found in the low octanal concentration (~900 ppb) experiments even RH was extremely low (<1% and 10%, sulfuric concentration >80 wt% and ~64 wt%, respectively), which indicates that both gas-phase aldehyde concentration and RH are important parameters for those reactions to occur. As extremely low RH and high aldehyde concentration may not coexist in ambient conditions, the acid-catalyzed aldehyde reactions may not be as significant as expected in organic aerosol formation.

References

Acknowledgement
This work was supported by the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST600303).
Uptake of Octanal Vapor in the Presence of Acidic Seed Particles. ALEX K. Y. LEE(1), Yong Jie Li(2), Arthur P S. Lau (3), Chak K. Chan(1), (1) Department of Chemical Engineering, Hong Kong University of Science and Technology, Hong Kong. (2) Environmental Engineering Program, Hong Kong University of Science and Technology, Hong Kong. (3) Institute for the Environment, Hong Kong University of Science and Technology, Hong Kong.

Reactive uptake of volatile organics, especially carbonyl compounds, into preexisting acidic particles has been recently proposed to explain the huge abundance of secondary organic aerosol (SOA) in the atmosphere. In this study, an electrodynamic balance (EDB) was used to investigate the uptake of octanal vapor by single sulfuric acid droplets levitated under various relative humidity (RH) conditions (10-50%) and gas-phase octanal concentrations (both ppb and ppm levels). The EDB has been shown to be very useful in examining particle hygroscopicity because of its high sensitivity to any changes in particle mass in response to changes in the surrounding air. This feature also makes the EDB an ideal tool to directly measure the mass yield (or loss) of levitated particles when they interact with gas-phase reactants.

In the high octanal concentration experiments (200-300 ppm), we observed that the organic mass yield depended on the acidity of the sulfuric acid droplets and significant uptake of octanal only occurred when the RH was about 10% (H2SO4 wt% ~ 64%). Furthermore, reversible partitioning of condensed organic compounds was observed after active dilution with octanal-free compressed air. This finding indicates the potential importance of reversible partitioning of condensed organics in affecting the organic mass fraction and chemical composition of atmospheric organic aerosols. When a relatively lower octanal concentration (700-900 ppb) was used, no significant uptake of octanal vapor by the sulfuric acid droplets was observed even at 10% RH with long exposure time (> 25 hrs). Our findings suggest that both particle acidity and gas-phase octanal concentration are the critical factors that influence the organic mass yield of levitated acidic droplets. Because of the severe conditions of low RH and high octanal conditions required to effect the reactions, the reactive uptake of octanal into acidic particles may not be an important pathway in SOA formation under actual atmospheric conditions.

Acknowledgment

The work was supported by the Research Grant Council of the Hong Kong Special Administrative Region, China (Project No. HKUST600303).
Secondary organic aerosol (SOA) formation from the photooxidation of toluene was studied in a 2 m3 indoor Teflon film chamber under three different NOx levels: low (<1.5 ppb), middle (~90-135 ppb) and high (~280 -315 ppb) NOx concentrations. All SOA experiments were conducted in the presence of either neutral or acidic seed aerosols under two different humidity levels (RH~15 -22% or 38-49%). The NOx concentration in the chamber affected not only the SOA yields but also the SOA growth pattern described by the ‘time-depend growth curve’ (produced organic mass (OM) as a function of consumed toluene concentration) over the course of the individual SOA experiment. Overall, SOA yields with low and the middle NOx concentrations were higher than those with high NOx conditions. For the low and the middle NOx experiments, SOA yields remained almost constant throughout the entire experiments while SOA yields were represented by the conventional partitioning mode (sigmoid curve) under the high NOx conditions. The particle acidity effects on toluene SOA formation varied with different NOx concentrations. For the low and the middle NOx experiments, SOA yields with acidic seed noticeably increased compared to those with neutral seed. However, no significant particle acidity effect was observed for the SOA created in the high NOx experiments.

A predictive model for secondary organic aerosol (SOA) formation through both partitioning and heterogeneous reactions was developed for SOA produced from oxidation of toluene in the presence of inorganic seed aerosols. The explicit gas-phase chemistry of toluene, gas-particle partitioning, and heterogeneous chemistry were implemented in the SOA predictive model. The SOA model was investigated and tested for a large body of the experimental SOA data that was generated in a 2 m3 teflon film indoor chamber under various experimental conditions (e.g., humidity, inorganic seed compositions, light conditions, NOx concentrations). The predictive SOA mass was decoupled into partitioning (OMP) and heterogeneous aerosol production (OMH), which provided a unique approach for us to operate both partitioning and heterogeneous reactions for SOA formation under a specific condition. The model allows us to evaluate the relative importance of partitioning and heterogeneous chemistry in SOA formation. The SOA model was successfully assessed in terms of the ozone formation, the NO to NO2 conversion and the decay of toluene in the gas phase as well as the production of SOA mass using a variety of SOA experiments that were generated under relevant atmospheric conditions. The results showed that our model improved the predictability of SOA mass compared to the SOA model developed from the partitioning theory alone.
SE.13
Heterogeneous Reactions of NO3 Radicals with Organic Liquids and Monolayers that Simulate Organic Aerosol Surfaces. SIMONE GROSS, Daniel A Knopf, Allan K Bertram, University of British Columbia, Vancouver

The nitrate radical NO₃ is an important nighttime oxidant in the troposphere, especially in polluted urban areas. While homogeneous gas-phase reactions of NO₃ with organic substances of atmospheric importance have been studied in detail, little research has focused on heterogeneous reactions of NO₃ with atmospheric organic particles. As reaction rates, products, and mechanisms may be very different in heterogeneous reactions compared to the corresponding homogeneous reactions, there is a need for more investigations on these heterogeneous processes. Reactions on atmospheric particulate matter can also have a major effect on important properties of aerosol particles (e.g. hydrophilicity, toxicity, and optical properties).

Alkanes, alkenes, and carboxylic acids are tropospheric aerosol components that result from plants, microbes, fossil fuel combustion, meat cooking processes, etc. To gain insight into heterogeneous reactions of these classes of compounds, liquid films of representative substances were exposed to gas phase NO₃ radicals using a flow tube reactor coupled to a chemical ionization mass spectrometer. The reactive uptake coefficients of these reactions were determined. Results showed a very fast reaction of NO₃ with compounds containing carbon-carbon double-bonds. Determination of gas-phase products provided information on the mechanisms for these heterogeneous reactions.

Self assembled monolayers (SAMs) are frequently used as model substrates for organic aerosol surfaces. To study heterogeneous reactions of alkane and alkene surfaces, SAMs of octadecanethiol and undecenethiol on gold substrates were exposed to NO₃ radicals using a flow tube reactor coupled to a chemical ionization mass spectrometer. The reactive uptake coefficients of these reactions were determined. Results showed a very fast reaction of NO₃ with compounds containing carbon-carbon double-bonds. Determination of gas-phase products provided information on the mechanisms for these heterogeneous reactions.

SE.14

Laboratory smog chamber experiments have been carried out to investigate the secondary organic aerosol (SOA) formation from the photooxidation of a series of normal alkanes, ranging from n-octane to n-tetradecane. Two sets of experiments were conducted as part of this study. The first set of experiments examined the photooxidation of individual alkanes in the presence of NOx with methyl nitrite added as a radical source. The second set of experiments were conducted in the absence of NOx using hydrogen peroxide as a source of OH radicals.

SOA yields were determined for each of the experimental systems, and were found to increase for parent alkanes of higher chain lengths. In addition, simultaneous measurements of SOA mass via filter collections and secondary organic carbon (SOC) concentrations using a semi-continuous OC-EC instrument allowed for the calculation of SOA/SOC ratios for a series of alkane photooxidation experiments. Finally, effective enthalpies of vaporization were obtained for each n-alkane/hydrogen peroxide experiment by measuring the volume concentrations of the steady-state SOA following passage through a heated inlet tube that was operated over a temperature range of 298 to 523 K. The effective enthalpies of vaporization were found to be well correlated with the chain length of the parent alkane used in each experiment.

This work has been funded wholly or in part by the United States Environmental Protection Agency under Contract EP-D-05-065 to Alion Science and Technology. It has been subjected to Agency review and approved for publication.
5E.15
Light-Induced Degradation of Nitro-Aromatic Compounds.
R. Aaron Vogt, AMY M. SAGE, Carlos E. Crespo-Hernandez,
Case Western Reserve University

Nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) are formed directly from incomplete combustion processes and in situ by the gas-phase oxidation of PAHs. They are believed to be responsible for a significant fraction of the mutagenicity of diesel particulate matter.

Photochemical degradation is the most important natural removal pathway for nitro-PAHs. Due to their conjugated ring structure, many of these compounds absorb visible light. Light absorption results in the formation of metastable electronic excited states, which can decay to produce secondary products. These products may act as efficient energy-transfer species (photosensitizers), or they may display enhanced toxicity relative to the parent compounds. Characterization of the excited states of nitro-PAHs and their relaxation pathways is essential to understanding their light-induced degradation.

The Chapman orientation-photoreactivity relationship states that the orientation of the nitro group relative to the plane of the aromatic moiety controls both reaction rates and the identities of reaction intermediates and products. However, this relationship assumes that ground-state molecular geometry can predict a molecule's excited state reactivity. To test this assumption we have studied the photophysics and photochemical degradation of two nitro-PAHs: 1-nitropyrene and 1-nitronaphthalene. The perpendicular orientations of the nitro-groups in these two compounds suggest that they should both be photoreactive. In organics solvents, we observe electronically excited 1-nitropyrene decaying rapidly back to the ground state, while 1-nitronaphthalene undergoes photochemical reactions to form at least two products.

5E.16
Measurements of the Henrys Law Coefficient of Toluene.
F. Rifkha Kameel, Deirdre Manion-Fischer, Mahinda Gangoda,
Shan-Hu Lee, Kent State University, Department of Chemistry, Kent, Ohio

Solubility of a compound is an important parameter that determines if the compound can be participated in aerosol formation and cloud formation. There are hundreds of organic compounds in the atmosphere but their solubilities, especially in organic solutions, are not well studied. We have developed a system to measured Henrys law coefficient (solubility) of organic compounds with a gas chromatography - flame ionization detection - mass spectrometer (GC-FID-MS). We tested our experimental system with the measurements of Henrys coefficient of toluene in water and compare with the literature data. With this system, we measure Henrys coefficient of toluene in n-octanol solution; n-octanol has been widely used to represent the typical non-polar media of organics aerosols in other studies.
5E.17
Determination of the Evaporation Coefficient of Semi-Volatile Organic Aerosols. RAWAD SALEH, Andrey Khlystov, Duke University

In this work, the Tandem Differential Mobility Analyzer (TDMA) method is used to estimate the evaporation coefficient of pure organic semi-volatile aerosols relevant to ambient organic aerosols. In the TDMA method, the size changes of a quasi-monodisperse aerosol are measured as the aerosol is heated in a thermodenuder. Traditionally, the TDMA method has been used to obtain the saturation pressure and surface tension of the aerosol particles by optimizing the evaporation kinetics to reproduce the observed size changes. The evaporation coefficient has been assumed to be unity, since it is impossible to optimize for the 3 parameters involved in the kinetics - saturation pressure, surface tension, and evaporation coefficient - at the same time. In this study, the saturation pressure and surface tension are constrained, and the TDMA method is used to optimize solely for the evaporation coefficient. To constrain the surface tension, measurements are performed for particle sizes ranging between 200 nm and 500 nm, where the Fuchs effect (and thus the evaporation coefficient) is prominent, while Kelvin effect (and thus the surface tension) is negligible. As for the saturation pressure, the TDMA method is supplemented with the Integrated Volume Method, which provides data on saturation vapor pressure at quasi-equilibrium conditions, i.e. without any assumptions on the evaporation coefficient.

5E.18
Challenges in the Interpretation of Aerosol Volatility Measurements using Thermodenuders due to Mass Transfer Limitations. BYONG-HYOEK LEE (1), Jeffery R. Pierce (1), and Spyros N. Pandis (1,2), (1) Carnegie Mellon University (2) University of Patras, Patra

Thermodenuders are routinely used to obtain information about the chemical composition and properties of atmospheric aerosols by measuring their volatility. The operating characteristics of existing thermodenuder systems vary dramatically from instrument to instrument. For example, the centerline residence time in the heated zone of the thermodenuder is as small as 1 s in some designs and as large as 30 s in others. The effects of this residence time in the thermodenuder and the corresponding operating temperature range on volatility measurements of secondary organic aerosol (SOA) and ambient aerosols are investigated. The potential existence of resistances to mass transfer in the particulate phase is a major focus of this work.

The volatility of SOA from the ozonolysis of alpha-pinene, beta-pinene, and limonene at diverse conditions (NOx levels, relative humidity). 95% of the alpha- and beta-pinene SOA evaporates at 75 degrees C after approximately 16 s. Limonene SOA is less volatile requiring heating to 90 degrees C for the same degree of evaporation. An aerosol dynamics model is used to reproduce the behavior of these SOA particles in the thermodenuder. The model shows an existence of resistances to mass transfer in the initial stages of the evaporation of the particles that seems to disappear after the particles shrink by approximately 30%. Due to these resistances in the particulate phase or at the interface, an effective accommodation coefficient of 0.05 is needed for the description of the beginning part of the evaporation. The model also suggests that particles do not reach equilibrium with the surrounding gas phase even after 16 s. This implies that the thermodenuder needs to be operated at even longer residence time in order to decouple the mass transfer effects from the actual volatility of the SOA.
**SE.19**

**Problems and Prospects for Predicting SOA Production Through Cloud Processing.** BARBARA TURPIN (1), Annmarie G. Carlton (2), Barbara Ervens (3), Katye E. Altieri (1), Mark J. Perri (1), Yi Tan (1), Mary Moore (1), Sybil Seitzinger (1, 4), (1) Rutgers University, New Brunswick, NJ, (2) US Environmental Protection Agency, Research Triangle Park, NC, (3) CIRES, University of Colorado and NOAA, Boulder, CO, (4) NOAA Cooperative Marine Education and Research Program, New Brunswick, NJ

Water-soluble products of the gas phase oxidation of alkenes and aromatics partition into atmospheric waters where they react further to form low volatility products. When this happens in clouds, these products remain in part in the particle phase after droplet evaporation, forming secondary organic aerosol (SOA). Similar aqueous phase reactions could plausibly occur in aerosol water as well, adding SOA mass. Zero-dimensional cloud chemistry and cloud microphysical modeling of in-cloud SOA formation have demonstrated the kinetic feasibility of such a process. Recently, addition of this process to a chemical transport model (CMAQ) has been shown to improve capture of the variability in organic aerosol concentrations on a limited number of simulated days in the northeastern US. Such model improvements are needed to accurately predict the impact of air quality management strategies.

Accurate prediction of in-cloud SOA is hampered by the poor understanding and the complexity of atmospheric aqueous phase organic chemistry, and by the dependence of product yields on cloud presence, cloud contact time, liquid water content and VOC/NOx. This poster will demonstrate the interactive process by which aqueous phase photooxidation experiments validate and refine aqueous chemical kinetic models that are incorporated into cloud chemistry/parcel models to 1) generate atmospherically-relevant yields or 2) simplify the chemistry for direct incorporation in chemical transport models. The poster will make use of product analyses from aqueous photooxidation experiments conducted at different concentrations, with and without sulfate/nitrate and with different precursors (glyoxal, methylglyoxal, glycolaldehyde, and pyruvic acid). One advance is our ability to conduct experiments at cloud-relevant concentrations with real-time product analysis. Products include oxalic, glycolic, pyruvic, succinic, acetic and formic acids, larger multifunctional compounds, and oligomers formed through esterification. Issues involved in the construction of an atmospheric chemistry model from laboratory findings will be discussed.

**SE.20**

**The Comparison of Two Types of Photocatalysts Efficacy in Inactivation/Destruction of Virus and Bacteria Aerosols.** ALEKSANDR S. SAFATOV (1), Sergei A. Kiselev (1), Vasily Yu. Marchenko (1), Artem A. Sergeev (1), Maxim O. Skarnovich (1), Elena K. Emel'yanova (1), Maria A. Smetannikova (1), Galina A. Buryak (1) Aleksandr V. Vorontsov (2), (1) Federal State Research Institution State Research Center of Virology and Biotechnology "Vector", Koltsovo, Novosibirsk region, Russia (2) Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

The evaluation of photocatalysts activity for inactivation/destruction of microorganisms in a liquid film is inapplicable for estimation of efficiency against particles in aerosol. Photocatalytic activity at inactivation/disintegration of microorganisms in aerosol is evaluated more correctly when aerosols are deposited on the photocatalyst-coated glass slides and present under natural-environmental conditions of ambient relative humidity.

Experiments were performed with Mycobacterium smegmatis, vaccinia virus and influenza virus strain A/Aichi/2/68 (H3N2). Aerosol of one of microorganism was sterile deposited onto glass slides. Using the stable fluorescent label one can easily evaluate the degree of microorganisms' inactivation under experimental conditions. Unevenness of aerosol mass distribution over glass slides made up less than 10%.

Two types of photocatalysts applied to glass slides were studied: "pure" titanium dioxide (anatase 100 %, particle diameter 6 - 10 nm) and platinized titanium dioxide. Exposure of samples to mild ultraviolet radiation was performed from 1 to 30 minutes with the lamp PHILIPS PL-S 11W/10/2P; the exposure radiation power was 0.65 +/- 0.05 mW/cm2.

Unirradiated slides covered with photocatalyst and "pure" slides irradiated for 30 min, both with deposited microorganisms' aerosol serves as controls. Under the influence of "pure" TiO2, the number of viable mycobacteria decreased by a factor of 5.6 after 30 minutes of exposure, and under the influence of platinized TiO2 - by a factor of over 30 compared to controls. Under the same experimental conditions the decrease of vaccinia virus activity was 10 and 20 times for "pure" and platinized TiO2, respectively. The rate of influenza virus inactivation in both cases is higher than for vaccinia virus.

Thus, platinized TiO2 is much more active at inactivation/disintegration of microorganism aerosols compared to "pure" TiO2.

This work was partially supported by the NATO "Science for Peace" Program, grant No. SfP - 981461.
5G.01
Spin trapping for identification and characterization of particle-bound reactive radical species. Jelica Pavlovic, Xi Chen, Philip K. Hopke, Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY

Reactive oxygen species present in the atmosphere on respirable particles to which we are exposed are short lived species and it is anticipated that many of those species are organic peroxides and peroxy radicals. Some previous studies used electron paramagnetic resonance (EPR) method to determine overall oxidative capacity of particles. The objective of our work is to analyze nature and chemical composition of these reactive radical species. However, to separate and identify these species, it is necessary to preserve them for a sufficiently long time as to permit analyses to be done. Spin trapping is method of our choice and it is widely used for studying radicals in biological systems but it has not been widely used in atmospheric chemistry. In order to develop our methods, samples were collected from an alpha-pinene - ozone reaction in an aerosol chamber reactor. 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used to capture and passivate reactive species. Extraction with methanol is followed by analysis with liquid chromatography coupled with mass spectrometry (LC-MS) with electrospray ionization (ESI) in positive mode, for the separation and identification of the radical species. Results of these studies will be presented.

5G.02
Effects of Organic Carbon Pyrolysis Correction on the Estimation of Carbon Conversion in Hydrogasification of Coal. Kwangsam Na (1), Chan Seung Park (1), Joe Norbeck (1, 2), (1) Bourns College of Engineering?Center for Environmental Research and Technology (CE-CERT), University of California, Riverside (2) Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, Riverside

The United States currently imports approximately 60% of its transportation fuels and is faced with increasing demand in the future. Research on the development of alternative fuel sources such as synthetic fuels from carbonaceous sources including coal and biomass is gaining significantly increased attention. The University of California, Riverside has developed a thermochemical process for the conversion of carbonaceous materials into synthetic hydrocarbon fuels such as the Fischer-Tropsch diesel. This process involves the gasification of feedstocks such as coal or wood and reforming the product gas to generate synthesis gas. An important property of these feedstocks is the elemental carbon (EC) and organic carbon (OC). The EC has higher heating value but does not gasify readily. The unconverted EC is collected as char and can be burnt to generate necessary process heat. The ratio of EC to OC in the particular feedstock is a critical parameter in identifying the process conditions that can lead to desired conversions. Thermo Gravimetric Analyzers (TGA) have been conventionally used to quantify EC and OC. However this method has disadvantages such as interference by moisture and also fails to account for the pyrolysis of OC that can cause inaccuracies. In this study, a commercial OC/EC analyzer was used to quantify EC and OC from coals. It was found that the ratio of OC to EC ranged between 0.68 and 0.73 when considered for pyrolysis correction. Without the correction, the proportion of OC in the total carbon was underestimated by 20-30%. This shows that pyrolysis correction in OC should be considered in quantification of EC and OC in order to accurately estimate the total carbon conversion. In this study, the comparison between TGA values and OC/EC analyzer values will be presented. The effect of OC pyrolysis correction on carbon conversion will also be assessed in terms of the kinetic data.
5G.03
Highly Time Resolved Measurements of Aerosol Carbon Using the Water Cyclone: An Ambient Comparison against the Sunset-ECOC Analyzer. Douglas A. Orsini (1), MIN-SUK BAE (2), James J. Schwab (2), Kenneth L. Demerjian (2), and Kevin P. Rhoads (3), (1) The Institute for Tropospheric Research, Leipzig, Germany, (2) Atmospheric Sciences Research Center, University at Albany, State University of New York, (3) Department of Chemistry and Biochemistry, Siena College, Loudonville, New York, USA

The water cyclone*, developed to collect and preserve biological aerosols in a small liquid flow, was interfaced to the Sievers TOC analyzer (GE 900, time resolution of 4 min, measurement range 0.03 ppb - 50 ppm TOC concentration) to measure aerosol organic and inorganic carbon fractions. The total carbon was compared against parallel measurements of EC and OC using the Sunset Real Time ECOC Analyzer. A NIOSH-like protocol for the Sunset measurement included four temperature steps ending at 840 degrees C for OC in a helium atmosphere followed by two temperature steps ramped to 850 degrees C for EC in a helium-oxygen atmosphere. The comparison of the carbon data between the cyclone-TOC and the Sunset analyzer indicates good agreement with an R2 = 0.92 and a linear regression slope = 0.94. In addition, the inorganic carbon signal from the water cyclone, which is characterized by CO2 production at pH = 2, tightly correlates with an extracted peak area appearing at 840 degrees C in the helium atmosphere of the Sunset Analyzer. The correlated inorganic carbon signals could reveal a fine aerosol carbonate carbon fraction and shed light on its source mechanism when combined with and compared to SMPS size distributions and TEOM PM2.5 mass concentrations.

* A Water Cyclone to Preserve Insoluble Aerosols in Liquid Flow - An Interface to Flow Cytometry to Detect Airborne Nucleic Acid, by: Orsini; Rhoads; McElhoney; Schick; Koehler; Hogrefe. In press at Aerosol Science and Technology.

5G.04
Effect of Vaporizer Temperature on Ambient High-Resolution Time-of-Flight Aerosol Mass Spectrometer Organic Mass Spectra. KENNETH S. DOCHERTY and Jose L. Jimenez, Cooperative Institute for Research in Environmental Sciences and Department of Chemistry and Biochemistry, University of Colorado, Boulder

Thermal vaporization is commonly used in many real-time aerosol chemical speciation instruments to desorb components of the aerosol prior to ionization and mass selection. Due to the wide variety of chemical species present in ambient aerosols combined with their wide range of volatilities, elevated vaporization temperatures are routinely used to ensure complete desorption of low volatility species such as ammonium sulfate. However, these high temperatures can cause thermal fragmentation of organic species, particularly for labile compounds, thereby lessening the quality of data with respect to identification of complex organic species. The high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) normally vaporizes species at 600C during ambient sampling, which can cause degradation of organic mass spectra as a result of thermal fragmentation.

An HR-ToF-AMS was modified to allow automated vaporizer temperature stepping from 600C to a minimum of 200C with 4 steps over a period of ~25 minutes. This instrument was deployed during the summer 2005 Study of Organic Aerosols in Riverside (SOAR-1) and also during the 2007 Biosphere Effects on Aerosols and Photochemistry Experiment (BEARPEX) to characterize the impact of vaporizer temperature on HR-ToF-AMS organic aerosol mass spectra. Here we present the results of positive matrix factorization (PMF) of organic aerosol mass spectra collected during periods of vaporizer temperature cycling. PMF results are presented both from the analysis of individual vaporizer temperatures (i.e., for each cycling temperature) and from the analysis of all cycling temperatures combined. The potential for gaining information regarding the volatility of individual organic aerosol components using PMF analysis of variable vaporizer temperature data will also be presented.
5G.05
Validating a Liquid Based Calibration of a Thermal Desorption Aerosol Gas Chromatograph Mass Spectrometer (TAG). NATHAN M. KREISBERG (1), Susanne S. Hering (1), David R. Worton (2), Brent J. Williams (2) and Allen H. Goldstein (2), (1) Aerosol Dynamics Inc., (2) University of California, Berkeley

The Thermal desorption Aerosol Gas chromatograph (TAG) is a new instrument for the in-situ, hourly measurement of organic aerosols on a compound level (Williams et al., 2006). PM$_{2.5}$ aerosol collected via humidified impaction is thermally desorbed to the head of a gas chromatographic column for standard GS-MS analyses.

TAG is similar to traditional filter based organic speciation methods, relying on authentic standards for instrument calibration. Liquid standards are currently injected into the collection cell and analyzed like ambient samples. Since many factors can affect the collection efficiency of organic aerosols complicating comparisons, a method of validating TAG calibrations independent of aerosol collection characteristics was developed. One or two small punches of a particulate standard NIST material (RM8785) where inserted into the cell for analysis.

The eight most abundant low-volatility polycyclic aromatic hydrocarbons (PAH) present on the NIST filters were selected for comparison, providing sufficient quantities for TAG detection. Repeat thermal desorptions indicate 90-100% recovery after the first desorption. Because the second desorption levels were at or below detection limits no corrections were made for these losses. TAG's calibrated response was compared to published NIST reference values (Schantz et al., 2006). Linear regression results for TAG vs NIST give a slope of 0.92 +/- 0.05 and intercept of 0.02 +/- 0.04 with a high degree of correlation (R= 0.98). All eight compounds analyzed exhibit a ratio of means (TAG to NIST) within one standard deviation of unity. Since no corrections were made to the single desorption responses, the small negative bias for TAG can be mostly attributed to the unrecovered fraction (<10%), thereby indicating that within the measurement uncertainty no bias exists in using a liquid based calibration for this instrument.


5G.06
On The Use of Ion Selective Electrodes for Online Measurement of Aerosol Inorganic Composition. Neeraj Rastogi (1), Rodney J. Weber (1), James J. Schauer (2), Martin Shafer (2), (1) Georgia Institute of Technology, Atlanta, GA (2) University of Wisconsin-Madison, Madison, WI

A number of instruments have been developed in recent years for online measurements of aerosol inorganic chemical components. The benefits of the data generated by these semi-continuous methods have been widely recognized and steps are being taken to deploy the instruments at monitoring sites. These types of applications require a relatively inexpensive instrument capable of operating autonomously over extended periods of time. One approach considered for these types of applications is the collection of ambient particles into water followed by analysis through Ion Chromatography. Although this method provides a highly quantitative measurement of a suite of species, the complexities associated with Ion Chromatographs present challenges when operated over extended periods of times. An alternative analytical method to Ion Chromatography for quantifying ions in the aqueous phase is through Ion Selective Micro-Electrodes (ISEs). This paper will present work in the development and characterization of ISEs, and their coupling to a Particle-Into-Liquid Sampler (PILS) for ambient measurements of fine particle composition.
Iron Speciation in Particulate Matter

Iron Speciation in Particulate Matter.
Nabin Upadhyay,
Pierre Herckes, Arizona State University, Dept. of Chemistry and Biochemistry, Tempe, AZ

The oxidation states of Fe play important roles in its solubility and reactivity in the environment. Since Fe(II) is more soluble than Fe(III), it is more reactive and produces oxidants that can affect the chemistry of atmospheric aqueous phase. Soluble Fe from deposition fluxes of particulate matter (PM) is an important micronutrient in the marine environment. However, little is known about oxidation states of Fe in PM and the redox behavior of Fe in urban PM and in clouds.

We will present results on the occurrence of soluble Fe(II) and Fe(III) in atmospheric PM collected from different environments. Fine (PM2.5) and coarse (PM>2.5) particle samples were collected in Nogales (AZ) at the US-Mexico border as well as in Tempe (AZ) on the campus of Arizona State University (ASU), including inside a parking structure. Samples were collected using HiVol samplers. A small section of the filter samples was extracted in an acetate buffer (pH = 4.3±0.1) followed by the photometric determination of Fe(II) using the Ferrozine method. Fe(III) was determined similarly after reducing it to Fe(II) by hydroxylamine hydrochloride. Total Fe in acid-digestion and the acetate buffer soluble Fe were determined using inductively coupled plasma mass-spectrometry (ICP-MS).

Redox artifact formation during the extraction process was evaluated using Fe salts. Excellent linearity with R^2>0.999 was obtained for the tests using Fe(II) and Fe(III) salts (ammonium iron (II, III) sulfates, FeSO_4·7H_2O and FeCl_3·6H_2O) in the acetate buffer covering the range of 5-500 microgram/L Fe(II). For ambient samples, Fe(II) was the dominant form of soluble iron in both coarse and fine PM, with concentrations ranging from 25-82 ng/m^3 and 0.5-12 ng/m^3, respectively. Soluble Fe(II) levels in PM2.5 accounted for only 1-2% of total Fe and for <0.01% of total Fe in PM>2.5. A substantial amount of Fe(III) (3.6+-2.4 ng/m^3) was present in PM2.5 in the parking structure. We will furthermore present results of kinetic investigations of redox behavior of Fe in artificial cloud samples irradiated with the simulated sunlight in the presence of other transition metals such as Cu and Mn.

New sampler holder for mass limited samples for speciation studies of Fe, Mn, Ni by XANES.

New sampler holder for mass limited samples for speciation studies of Fe, Mn, Ni by XANES.

SAUGATA DATTA (1), Janessa Hartmann(1), Tom Protus(2), Jana Mihalic(3), Ana Rule (3), Juan Ramos-Bonilla(3), Alison Geyh(3), Patrick Breysse (3) and Steven N. Chillrud(2), (1) Georgia College and State University, Milledgeville, (2) Lamont-Doherty Earth Observatory, New York, (3) Johns Hopkins University, Bloomberg School of Public Health, Baltimore

This work focuses on comparing different sample geometries for mass-limited samples of ambient airborne particulate matter (PM) for analysis of Fe, Mn and Ni by X-ray Absorption Near Edge Spectroscopy at National Synchrotron Light Source. Ambient PM from Baltimore, NIST 1648, and BCR 723 were used in these experiments. Preparations included transferring PM onto multiple layers of kapton or scotch tape which were then stacked, analyzing directly from quartz filters used to collect PM, and transferring PM to a new slotted sample holder designed to place the entire sample in the beam of the synchrotron. A traditional method for powdered samples is to stack multiple layers of filter or tape assuming that any potential inhomogeneities on one layer will be averaged in the other layers. However, this method results in the majority of the sample outside of the synchrotron beam. Furthermore, at low concentration it is difficult to get enough mass of element of interest into the beam since each layer of tape absorbs an appreciable amount of the beam (10%/layer scotch tape, 30%/layer kapton tape, 30%/layer quartz filter). Therefore, a custom holder was made of polycarbonate, 1.6 mm thick with a slot 9.3mm long and 1.6mm wide, holding ~20 mg of PM (layer of scotch tape top and bottom). Concentrations of Fe, Mn, and Ni in the Baltimore PM were 16,861 ppm, 802 ppm, and 19 ppm, respectively. Oxidation states for the Baltimore sample were Ni (+2), Mn (+2, +4) and Fe (+2, +3). For Baltimore PM and the reference materials, the best data were found with the new sample holder, even though the Ni concentration was relatively low in the Baltimore sample. Data obtained from the new sample holder were an overall improvement compared to the other sample preparation methods.
Emission based maintenance is becoming an option to reduce particulate in diesel emissions specifically in the mining industry but a better way of determining tailpipe emissions is needed. Determining the particulate in the tailpipe is also important when evaluating control technologies such as diesel particulate filters and determining potential ambient concentrations resulting from vehicles. Current methods for measuring tailpipe are expensive and bulky. There are not many portable instruments that can give accurate particulate concentrations. Most of the instruments currently in the mining industry only give relative particulate emissions. NIOSH investigated several portable instruments that could be used to determine tailpipe particulate in real time. These instruments give the advantage of being portable to take in remote locations such as underground mines and weighing stations and give actual concentrations of particulate. NIOSH tested a prototype EC monitor that will be commercially available in 2009, Thermo Electron Personal Dust Monitor, and a Prototype Magee Scientific instrument. These instruments were tested in an underground mine laboratory. Their results were compared to elemental carbon (EC) in the tailpipe and samples (total particulate, EC, Total carbon, etc.) taken downstream of the vehicle. The accuracy and benefit of each instrument is discussed in this paper.

Field Validation of Semi-continuous Monitoring of Sulfate and Carbonaceous Species at the Harvard-EPA Supersite.

Fine particulate (PM2.5) sulfate and carbonaceous species were monitored semi-continuously at the Harvard-EPA supersite during the period of January, 2007 through April, 2008. A Sulfate Particulate analyzer (Thermo Electron Co., MA) measured hourly concentration of sulfate and an OC/EC analyzer (Sunset Lab. Inc., OR) with an organic gas denuder measured hourly concentrations of organic and elemental carbon (OC and EC). Fine particulate BC (black carbon), a surrogate for EC, was also measured continuously by optical transmission using an Aethalometer (Magee Scientific Co., CA). In addition, 24-hr PM2.5 samples were collected on teflon and quartz-fiber filters, and then analyzed for sulfate and carbonaceous species using ion chromatography and thermal optical reflectance methods, respectively. In order to compare with 24-hr integrated filter samples, hourly monitoring data were averaged for corresponding 24-hr intervals. Hourly sulfate results was higher than the 24hr integrated results, with a slope of 1.17 (R²=0.98). Hourly OC was lower, with a slope of 0.96 (R²=0.74), and hourly EC was higher, with a slope of 1.14 (R²=0.76). Hourly BC was higher than hourly EC, with a slope of 1.38 (R²=0.88). This slope was similar to values reported in previous studies. Overall, these intercomparisons showed relatively good agreement between continuous and integrated measurements.
Stabilization Of Positively Charged Water And Sulfuric Acid-Water Pre-Nucleation Clusters By Protonated Ammonia. ALEXEY NADYKTO, Fangqun Yu, Jason Herb, State University of New York at Albany. ASRC, Albany, NY 12203, USA

Molecular cluster ions in the atmosphere are largely hydrated. The hydration of atmospheric ions directly influences the ion mobility, thermochemical stability and lifetime that have a profound effect on nucleation rates. In the present study, the gas-phase hydration of binary ionic clusters containing protonated ammonia (NH4+)(H2SO4) (H2O)n have been studied using the Density Functional Theory (DFT). The hydration enthalpies, entropies and Gibbs free energies have been calculated, and the thermodynamic analysis of the cluster stability has been carried out. It has been found that the protonation of ammonia leads to substantial enhancement in both the hydration strength and the overall clusters stability. In contrast, the presence of the sulfuric acid in (NH4+)-(H2O) clusters has does not have a profound effect of the hydration thermochemistry. The conversion of common atmospheric (H2SO4)(H3O+)(H2O)n clusters into (NH4+)(H2SO4)(H2O)n+1 by addition of NH3 has been investigated and found to be favorable thermodynamically. These considerations leads us to conclude that while NH4+ works as an efficient stabilizer of neutral clusters composed of atmospheric precursors, NH3 plays an important role in the conversion of positively charged sulfuric acid hydrates into protonated ammonia-sulfuric acid-water clusters.

Growth of Newly Formed Sulfuric Acid Nano-particles. Lin Wang, Alexei Khalizov, Renyi Zhang, Department of Atmospheric Sciences and Department of Chemistry Texas A&M University, College Station, TX 77843, USA

The processes governing the formation of new atmospheric particles and their subsequent growth represent a critical aspect of atmospheric aerosols but remain poorly understood. Nano-particle growth through condensation of organic and inorganic vapors, potentially followed by chemical reactions within the particle-phase, is of importance since it may impact the regional and global climate.

In this study, sulfuric acid aerosol particles were produced by homogeneous binary nucleation of H2SO4 and H2O vapors in a laminar flow reactor. The growth of the newly formed 4-20 nm sulfuric acid particles by uptake of several carbonyls, including 2,4-hexadienal and glyoxal, was studied using a nano-tandem differential mobility analyzer (nano-TDMA). Our results indicate that the initial size and the relative humidity are two key factors that determine the growth of sulfuric acid particles exposed to organic vapors. In addition, the change in the aerosol chemical composition was confirmed by the observation of new functional groups in sulfuric acid particles deposited on ZnSe crystal and exposed to 2,4-hexadienal and glyoxal, using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FT-IR). Our preliminary results indicate that the combination of nano-TDMA and ATR-FT-IR techniques provides a powerful tool to investigate the growth behavior of the newly formed particles.
6E.03
Laboratory-Measured Sulfuric Acid-Water Binary Homogeneous Nucleation from the SO2 + OH Reaction.
Dave Benson, Li-Hao Young, Rifkha Kameel, Shan-Hu Lee, Kent State University, Department of Chemistry, Kent, Ohio

We have developed an experimental setup for sulfuric acid and water binary homogeneous nucleation studies. We measured H2SO4-H2O nucleation rates (J) at atmospheric pressure, 288 K and 10 - 55 % relative humidity (RH). Sulfuric acid vapor was produced from the SO2 + OH -> HSO3 reaction and was measured with a chemical ionization mass spectrometer (CIMS). The CIMS-measured sulfuric acid concentrations required to produce the unit J ranged from e7-e8 per cubic centimeter, but if wall loss is taken into account the threshold sulfuric acid concentrations were at the e8-e9 per cubic centimeter, much higher than the atmospheric conditions. The measured J was proportional to sulfuric acid concentration with the second to tenth powers and proportional to RH with the eleventh to fifteenth powers. The measured aerosol sizes were proportional to log RH, showing a weak dependence of aerosol growth on RH. But the RH effects were more pronounced at higher sulfuric acid concentration, indicating that RH is more important for aerosol growth in the H2SO4 rich environment.


6E.04
A Quantitative Chemical Mechanism for Modeling the Formation of Secondary Organic Aerosol from the Reaction of OH Radicals with Linear Alkenes.
AIKO MATSUNAGA (1), Kenneth S. Docherty (2), Yong B. Lim (1), Paul J. Ziemann (1), (1) University of California, Riverside (2) University of Colorado, Boulder

Secondary organic aerosol (SOA) is formed by the oxidation of volatile organic compounds by OH radicals, NOx radicals, or O3, and many studies have focused on the development of detailed models of SOA formation. Current models tend to under-predict atmospheric SOA mass concentrations with one reason being poorly understood chemical mechanisms, especially alkene reactions with OH radicals. Alkenes, such as monoterpenes, comprise a significant fraction of the atmospheric hydrocarbon burden, and OH radicals are the major atmospheric oxidant. In this study, we investigated the products and mechanisms of the reactions of C8 - C17 linear alkenes with OH radicals in the presence of NOx. The study was carried in a ~6000 liter environmental chamber with OH radicals generated by photolysis of a methyl nitrite/NO mixture. Particle composition was analyzed using a thermal desorption particle beam mass spectrometer and SOA yields were determined from SMPS measurements of SOA mass and GC-FID measurements of the alkene. An HPLC with an UV detector was used to quantify multifunctional nitrate products. The major SOA products are primarily formed by reactions initiated by OH radical addition to the C=C double bond and include beta-hydroxynitrates, dihydroxynitrates, cyclic hemiacetals, dihydrofurans, and dihydroxycarbonyl dimers. Measured beta-hydroxynitrate and dihydroxynitrate were used with literature data and structure reactivity methods to develop a quantitative chemical mechanism of the reactions, and the mechanism was used to model SOA formation. The modeled results agreed well with the measured values above C8_(15), but for smaller carbon numbers the agreement depends on the treatment of dihydroxy carbonyls with respect to gas-particle partitioning and particle-phase reactions. The results of this study add substantial new insights into the products and mechanisms of alkene-OH reactions and SOA formation.
6E.05
Development and Application of a Stochastic Particle-Resolved Aerosol Model. NICOLE RIEMER (1), Matthew West (1), Rahul A. Zaveri (2), Richard C. Easter (2), James C. Barnard (2), (1) University of Illinois at Urbana-Champaign, (2) Pacific Northwest National Laboratory, Richland

Atmospheric aerosols can be composed of a complex mix of compounds such as soluble inorganic salts and acids, insoluble crustal materials (dust), trace metals, and carbonaceous materials, which include primary and secondary organic compounds of anthropogenic and biogenic origins as well as soot formed as result of fossil fuel combustion and biomass burning.

The mixing state of atmospheric aerosol particles is of crucial importance for assessing their macroscopic impacts. However, tracking the mixing state in conventional aerosol models requires treating a multidimensional size distribution, which is computationally prohibitive. Therefore current models usually assume an internal mixture within one mode or size section. The uncertainties associated with this assumption, which artificially ages freshly emitted particles instantly, are not well quantified.

In this study, we present a new approach, the stochastic particle resolved model PartMC-MOSAIC, which explicitly resolves the composition of individual particles in a given population of different types of aerosol particles, and accurately tracks their evolution due to emission, dilution, condensation and coagulation. PartMC-MOSAIC is applied to an idealized urban plume case to simulate the evolution of urban aerosols of different types due to coagulation and condensation. For this urban plume scenario we quantify the individual processes that contribute to the aging of the aerosol distribution.

7E.01

The presence of methyl tetrals (2-methylthreitol and 2-methylerythritol) has been found in PM$_{2.5}$ in numerous urban and rural environments. These compounds have also been detected in secondary organic aerosol (SOA) from laboratory oxidations of isoprene in the presence of acidic and nonacid seed aerosol. With ammonium sulfate seed aerosol, these compounds (following derivatization and GC-MS analysis) have been found in systems with and without NOx. In the absence of NOx, their formation has been shown indirectly from isoprene-ozonolysis experiments. In addition, from LC-MS analysis, organosulfate compounds have also been reported in the irradiated isoprene/NOx system with acidic sulfate aerosol present, for which the methyl tetrals might have been the precursors.

In the present study, laboratory experiments have been carried out to investigate the formation of SOA products from the OH-isoprene reaction in the absence of NOx, where OH was generated from the photolysis of H$_2$O$_2$. Chamber experiments were conducted in a dynamic (or flow) mode to permit SOA collection under highly controlled conditions. Gas phase constituents were also measured by utilizing an extractable denuder. Aerosol measurements were made for SOA, secondary organic carbon (SOC), the SOA-to-SOC ratio, the integrated volume from 20-900 nm, and the effective enthalpy of vaporization, deltaH$_{ev}$. Filters were also collected and analyzed for the presence of 2-methylglyceric acid and the methyl tetrals.

The results of the GC-MS analyses from laboratory samples were consistent with those from isoprene ozonolysis experiments (where OH formation was not suppressed) showing the methyl tetrals were formed in the absence of NOx. Measurements in the gas phase showed the presence of two dihydroxy compounds which are probable precursors to the methyl tetrals. The results suggest that isoprene emissions in areas where NOx is negligible can lead to SOA formation from the types of processes represented in this study.

This work has been funded wholly or in part by the United States Environmental Protection Agency under Contract EP-D-05-065 to Alion Science and Technology. It has been subjected to Agency review and approved for publication.
Can Secondary Organic Aerosol Formed in Atmospheric Simulation Chamber Be Continuously Aging? Li Qi, Shunsuke Nakao, Quentin Malloy, Bethany Warren, and David Cocker III, Department of Chemical and Environmental Engineering, Bourns College of Engineering, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, CA 92507, USA

Recent smog chamber studies have found that the oxidative processing (i.e. aging) of organic aerosol affects the chemical and physical properties for both aromatic and terpene aerosol precursors. Evidence from laboratory experiments suggests that organic aerosol can be converted from a hydrophobic to a hydrophilic state with aging. One possible chemical aging mechanism proposes that gas-phase oxidants react heterogeneously with aerosol to form large molecules such as oligomers. Experiments conducted in the UC Riverside/CE-CERT environment chamber have not shown changes in hygroscopic properties from alpha-pinene and meta-xylene systems even after aging sixteen hours. In this study, we simulate chemical aging of carbonaceous aerosol generated from alpha-pinene oxidation (O3, OH and NO3) with an emphasis on the further uptake of oxidants, the evolution of aerosol hygroscopicity, and particle density. Particle hygroscopicity and density were continuously measured by hygroscopic tandem differential mobility analyzer and aerosol particle mass analyzer-scanning mobility particle sizer respectively. Particulate phase composition was also monitored by online high resolution time-of-flight aerosol mass spectrometry to provide an insight into the variation of chemical composition with aging process.


The formation of secondary organic aerosol (SOA) from the reactions between OH radicals and semivolatile (SVOC) and intermediate volatility (IVOC) organic compounds was investigated in the Carnegie Mellon University smog chamber. SVOC and IVOC are operationally defined by their effective saturation concentration ($C^*$) as $0.1 \text{ microgram m}^{-3} < C^* < 1000 \text{ microgram m}^{-3}$ and $1000 \text{ microgram m}^{-3} < C^* < 100,000 \text{ microgram m}^{-3}$, respectively. The goals of this work are to understand the SOA yield and chemical composition from oxidation of low volatility vapors at atmospheric concentrations and oxidant levels. The results obtained during this study will be used to better interpret earlier experiments with dilute diesel exhaust and wood smoke.

IVOCs exist mostly as vapors in the atmosphere, while SVOCs are partitioned between the vapor and particle phases. Due to their low volatility, SVOC and IVOC vapors should have the potential to generate SOA with high mass yield. Mass emissions of SVOC and IVOC vapor from diesel engines and other combustion systems are significant compared to POA emissions; thus the oxidation of SVOCs and IVOCs could serve as a significant source of SOA in the atmosphere. Previous results from this laboratory indicated that only a small fraction of SOA formed from the photo-oxidation of diesel exhaust could be described by oxidation of traditional SOA precursors such as light aromatics. Oxidation products of SVOC and IVOC vapors are the likely source of this unexplained SOA.

We present results of SOA production from the oxidation of multiple classes of compounds, including n-alkanes and alkenes consistent with components of diesel fuel and lubricating oil. The oxidation of large n-alkanes results in sustained production of SOA with high mass yield. Q-AMS data is used to investigate the composition of the SOA and to compare it to ambient oxidized organic aerosol.
7E.04  
Do Solid and Liquid Organic Particles Get Oxidized Differently in the Atmosphere? GEFFREY D. SMITH, Lindsay Renbaum, University of Georgia

Reactions of organic aerosol constituents are influenced by the chemical and physical properties of the particles. In some cases the rate of reaction may change by several orders of magnitude if mass transport into the particle is affected by the presence of other species. Furthermore, the phase, morphology and compositional heterogeneity of the particle can alter the rates and products of these organic reactions. We have investigated such effects in the reaction of model organic aerosol particles with the gas-phase oxidants O3 and Cl (as a surrogate for OH). The rates of reaction and yields of oxidation products were measured for supercooled (i.e. liquid) as well as solidified erucic acid (CH3(CH2)7CH=CH(CH2)11C(O)OH) particles using Aerosol Chemical Ionization Mass Spectrometry. Additionally, size change upon reaction was measured using a scanning mobility particle sizer. By comparing reactions of liquid and solid particles of identical chemical composition and size it is possible to assess the importance of phase in their oxidation. Results from similar experiments on particles of brassidic acid, the trans isomer of erucic acid, provide further insight into the role that particle morphology may have in influencing the oxidation reactions.

7E.05  
Photodegradation of secondary organic aerosol derived from oxidation of terpenes. SERGEY A. NIZKORODOV (1), Adam P. Bateman (1), Stephen A. Mang (1), Dana Henricksen (1), Xiang Pan (1), Mads P. S. Andersen (1), Donald R. Blake (1), Julia Laskin (2), Alexander Laskin (2), (1) University of California, Irvine, (2) Pacific Northwest National Laboratory

SOA (secondary organic aerosol) generated by oxidation of biogenic volatile organic compounds makes a significant contribution to the global aerosol budget. This presentation focuses on direct photodissociation processes taking place inside SOA (secondary organic aerosol) particles derived from oxidation of terpenes. Model SOA particles are generated by oxidation of monoterpenes by O3 and NO3 in darkness. Particles are collected on filters and exposed to tunable UV radiation. Gas-phase photodissociation products are detected by cavity ring-down spectroscopy, chemical ionization mass-spectrometry, and gas-chromatography. Composition of SOA particles before and after irradiation is probed with high-resolution ESI-MS (electrospray ionization mass spectrometry). The majority of observed SOA photodegradation pathways can be explained by weak absorptions by carbonyl and peroxy functional groups. Results suggest that direct photochemical processes occurring inside SOA particles change SOA chemical composition on atmospherically relevant time scales.

The chemical composition of particulate matter (PM) in the atmosphere is complex and the organic carbon portion is not well characterized. The complexity is a direct result of the numerous volatile organic compounds emitted from vegetation and many anthropogenic sources. These precursors to PM react with oxidants, such as ozone, and some of the products partition to the condensed phase resulting in secondary organic aerosol (SOA). In typical laboratory studies a single precursor is oxidized to estimate the SOA yield and composition. While these studies are helpful for understanding individual reaction mechanisms, they do not give a realistic view of atmospheric SOA chemistry where numerous precursors react. The focus of this research is to investigate how a complex precursor mixture, that more closely mimics atmospheric environments, affects SOA-forming reactions and SOA yields. Precursor mixtures of biogenic monoterpenes of known concentrations and compositions are volatilized into a 5.5 m3 Teflon chamber where they react with ozone (in excess) and in the presence of a radical scavenger 2-butanol. The concentrations of the reactants are monitored during the reaction by sampling with solid-phase microextraction and GC-MS analysis. The PM is sampled onto filters and analyzed off-line by GC-MS. The size and number of particles are monitored by a Scanning Mobility Particle Sizer (SMPS). The results of the SOA measurements show that the SOA yield produced from the ozonolysis of a coniferous pine oil extract samples is different from the SOA yield produced from an equivalent amount of alpha-pinene, which is one the components of the extract. These chamber experiments allow for the correlation of atmospherically-relevant precursor mixtures to aerosol yields and oxidation product compositions which help in the understanding of PM health effects and global climate change.

The Chemical Composition of alpha-Pinene SOA Particles is Increasingly Oxygenated at Lower Particle Mass Loadings. SCOT T. MARTIN (1), John E. Shilling (1), Qi Chen (1), Stephanie M. King (1), Thomas Rosenoern (1), Jesse H. Kroll (2), Douglas R. Worsnop (2), Peter F. DeCarlo (3), Allison C. Aiken (3) Donna Suerper (2,3) Jose L. Jimenez (3), (1) Harvard University, Cambridge (2) Aerodyne Research Inc, Billerica (3) University of Colorado, Boulder

The chemical composition of secondary organic aerosol (SOA) particles, formed by the dark ozonolysis of alpha-pinene, was characterized by a high-resolution time-of-flight aerosol mass spectrometer. The experiments were conducted using a continuous-flow chamber, allowing the particle mass loading and chemical composition to be maintained for several days. The particle mass loading was varied from 0.5 to greater-than or equal to 140 ug/m3 by adjusting reacted alpha-pinene from 0.9 to 91.1 ppbv. Other reaction conditions were 25 degrees C, 40% RH, dry ammonium sulfate (AS) seed particles, and excess 1-butanol. The mass spectra of the particles varied strongly with mass loading. The m/z 43 signal intensity, suggestive of a more reduced particle composition, was greater than that of m/z 44, suggestive of a more oxidized particle composition, for loadings exceeding 5 ug/m3. Based on the high-resolution particle mass spectra, the mass fraction of fragments containing carbon, oxygen, and possibly hydrogen (C/H/O) monotonically decreased from 0.54 to 0.45 as mass loading increased from 0.5 to greater-than or equal to 140 ug/m3. Correspondingly, the mass fraction of C/H fragments increased from 0.46 to 0.55. Overall, the molar oxygen-to-carbon ratio decreased from 0.45 to 0.28. Chemical composition changed most abruptly for lower loadings (< 0.5 and 15 ug/m3), with smaller changes observed from 15 to greater-than or equal to 140 ug/m3. Accompanying these chemical changes were concomitant changes in organic mass density. For the lowest loadings, the particle mass spectra resembled observations reported in the literature for some atmospheric particles.
The sensitivity in predicted levels of atmospheric organic particulate matter (OPM, ug/m³) to changes in the governing gas/particle partitioning constants due to variations in temperature, relative humidity (RH), and other system parameters will be discussed. The sensitivity is considered in the context of the OPM level being given by the difference between: a) the sum of the total levels of the relevant condensable compounds; and b) the corresponding sum for the gas-phase levels of those compounds. A generic system with three condensable compounds will used to demonstrate how the relative sensitivity in predicted OPM levels increases rapidly as OPM levels become small relative to the concentrations of condensable compounds. Moreover, as the latter decreases, the gas phase becomes increasingly capable of holding the majority of each of the compounds, and small changes in system parameters can cause large relative changes in the OPM level. The latter effect will be illustrated using predictions for a number of relevant secondary-OPM and secondary+primary OPM cases.

Most regional and global models rely on the N*2p approach of Odum et al. (1996) to predict ambient levels of organic particulate matter (OPM). In the N*2p approach, up to two lumped products (p) are used to represent the partitioning oxidation products of N number of parent hydrocarbons. Using alpha-pinene as an example HC, the gas/particle partitioning constants (Kp) of the lumped products p1 and p2 typically cover the ranges of .003-.020 m³ ug⁻¹ and .090-0.80 m³ ug⁻¹, respectively, which would lead to a fractional amount of approximately .03-.20 and .50-.90 in the particle phase under atmospherically relevant conditions (based on Pankow, 1994a,b). There is growing evidence that compounds with higher- and lower-volatility are important for atmospheric OPM formation and may not be represented by such lumped products and their static Kp values. We recently presented the N*p + P model approach, which allows for the consideration of: a) the time dependence in the number of products that form from a particular parent HC; b) the time-dependent properties of the products (e.g., increasing polarity due to continued oxidation); and c) the formation of essentially non-volatile polymeric material (P) by accretion reactions. Here we compare simulated OPM levels with measured OPM levels for two sets of alpha-pinene ozonolysis chamber experiments. Using the N*p + P model approach our predictions improve significantly over the traditional N*2p approach.
**8E.04**

**Effective Enthalpies of Vaporization of SOA Produced from Biogenic, Aromatic and Normal Aliphatic Hydrocarbons.**

John H. Offenberg(1), Michael Lewandowski(1), Edward O. Edney(1), Tadeusz E. Kleindienst(1), Mohammed Jaoui(2), (1) National Exposure Research Laboratory, U.S. Environmental Protection Agency, RTP, NC, (2) Alion Science and Technology, RTP, NC

Volume concentrations of steady-state secondary organic aerosol (SOA) were measured in several laboratory experiments after passing through a constant temperature heated tube (298-523 K). Higher temperatures resulted in greater decrease of particle volume. The measured effective enthalpies of vaporization ($\Delta H_{\text{eff}}$) for SOA range from -6 to -70 kJ mol$^{-1}$, and depend upon the reactant hydrocarbon class (aromatics, terpenes, n-alkanes, isoprene) as well as compound specific structure (e.g. normal alkane chain length or substitution on phenyl ring of aromatic hydrocarbon). A positive correlation between $\Delta H_{\text{eff}}$ and n-alkane chain length are observed for SOA formed from the photolysis of hydrogen peroxide in the presence of n-alkanes. Additionally, $\Delta H_{\text{eff}}$ for aromatic hydrocarbons increases in magnitude with increasing methyl substitution. These laboratory measurements suggest that the thermodynamic behavior of SOA depends upon the reactant hydrocarbon composition.

This work has been funded wholly or in part by the United States Environmental Protection Agency under Contract EP-D-05-065 to Alion Science and Technology. It has been subjected to Agency review and approved for publication.

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**8E.05**

**Enthalpy of Vaporization and Saturation Vapor Pressure for Semi-Volatile Organic Aerosols: the Integrated Volume Method.**

RAWAD SALEH, Andrey Khlystov, Duke University

This study presents the Integrated Volume Method for determination of the saturation vapor pressure and enthalpy of vaporization of semi-volatile aerosols. In this method, the change of the total volume of pure semi-volatile aerosol particles as they are heated from a reference state to higher temperature states is used to estimate the saturation pressure and enthalpy of vaporization based on the Clausius-Clapeyron relation. The initial and final total volumes are measured by 2 SMPS systems, and the heating is done in a thermodenuder. Transport and aerosol dynamics computational models are developed to investigate the 2 main conditions for this analysis to be valid: 1) the aerosol should be at equilibrium at the exit of the thermodenuder; 2) there should be no re-condensation or further evaporation downstream of the thermodenuder. The integrated volume method is used to estimate the saturation pressure of organic aerosols when present in binary organic-organic and organic-inorganic mixtures. The reduction in total volume changes of mixtures relative to those of pure aerosols is used to estimate the reduction in saturation pressure. Results for pure components, as well as binary organic-inorganic and organic-organic mixtures will be presented.
9E.01
Numerical Modeling of Si Nanoparticle Formation during Silane Pyrolysis. Jaejung Seo, Taesung Kim, Sungkyunkwan University, Suwon

Fundamental studies in particle formation in gas-phase processes were experimentally and numerically studied in the past by various researchers. As nanoparticles are one of the building blocks of novel materials with superior quality, more work is needed in nanoparticle production to increase the generation rate and maintain high quality of the product. In this study, we report a numerical modeling of silicon nanoparticle formation during silane (SiH4) pyrolysis, which comprises nucleation, growth, coagulation and transport. Dynamic aerosol modeling was carried out using a commercially available chemical modeling software called CHEMKIN for the evolution of the particle size distribution function by using the method of moments (MOM). We have evaluated the previous experimental results by performing two-dimensional simulations of chemically reacting fluid flow and particle formation. Simulation studies were successfully carried out for various parameters such as reactor temperatures, flow rate, silane (SiH4) concentration and pressure which play key roles during manufacturing of Si particles. It is well understood that the nucleation takes place at the beginning of the process due to irreversible chemical reaction, which was confirmed by our simulation studies. Our simulation agrees that, due to coagulation and surface reactions, silane particle concentration found to be decreased during further particle growth. The simulation results reveal that, the effect of influence of reactor temperature, flow rate, silane concentrations and pressure made a good agreement with previous experimental result.

9E.02
TDMA and DMA/APM Measurement of Nickel Nanoparticle Oxidation Kinetics. LEI ZHOU, Ashish Rai, Michael R. Zachariah, University of Maryland

Nano-scaled nickel particles have attracted interest for its potential use as a fuel in energetic materials. In this work, we combined two ion-mobility spectrometry approaches; tandem differential mobility analysis (TDMA) and tandem differential mobility - particle mass analysis (DMA-APM) to study the size resolved reactivity of nickel nanoparticles. Nickel nanoparticles were generated in-situ using gas-phase thermal pyrolysis of nickel carbonyl. Four particle sizes (40, 62, 81 and 96 nm, mobility size) were then selected by using a differential mobility analyzer. These particles were sequentially oxidized in a flow reactor at various temperatures (25 - 1100 degrees C). The size and mass change of the size selected and reacted particles were then measured by a second DMA, or an APM. We found that both particle size and mass were increased as the temperature increased. However, at higher temperature (600-1100 degrees C), a different mass and size change behavior was observed which could attribute to a phase transition between NiO and Ni2O3. A shrinking core model employed to extract the size-resolved kinetic parameters shows that the activation energy for oxidation decreased with decreasing particle size. The burning time power dependence on particle size was found to be less than 2 and nickel particles were found to be kinetically more active than aluminum.
9E.03  

The experimental vapor nucleation rate surfaces for glicerin-carbon dioxide systems are considered for case when a condensed phase has a phase transition. It is well known that glycerin has melting point near the room temperature. Melting was used to get impression on a first order phase transition impact on a vapour nucleation rate surface topology. Very clear S - shape fold on the nucleation rate surfaces were found experimentally for different total pressures of nucleation media. That fold is caused by the glycerin melting point. Melting temperature is movable in the result of carbon dioxide pressure variation. That kind of behaviour can be explained reasonable in binary liquid solution approximation. Surprisingly one more phase transition was revealed. That transition is initiated when system gets near subcritical conditions. It can be concluded that each phase transition of a matter condensed state generates a fold on a vapor nucleation rate surface. That result is applicable for all cases of nucleation when a new phase has phase transition of the first order.

Research is supported by RFBR grants No 07-08-13529-ofi and 07-03-00587-a;.

9E.04  
Phase-Transition Behavior of Ammonium/Hydrogen/Sulfate Aerosol Nanoparticles of Varying Acidity. MACKENZIE SMITH, Amanda Mifflin, Scot Martin, School of Engineering and Applied Sciences, Harvard University

Atmospheric aerosol particles play a significant role in the radiative budget of the earth, although the overall impact of their effects on climate and radiative forcing are still not fully understood. The degree to which aerosols affect the climate, such as through scattering and absorption processes, is largely dependent on their phase. A hygroscopic tandem nano-differential mobility analyzer system (HnTDMA) was used to investigate the phase-transition behavior of a variety of ammonium/hydrogen/sulfate species of acidities ranging between ammonium bisulfate, X = 0.5, and ammonium sulfate, X = 1.0. and to quantify the dependence of this behavior on a variety of particle chemical properties. Measurements were conducted on particles having diameters less than 100 nm. At this small size, the increased importance of the surface to the overall free energy of the particles may induce various effects that are unique to nano-sized particles, called nano-size effects. Such effects may include shifts in the deliquescence relative humidity (DRH) or efflorescence relative humidity (ERH), changes in hygroscopic growth factor, and possible formation of hydrates.

Preliminary studies of an X = 0.65 composition show the presence of multiple DRH values and a continuous phase transition between 40 and 65% RH, which suggests that acidic aerosol particles may form externally mixed compositions. These studies will contribute to better predictions of radiative forcing and global transport of aerosol particles, and can ultimately be used by policy makers in decisions about future emissions standards.
Aerosol Chemistry

9E.05
Sign preference in binary sulfuric acid-water nucleation.
ALEXEY NADYKTO, Fangqun Yu, Jason Herb, State University of New York at Albany, ASRC, Albany, NY 12203, USA

A clear understanding of the molecular nature of atmospheric nucleation is critically important. The role of the ion sign in the binary H2SO4-H2O nucleation remains unclear despite significant progress in both theory and instrumentation achieved within the last decade. While measurements generally show higher activity of binary negative ions, positive ions have also been observed to be involved in the atmospheric nucleation and even dominate the particle formation on some nucleation event days. In order to resolve the aforementioned phenomena, quantum-chemical study of binary sulfuric acid-water ionic clusters nucleating in the atmosphere has been carried out. We found a profound sign effect caused by the pronounced difference in the structure and properties of clusters formed over core ions of different sign. The sign preference is found to be controlled by two somewhat competing factors: hydration and sulfuric acid attachment. While hydration of cations is clearly favorable, the affinity of sulfuric acid, which largely controls the nucleation intensity, to negative ions is much higher than that to positive ions. The presence of a very large difference in the affinity of sulfuric acid between positive and negative ions suggests that nucleation of negative ions is likely favorable.

9E.06
Atmospheric Observations of Aerosol Sizes and Aerosol Precursors Measured in Kent, Ohio.
Chandra Mouli PAVULURI, Rifkha Kameel, Brian Dailey, Dave Benson, Shan-Hu Lee, Kent State University, Department of Chemistry, Kent, Ohio

We are conducting atmospheric observations of new particle formation in Kent, OH. We have measured aerosol sizes and concentrations for particles in the size range from 3-102 nm semi-continuously from December 2005 and for particles from 3-1000 nm continuously from September 2007 in Kent, Ohio. We also simultaneously measure sulfuric acid and ammonia, two most important aerosol precursors, with two chemical ionization mass spectrometers (CIMS). Kent, located in Northeastern Ohio, is relatively rural itself, but is also surrounded by several urban cities within 40 miles. So far, most of new particle formation observations made in US were at relatively polluted areas (e.g., Atlanta, Pittsburgh, and Detroit). Because of the combination of its relatively rural environment (hence low surface areas of aerosol particles), active vegetation (organic and ammonia emissions), and possible transport of aerosol precursors from the surrounding urban and industrialized areas, Kent is a unique location to make new particle formation studies. We will present our ground-based, long-term measurements of aerosol sizes and concentrations measured in Kent and discuss how aerosol precursors, RH, temperature and photochemistry affect new particle formation in this rather rural Midwestern town.
A study on real-time formation and neutralization of secondary inorganic species by considering different calibrations for NH$_4^+$ in PM2.5 in Toronto, Canada.

Xiaohong Yao, Kerolyn Shairsingh, Greg J. Evans, University of Toronto

Recently, several semi-continuous gas/particle instruments have been developed for measuring real-time gases and particle chemical components in the atmosphere. The Dionex Gas Particle Ion Chromatograph (GP-IC) system is an automated instrument which can measure concentrations of HCl, HNO$_2$, HNO$_3$, SO$_2$ and NH$_3$ in the gas phase and Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ in PM2.5 (atmospheric particles with diameter less than 2.5 μm) every 15 minutes. This high time resolution measurement allows for the investigation of real-time variations of these secondary inorganic species in PM2.5 and their corresponding formation pathways and extent of neutralization. In this study, we found that when the NH$_4^+$ concentration in PM2.5 is less than 40 neq m$^{-3}$ and larger than 340 neq m$^{-3}$, the concentration response for NH$_4^+$ using the GP-IC is not linear. To evaluate the impact of this non-linear response, four calibration approaches were used for estimating NH$_4^+$ concentration in PM2.5. The chemical composition of PM2.5 in Toronto, Canada was interpreted for a variety of scenarios. Five types of formation pathways for sulphate and nitrate, i.e., local vehicle emissions followed by chemical conversion, in plumes from local gas-fired combustion sources, from local SO$_2$ point sources followed by chemical conversion, via cloud-processing and in transported air mass, were identified, which produced different particle acidities. It was also found that different calibration approaches for NH$_4^+$ greatly affected the interpretation of formation and neutralization of secondary inorganic species in PM2.5.

Spatial distribution of settled under influence of atmospheric and air pollution in Mitrovica with heavy metals. Syle Tahirsylaj (1), Letafete Latifi (2), Merita Shkodra (3), (1) University of Prishtina, Faculty of Mining and Metallurgy 40000 Mitrovica, Kosovo (2) Ministry of Environment and Spatial Planning, 10000, Prishtin, Kosovo (3) University SHTUL, in Tetova, FRY Macedonia

This study (research) was carried out in the city of Mitrovica, which is situated in Kosovo north with geographical coordinates 42 degrees and 53 min in Kosovo north and 20 degrees and 52 min in the east. More concretely, the monitoring covers the area in north-east part of Mitrovica, where the scope of monitoring is 7 km of air space. Total number of monitoring points is 9, which cover the urban area with a higher density of population.

From the use of Lead and Zinc Mine in Stan-Terg and activities carried out by chemical industries in the area in the past, a serious problem was caused in this part of Mitrovica in environment degradation with the created dust depositions dumps from the remains of chemical-technological processes of the mine in Zvecan and other industrial activities. These depositions are a permanent source of air pollution, which was suspended in air at any time. Exposure to certain types of settled dust and its associated contaminant load can be detrimental to human health.

In this study, we are focused on researching air pollution by dust deposition during years 2006 and 2007, and dustfull ranged from 78.361 to 2806.10 mg/m$^2$day according to our study, where we can conclude that there is an enormous excess in air quality according to WHO standards.

We did a comparison of air pollution for this period and we monitored the meteorological conditions in the spread of dust from the created depositions from the mine use and industrial activities. As well is determination and concentration heavy metals in the dust deposition, where we see from the made analysis that we have high concentration with Pb, Zn, Mn.
9E.10
Sources of submicron particles in the Mexico City Metropolitan Area from FTIR and XRF Analyses with PMF. SHANG LIU(1), Satoshi Takahama(1), Lynn M. Russell (1), Stefania Gilardoni(2), (1) Scripps Institution of Oceanography, University of California, San Diego, La Jolla, USA (2) Joint Research Centre, Ispra, Italy

Positive Matrix Factorization (PMF) was applied to distinguish sources of fine particles (PM1) for a study conducted during March 2006 in Mexico as part of MIRAGE/MILAGRO campaign. The goal was to identify aerosol sources in the metropolitan area and transportation of pollutants. Submicron particles were collected at three sites: Mexico city, which is an urban site; Altzomoni site, which is a high elevation site, and aircraft measurements, based in Veracruz. Fourier Transform Infrared Spectroscopy (FTIR) was used to quantify particulate organic functional groups, including saturated aliphatic (alkane), unsaturated aliphatic (alkene), aromatic, alcohol, carbonyl, amines, and organosulfur compounds. X-Ray Fluorescence (XRF) was used to quantify elemental concentrations heavier than Na. Positive Matrix Factorization (PMF) technique was applied to mass-weighted FTIR spectra of all three sites data, 7-9 factors were selected for PMF analysis. The model reproduced data very well, and the factors identified by PMF were correlated to elemental concentrations to investigate possible sources. The main sources are dominated by fuel combustion and biomass burning.

9E.11
An automated sampling system for particle bound reactive oxygen species. LIPING SUN, Jelica Pavlovic, Xi Chen, Philip K. Hopke, Center for Air Resources Engineering and Science, Clarkson University, Potsdam

Reactive oxygen species (ROS) include molecules like H2O2, ions like hypochlorite ion (OCl⁻), radicals like hydroxyl (OH) radical and superoxide anion (O2⁻). Previous studies found that ROS species are associated with particulate matter especially ultrafine particles, and those particle-bound ROS may have adverse effects on human health. In these prior studies, a manual filter method has been used to measure the ROS concentration. However, this method may underestimate those ROS constituents with shorter lifetimes (higher reactivity) because they react during the sample collection process. A continuous ROS sampling system was developed in which dichlorofluorescin (DCFH) fluorescence is measured as a non-specific, general indicator as particle-bound oxidants. A particle into liquid sampler (PILS) is used to collect atmospheric particles into an aqueous slurry that is then reacted with DCFH and horseradish peroxidase. Subsequently, the fluorescence intensity is measured with a flow-through fluorometer. Quantification is through relating the sample's fluorescent intensity to that of equivalent quantities of hydrogen peroxide (H2O2). Data from automated sampling system was compared with the manual method permitting the determination of the loss of short-life ROS. The laboratory system has been converted to a field deployable system and is being deployed in a field study.
**9E.12**


Secondary organic aerosol (SOA) is formed in the atmosphere by complex physical and chemical processes that are not yet well understood. Recent research has shown significant amounts of SOA is formed from photo-oxidation of dilute exhaust from a diesel engine (Robinson et al., Science, 315, 1259 (2007)). Furthermore, traditional SOA precursors such as light aromatics only explain a small fraction of the SOA formed. To further investigate the sources of SOA in dilute diesel exhaust, a series of laboratory experiments were performed to examine the formation of SOA from emissions surrogates, including lubricating motor oil and diesel fuel. These emission surrogates are a complex mix of hydrocarbons that span a wide range of volatility. UV-initiated photo-oxidation was performed in the Carnegie Mellon University smog chamber at atmospherically relevant OH concentrations. Chemical and physical composition of particles were monitored using an SMPS and quadrapole AMS. The AMS data are decomposed to determine the spectral signature of the SOA and to track its evolution with time. These data are compared to reference spectra from previous field and laboratory experiments, including ambient oxidized organic aerosol (OOA) and laboratory results for diesel exhaust.

**9E.13**


We present a method for generating organic aerosol using a resistively heated graphite tip. The tip is a 1"x1"x0.125" thick graphite block that contains a circular well with a volume of 100 microliters and has a resistance of 0.1-0.5 Ohms at room temperature (which decreases upon heating). Alternating current is provided by a transformer operated between 1 and 1.5 V, and the resulting current through the tip is approximately 10 A. Nominal power dissipation of the tip is 10-20 W, resulting in a heating rate of about 300°C/minute.

The method presented here offers three primary advantages over a collision atomizer: (1) Solvent is removed offline prior to injection of the target aerosol species, allowing quantitative amounts of aerosol to be introduced directly to a smog chamber without the use of multiple diffusion driers. (2) Large quantities of aerosol (>100 micro-gram m^-3) can be generated in a few minutes, as compared to tens of minutes or even hours using an atomizer. (3) Resultant particles are small, with the initial modal diameters for both number and volume distributions typically smaller than 100 nm.

The heated tip is capable of generating both single- and multi-component particles. Because of the high heating rate, we assume that the components of multi-species mixtures do not fractionate and rather form mixed particles. This assumption is confirmed using particle time-of-flight data obtained from an Aerodyne Q-AMS. AMS mass spectral data indicate that the vaporization of organic compounds and mixtures is repeatable and quantitative.

A potential complicating factor is the formation of aerosol from decomposition of the graphite tip, presumably through high energy electron impact. We demonstrate that the mass spectrum of this ‘graphite aerosol’ is unique and investigate its chemical stability. We also present applications where its presence can be an advantage rather than a hindrance.
Formation of 1,2- and 1,4-Naphthoquinone from the Photo-oxidation of Naphthalene with the Hydroxyl Radical. JIYI LEE, Douglas A. Lane, Environment Canada, Science and Technology Branch, Toronto, Canada

Naphthalene (Naph) is the most abundant polycyclic aromatic hydrocarbon (PAH) in the atmosphere of urban areas. The gas phase reaction of Naph with the OH radical results in numerous products which have vapor pressures that are lower than the Naph from which they were derived. This promotes the formation of secondary organic aerosol (SOA) which includes highly toxic chemical pollutants such as quinones. 1,2-naphthoquinone (NQ) and 1,4-NQ have been identified and quantified in diesel exhaust and ambient particles, and quinones have been postulated to contribute to the toxicity of both sources.

In this study, we applied GCxGC/TOF-MS to the identification of a number of toxic products from the photo-oxidation of Naph with the OH radical in a smog chamber. The formation yields of 1,2-NQ and 1,4-NQ were measured from this reaction. Although 1,4-NQ has been shown to be a photo-oxidation product of Naph, the formation of 1,2-NQ has not been observed. The formation yields of 1,2-NQ and 1,4-NQ were 0.019 +/- 0.002 and 0.041 +/- 0.021, respectively. The formation yields of 1,2-NQ was lower than that of 1,4-NQ (~46 % of 1,4-NQ). This study is the first to report the identification and quantification of 1,2-NQ as a product of the photo-oxidation of Naph with the OH radical. This presentation will also discuss the formation pathways that lead to the various products.

Characterization of Products from the Photo-oxidation of Phenanthrene with the Hydroxyl Radical using GCxGC/TOF-MS. JIYI LEE, Douglas A. Lane, Environment Canada, Science and Technology Branch, Toronto, Canada

Phenanthrene (Phen) is one of the most commonly found polycyclic aromatic hydrocarbons (PAH) in the atmosphere of urban areas. Phen exists primarily in the gas phase under ambient conditions. In the atmosphere, Phen undergoes photo-chemical oxidation and a number of oxygenated products which have lower vapor pressures than Phen are formed from this reaction. The oxygenated products, including quinones and nitrodibenzopyranones, are produced from the photo-oxidation of Phen and are mainly concentrated in the particle phase. They have also been shown to be highly mutagenic. However, only limited knowledge of the products of the photo-oxidation of Phen in the atmosphere is currently available.

In this work, we applied GCxGC TOF/MS to identify the products from the photo-oxidation of Phen with the OH radical. The newly identified products include phenanthrenediones, phenanthrenediols, hydroxy-phenanthrendiones, epoxy-phenanthrenediones, dibenzopyrones and ring-opening products. In addition, the possible pathways for the formation of these products are suggested and discussed.
9E.16
Photooxidation Kinetics and Intermediates of Substituted Dicarboxylic Acids. YANG LIMING (1), Liya E. Yu (2), (1) & (2) National University of Singapore, Singapore

Low molecular weight (LMW) C2-C9 dicarboxylic acids (DCAs) can easily partition into the particulate phase and subsequently alter chemical and physical properties of host aerosols. DCAs containing substituents, in particular hydroxyl- and oxo-groups, are of special interests because they have been present in the atmosphere, and can be generated during photooxidation of DCAs, as well as serve as precursors to smaller DCAs. This study experimentally investigates photooxidation kinetics and mechanisms of substituted C4-C7 DCAs simulating reactions in diluted fog and rain droplets in air. Results show that methyl-DCA exhibit degradation rates similar to corresponding base (straight chain) DCAs. Containing same carbon numbers, oxo-DCAs shows the highest degradation rate among tested substituted DCAs. This is expected because oxo-DCAs can be easily destabilized because of the high electronegativity of keto group. In addition, beta-keto-DCA can form a six-member cyclic structure by linking the proton of a carboxylic acid group to the oxygen of keto-group. Such a cyclic structure is often a transition state, which is unstable and could facilitate decarboxylation. During photooxidation of oxo-, methyl- and hydroxy-DCAs, 16 intermediates were identified, including unsubstituted secondary DCAs, methyl-DCAs, hydroxy-DCA, oxo-monocarboxylic acids (MCAs) and hydroxyl-MCAs. Secondary DCAs was most abundant, dominating over other intermediates when parent molecules contain more than six carbons. Based on molecular structure and concentration profiles of identified intermediates, secondary DCAs can be generated from photooxidation of oxo-DCAs and hydroxy-DCAs involving hydrogen-abstraction by OH and straight-chain (C-C bond) cleavage.

9E.17
Spectroscopic Characterization of the Ozonolysis of Octadecene Aerosols via AFT-FTIR. CINDY DEFOREST HAUSER, Moses Kim, Jonathan Huggins, Davidson College, Davidson

The ageing of atmospheric aerosols is an area of intense study utilizing a variety of methods. We have developed a method that combines an Aerosol Flow Tube with Fourier Transform Infrared Spectroscopy (AFT-FTIR) to study the heterogeneous chemical reaction of organic aerosols with ozone. With the validation experiments complete, we have focused our efforts on the interpretation of the information provided by the infrared spectra. In the Aerosol Flow Tube, we are able to probe the reaction by varying ozone concentrations or reaction times. These different conditions reveal information regarding reaction intermediates and products. Using infrared spectroscopic analysis we can identify these compounds in a unique way due to the functional group information provided. As the method employs gas phase analysis, in addition to functional group signatures, we can utilize peak areas to evaluate reaction kinetics. Here, we present results from the spectroscopic analysis of the reaction between octadecene aerosols and ozone.
9E.18

In our previous study (Song et al., Geophys. Res. Lett., 34, L20803, 2007), we showed that the presence of urban hydrophobic primary organic aerosols (POA) had no detectable effect on the secondary organic aerosol (SOA) yields from ozonolysis of alpha-pinene, suggesting that the SOA species may form a separate phase rather than a single well-mixed organic phase with the POA species. However, the urban hydrophobic POA may gradually become hydrophilic with time as a result of oxidation with the OH radicals. On the other hand, POA formed from biomass burning are already somewhat hydrophilic. In this study, we investigate the formation of alpha-pinene SOA in the presence of various surrogates of oxidized/hydrophilic POAs such as oxidized lubricating oil, oxidized bis(2-ethylhexyl)sebacate (BES), and fulvic acid. Organic species in the gas phase were measured with a Proton Transfer Reaction-Mass Spectrometer (PTR-MS) while the growth of aerosols and their composition were analyzed using a Scanning Mobility Particle Sizer (SMPS) and an Aerosol Mass Spectrometer (AMS), respectively. The data are interpreted with the gas-particle partitioning theory, and the implications of our results on modeling SOA formation will be discussed.

9E.19
Multi-box Model Studies of the Secondary Organic Aerosol Formation from Alpha-Pinenec Oxidation under a wider range of conditions. ADAM XIA, Craig Stroud, Paul Makar, Environment Canada

A subset of a near-explicit Master Chemical Mechanism (MCM v3.1) describing alpha-pinene oxidation (976 reactions and 331 compounds), coupled with a gas/particle absorptive partitioning model, is used for the study of secondary organic aerosol (SOA) formation within multi-box models. However, this study covers a wider range of conditions than those in our previous work (Xia et al, 2008).

Model results from the detailed mechanism for alpha-pinene oxidation were used to produce the isopleth maps for ozone, the total SOA mass, and the mass of the four functional groups (peroxynitrates, organic nitrates, organic peroxides, and organic acid) in the aerosol phase. For the total SOA mass, the slope of the transitional line (dNOx/dVOC) that separates VOC-sensitive to NOx-sensitive conditions is flatter than the transitional line for ozone. Among the four functional groups, nitrates dominate in region with high NOx and low VOC. Conversely, organic peroxides dominate aerosol mass in region with high VOC and low NOx. Peroxynitrates dominate in the region with high NOx and intermediate VOC, and organic acids dominate aerosol mass in regions with high VOC and intermediate NOx. Finally, the effect of the pre-existing organic seed on the SOA formation is also investigated. It is found that higher pre-existing organic seed leads to lower fraction of organic peroxides.

Currently, there is a large disconnect between ambient measurements of secondary organic aerosol (SOA) to model predictions based on environmental chamber experiments. PM-SAPRC08 is the second generation of PM-SAPRC07 and continues to utilize the gas phase reaction model SAPRC07 for aerosol formation modeling. PM-SAPRC08 has added formation mechanisms and optimization parameters for predicting SOA formation from meta-xylene photooxidation. The model currently follows two SOA formation pathways, alkylperoxys plus peroxys and xylenols plus nitrates, to explain experimental results for over 200 experiments. A comprehensive analysis; based on onset of formation, final aerosol mass formed, and time taken to reach 25% of the final mass, is conducted for all experiments under a variety of conditions; varying HC: NOx levels, varying k1’s, addition of light hydrocarbons, and addition of oxidant influencing compounds. Results indicate the model predicts best under NOx conditions (within 40% of final SOA formation for over 60 experiments) while onset of formation is over predicted under no NOx (H2O2) conditions.

Two original versions of the Model of Aerosol Dynamics, Reaction, Ionization and Dissolution (MADRID) exemplify different approaches for modeling organic aerosol (OA): based on empirical parameters (MADRID1) or on first principles using molecular constituents and properties (e.g., activity coefficients, vapor pressures, enthalpies of vaporization) (MADRID2). Sesqui-MADRID (MADRID1.5) combines these approaches. In sesqui-MADRID, both primary and secondary OA are modeled using surrogate molecular structures. Empirical partitioning characteristics guide the selection of surrogate secondary OA (SOA). Primary OA (POA) are represented by selecting key components of major source categories. Both POA and SOA are considered to be semivolatile. Water is also included in the absorbing medium in sesqui-MADRID, which allows phase separation when thermodynamically favorable.

Allowing POA to evaporate reduces the fraction of POA relative to SOA. The decrease can lead to a less-than-proportional decrease or increase in total OA due to changes in composition, activity coefficients, and partitioning of individual constituents. The inclusion of water in sesqui-MADRID increases the total OA concentration by increasing the absorbing medium. If activity coefficients are assumed to be unity, OA increases substantially. Treatment of non-ideality is essential in OA modules. Phase separation results in a small increase in total OA, because hydrophobic and hydrophilic compounds can exist in two liquid phases rather than repel each other in a single phase. The presence of water causes phase separation of OA in many instances.

The emissions model SMOKE is modified to generate speciated emissions for POA for use in a three-dimensional simulation for an episode in July 2002 in the southeastern United States. Compared to an existing model that treats POA as non-volatile and ignores water and activity coefficient effects, sesqui-MADRID predicts much lower primary OA with higher contributions from more-volatile and hydrophilic SOA constituents and similar concentrations for SOA constituents that are hydrophobic and less volatile.
Secondary Organic Aerosol Formation from Reactions of Tertiary Amines with Nitrate Radical. MARK ERUPE (1), Derek Price (1), Philip Silva (1), Quentin Malloy (2), Li Qi (2), Bethany Warren (2), David Cocker (2) , (1) Utah State University, (2) CE-CERT, University of California, Riverside

Recent work has shown that reactions of amines with the nitrate radical lead to the formation of significant amount of aerosol. In this study, secondary organic aerosol (SOA) formation from reactions of tertiary amines with nitrate radical was investigated using an aerosol mass spectrometer (AMS) and a proton transfer reaction mass spectrometer (PTR-MS). Three tertiary amines were reacted; Trimethylamine (TMA), Triethylamine (TEA) and Tributylamine (TBA). Results indicate that TBA forms the largest amount of aerosol mass followed by TMA and TEA respectively. Mass spectra from the AMS point to complex non-salt aerosol products, likely hydroxy amides. We propose a mechanism that proceeds via abstraction of a proton by the nitrate radical followed by RO2 chemistry. Rearrangement of the aminyl alkoxy radical through H-shift leads to the formation of aerosol products. These experiments show that night-time oxidation of tertiary amines by the nitrate radical can be an important source of SOA in regions with high mixing ratios of these species.

A Community Aerosol Thermodynamics Platform for Systems Containing Organic and Inorganic Compounds: the Extended AIM Model (E-AIM). SIMON L. CLEG (1,2), Anthony S. Wexler (2), (1) University of East Anglia, U.K., (2) University of California at Davis

Gas/aerosol equilibrium (thermodynamic) models of the soluble inorganic components of aerosols are relatively well developed, but this is not true of the many semi-volatile organic compounds that can partition in the atmosphere. Flexible methods of modelling inorganic/organic aerosol systems are needed, both to accommodate the range of approaches being explored by different groups and our evolving knowledge of the properties and reactions of atmospheric organic compounds.

We have developed a thermodynamic gas/liquid/solid partitioning model that is based on the inorganic AIM thermodynamics of Wexler and Clegg (2002), and is able to include an arbitrary number of water-soluble and/or hydrophobic organic compounds or surrogate species. The properties of these species (vapour pressure or Henry's law constant, activity coefficients, dissociation constants, solubility in water, and existence in the aerosol aqueous or hydrophobic phase) are specified by the user. Activity coefficients of organic compounds in the aerosol liquid phases can be calculated by UNIFAC, by a fitted equation that the user provides, or assuming Raoult's law.

Users can develop and maintain libraries of their own organic compounds, which are saved on the system. Access to these is either by login/password, or by a numeric code (unique to each user) that allows the compounds to be shared with students and colleagues. Thus E-AIM provides a community aerosol thermodynamics platform.

The inorganic thermodynamic model has been extended to include neutral and alkaline systems in which the dissociation of ammonia and water in the aqueous phase affect aerosol pH and hence gas/aerosol partitioning of ammonia and acid gases such as nitric acid. The influence of dissolved salts on the activity coefficient of ammonia - hence its vapour pressure - has been determined from literature data and is also included in the model.

The Extended AIM Model (E-AIM) has been implemented on the web (http://www.aim.env.uea.ac.uk/aim/aim.php) for free interactive use.

Reference:
New Pathway of SOA Formation through Nitrate Aerosol Photochemistry. Yong Yu (1), Michael J. Ezell (1), Stanley N. Johnson (1), Veronique Perraud (1), Emily Bruns (1), Barbara J. Finlayson-Pitts (1), Alla Zelenyuk (2), Lizabeth M. Alexander (2), Dan Imre (3), (1) Department of Chemistry, University of California Irvine, Irvine (2) Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland (3) Imre Consulting, Richland

Particulate nitrate is a significant component of aged urban aerosol and is expected to become more important in the future atmosphere due to predicted increase in nitrate precursor emissions and the decline of ammonium sulfate aerosols in wide regions on the earth. Compared to sulfate aerosols, nitrate aerosols have rich photochemistry and have the potential for gas-particle interactions with volatile organic compounds (VOC’s) which may lead to secondary organic aerosols (SOA) and modification of the physical and optical properties of the nitrate aerosol. Studies of SOA formation from nitrate aerosol photochemistry with selected biogenic and anthropogenic precursors in a laminar flow reaction chamber (0.5 m dia. & 6 m length) will be reported. Changes in the gas phase composition are measured using GC-MS, a NOx chemiluminescence analyzer, an O3 UV monitor, and Proton Transfer Reaction Mass Spectrometry (PTR-MS). Particle size distributions are characterized using SMPS and APS, and light scattering is measured using a three-wavelength nephelometer and compared to Mie calculations. The chemical composition and aerodynamic diameter of the particles are measured using a high-resolution aerosol mass spectrometer (AMS) and a second-generation Single Particle Laser Ablation Time-of-Flight mass spectrometer (SPLAT II), as well as combined chromatography-mass spectrometry with and without derivatization of filter-collected carboxylic acids, aldehydes and organic nitrates. The capabilities of this new system will be presented, along with results from the oxidation of alpha-pinene and other compounds, and the implications for SOA formation and loss in the atmosphere will be discussed.

Importance of Particle Phase in Heterogeneous Organic Nitrate Formation. Lindsay Renbaum Geoffrey D. Smith, University of Georgia

Radical initiated oxidation of organic compounds leads to the efficient production of alkylperoxy radicals in the presence of oxygen. The alkylperoxy radicals may then react by various pathways to create a variety of functionalized products. Under high NOx conditions, organic nitrates (RONO2) may be formed in significant yields. Organic nitrate formation from the reaction of alkylperoxy radicals with NO has been studied extensively in the gas phase, however little research has been carried out on condensed phase RONO2 formation in heterogeneous reactions between condensed phase alkylperoxy radicals and NO. Comprehending organic nitrate formation in organic aerosols is necessary in understanding the physical properties of organic aerosols because organic nitrates may 1.) significantly alter the cloud condensation nuclei (CCN) activity of the aerosol particles by affecting the hygroscopicity 2.) alter the UV actinic flux that reaches the earth’s surface 3.) affect the atmospheric lifetimes of organic species in the atmosphere and 4.) act as efficient reservoirs of NOx, making long-range transport possible. The formation of RONO2 in heterogeneous reactions of aerosols composed of various saturated and unsaturated condensed phase organics is observed and the importance of particle phase on RONO2 formation is discussed as well as the feasible mechanisms responsible for condensed phase organic nitrate formation.
Influence of Heterogeneous Chemistry on the Gas and Particle Partitioning of Semivolatile Organic Compounds.

GANG CAO (1), Myoseon Jang (2), (1) the University of North Carolina at Chapel Hill (2) University of Florida

Secondary organic aerosol (SOA) was generated from oxidation of toluene by OH radicals from photolysis of H2O2 in a 2 m3 indoor Teflon film chamber. The SOA experiments were performed under non acidic and acidic conditions by varying the composition of the inorganic seed aerosols. For the individual SOA experiment, the gas and particle phase products were tentatively identified by a gas chromatograph-ion trap mass spectrometer (GC-ITMS). The peak areas of the organic products in GC-ITMS were normalized by the internal standards and used for the calculation of experimental partitioning coefficient of each identified product. The theoretical partitioning coefficients were estimated by the conventional absorptive partitioning model incorporated with estimation of both the activity coefficients of the individual organic products in a given SOA composition using the UNIFAC and the vapor pressure of organic compounds by the group contribution method. The results showed a noticeable discrepancy between the experimental partitioning coefficients and those obtained by the theory suggesting that heterogeneous chemistry in the aerosol phase significantly affects the gas and particle distribution of organic compounds. In addition to SOA products, two deutrated alkanes (d40-nonadecane and d42-eicosane) that represented compounds not reactive for heterogeneous reactions were used to study the partitioning of the hydrophobic semivolatile organic compounds on two different SOA generated in the presence of neutral and acidic seed aerosols. The experimental partitioning coefficients of deutrated alkanes were significantly higher with neutral seed. Such results indicate that the SOA became less favorable for the partitioning of organics due to the large molecular weight compounds produced by heterogeneous acid-catalyzed reactions. Our study also shows that hydrophobic semivolatiles often found in automobile combustions are reluctant to partition on SOA. This study explains why the hydrophilic organic carbon fraction of PM is high in many field samples.

Temperature Programmed Reaction Spectroscopy of the Primary Ozonide: Towards a Better Understanding of Ozonolysis Kinetics.

SCOTT A. EPSTEIN  Neil M. Donahue , Carnegie Mellon University, Center for Atmospheric Particle Studies

Ozonolysis is an important oxidation pathway for gas- and condensed-phase alkenes in the troposphere. Since ozonolysis products often have lower vapor pressures than their reactant alkenes, these reactions are a significant source of secondary organic aerosol. In addition, ozonolysis reactions are a source of radicals that play a key role in tropospheric chemistry. Also, ozone uptake ages particles on a timescale that is relevant to the typical lifetime of an air mass.

The mechanism of ozonolysis involves many branch points, but in all cases it proceeds through an initial intermediate known as the primary ozonide (POZ). The decomposition of the POZ can proceed in up to four different ways leading to different subsequent chemistry and product distributions. However, the POZ decomposes too rapidly to be observed under normal conditions.

We have constructed an apparatus to conduct Temperature Programmed Reaction Spectroscopy (TPRS) of ozonolysis reactions on a liquid-nitrogen cooled surface under vacuum. Fourier Transform Infrared Spectroscopy (FTIR) is used to observe the decomposition of the POZ on the surface. We observe the decomposition of primary ozonides formed from different alkenes as the surface is warmed at multiple heating rates. Data from these experiments allows us to make estimations of the barrier heights for POZ decomposition and, in cases with multiple primary ozonides, the branching ratios of different reaction pathways. In addition, we observe the formation of carbonyl products and their subsequent desorption. These experiments will be extended to include alkenes that are significant secondary organic aerosol precursors in the atmosphere.
13E.02 Insights into Fog and Cloud Chemistry from High Resolution Mass Spectrometry. YELE SUN(1), Qi Zhang(1), Lynn Mazzoleni(2), Jeff Collett(3), Utpal Rowchowdhury(1), (1)Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, New York, 12203, USA, (2)Los Alamos National Laboratory, Los Alamos, NM 87545, USA, (3) Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA

Despite the fact that organic substances are ubiquitous and abundant in fog and cloud waters, their constituents are not well understood mainly due to analytical difficulties. We recently developed a technique to characterize the bulk composition of organic compounds in atmospheric aqueous samples using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). This method has been validated by several measurement techniques, including PILS-IC, PILS-TOC, OC/EC Analyzer, TEOM, and SMPS (this conference). In this study, fog samples collected at Fresno, CA during winter 2006 and cloud samples collected at the Whiteface Mountain (WFM), NY in summer 2006 and 2007 were analyzed. In addition, the aerosol samples collected at Fresno, CA during winter 2006 were also extracted and analyzed using the same method above. Our results indicate that organic substances contribute ~30-40% of total dissolved materials in fog, cloud and aerosol. N-containing organic compounds account for ~40% of total organic species in Central Valley (CV) fog waters and ~15-17% in WFM cloud waters and Fresno aerosols. High resolution mass spectra analysis shows that hydrocarbon (C_xH_y+) and oxygenated (C_xH_yO_z+) ions dominate the total organic ions in all fog, cloud and aerosol, while nitrogen-containing ions (C_xH_yN_p+ and C_xH_yO_zN_p+) in CV fog waters show much higher fraction than those in aerosol and cloud samples. Also much higher nitrogen content and atomic nitrogen-to-carbon ratio (N/C) were observed in CV fog waters (N% = ~6% and N/C = 0.10) than those in Fresno aerosol and WFM cloud (N% = ~2-3% and N/C = ~0.04). Several classes of organics with different functional groups are identified by the mass spectra signatures including primary amines (R-CH2-NH2, m/z 30 CH4N+), amides (R-CO-NH2, m/z 43 CHNO+ and m/z 44 CH2NO+), and amino acids (R-C(H2)-COOH, m/z 74 C2H4NO2+, m/z 57 C2H3NO+, and m/z 46 CH4NO+). The organics in fog, cloud, and aerosol are highly oxidized, showing similar mass spectra to those of humic/fulvic acids and high organic-carbon-to-organic-mass (OM/OC) ratio (~1.9-2.0) and atomic oxygen-to-carbon (O/C) ratio (~0.5-0.6). Finally, the overall mass spectral patterns of organics in fog and cloud are compared to those of ambient organic aerosol, from which more insights into the atmospheric processes of organics in fog and cloud are discussed.

13E.03 In-Cloud SOA Formation: Effects of Acidic Sulfate and Precursor Concentration on Organic Acid Yields. YI TAN (1), Mark Perri (1), Annmarie Carlton (2), Sybil Seitzinger (1), Barbara Turpin (1), (1) Rutgers University, New Brunswick (2) US Environmental Protection Agency, Research Triangle Park

Aqueous photooxidation of glyoxal, a water-soluble product of gas-phase photochemistry, yields low-volatility compounds including oxalic acid. When this chemistry takes place in clouds and fogs followed by droplet evaporation (or if this chemistry occurs in aerosol water) then products remain in part in the particle phase, forming secondary organic aerosol (SOA). Acidic sulfate exists ubiquitously in atmospheric water and is known to enhance SOA formation through aerosol phase reactions. In this work we investigate how the presence of acidic sulfate and starting concentrations of precursors effect product formation in aqueous-phase photochemical reactions of glyoxal and hydroxyl radical (OH) conducted at cloud-relevant pH.

Glyoxal (3 mM) was oxidized in the aqueous phase by OH (from photolysis of hydrogen peroxide, 15 mM). Experiments were conducted with 0, 0.28 and 0.84 mM sulfuric acid. Experiments were repeated with 300 and 30 micromolar glyoxal (with 1.5 mM and 0.15 mM hydrogen peroxide, respectively). Precursors and products were investigated using ion chromatography (IC) and electrospray ionization mass spectrometry (ESI-MS).

Products included oxalic, formic, malonic, succinic, and glycolic acids and larger multifunctional compounds. Malonic, succinic and glycolic acids were not previously identified as products of glyoxal oxidation. They were observed in these experiments as a result of improved analytical resolution. A possible formation mechanism will be discussed. With the exception of formic acid and trace glycolic acid, products did not form in the absence of OH. The presence of sulfate did not alter oxalic acid concentrations significantly. However, higher oxalic acid yields were observed in experiments conducted at lower precursor concentrations. Reaction vessel kinetic modeling captures the change in pH and predicts no change in oxalic acid behavior with addition of sulfate. We will discuss experimental observations, the ability of the mechanistic chemical modeling to reproduce these observations, and implications to SOA formation through cloud processing.
13E.04
Enhanced SOA formation due to water uptake by ambient particles. CHRISTOPHER J. HENNIGAN (1), Michael H. Bergin (1), Jack E. Dibb (2), and Rodney J. Weber (1), (1) Georgia Institute of Technology (2) University of New Hampshire

This study characterizes the partitioning behavior of a significant fraction of the ambient organic aerosol through simultaneous measurements of gas and particle water-soluble organic carbon (WSOC) in summertime Atlanta, Georgia. The partitioning of WSOC had no correlation with either temperature or particulate organic carbon mass concentrations, but did show a strong RH dependence that was attributed to aerosol liquid water. At elevated RH levels (> 69%), WSOC showed a significant increase in partitioning to the particle phase that followed the predicted water uptake by fine particles. The enhancement in particle-phase partitioning translated to increased median particle WSOC concentrations ranging from 0.3-0.9 μg C m⁻³. The results provide a detailed overview of the WSOC partitioning behavior in the summertime in an urban region dominated by biogenic emissions, and indicate that secondary organic aerosol formation involving partitioning to liquid water may be a significant aerosol formation route that is generally not considered.

13E.05
Aerosol Hygroscopicity at Nearly-activating (RH>99%) Conditions. CHRIS RUEHL (1), Patrick Chuang (1), Athanasios Nenes (2), (1) University of California, Santa Cruz, (2) Georgia Institute of Technology

Kohler theory predicts the relative humidity in equilibrium with a particle of known size and composition, and can therefore be used to predict both hygroscopic growth experienced under sub-saturated conditions and the critical supersaturation required to nucleate a cloud droplet. Recently the Kohler equation has been simplified by lumping all parameters determined by particle composition into a single parameter, and this parameter has been measured for various particles, including those generated for solutions of known composition, in smog chamber experiments, and those sampled during field campaigns. While many studies have been conducted at moderate relative humidities (~90% or lower) and at supersaturation (RH>100%), there have been relatively few studies conducted at nearly-saturated conditions (RH 99%-100%). We produced nearly-saturated conditions using a continuous-flow thermal gradient chamber with a decreasing temperature gradient (typically this instrument is used with an increasing gradient, resulting in RH>100%), and measured the hygroscopic growth factor for particles of known composition with dry diameters ranging from 100-500 nm. Droplet diameters between 1 and 3 microns were measured with a phase Doppler interferometer. After calibrating the instrument with sodium chloride, the hygroscopic growth of ammonium sulfate was slightly enhanced relative to theoretical predictions. This effect was seen in droplets of different sizes, suggesting it was more related to the Raoult effect (solution activity) than to the Kelvin effect (surface tension). Sodium dodecyl sulfate particles were fairly well described by the single parameter model, which suggests that surface tension reduction in droplets of this size and concentration may be relatively minor. We also report results from a variety of organic substances, including sugars, dicarboxilic acids, and fulvic and humic acids.
Phase transitions and hygroscopic properties of pure organic aerosols and inorganic particles mixed with various water soluble organic compounds have been investigated by many research groups (1, 2). However, much less is reported on the properties of less water solubility organics. Recently, some less water soluble organic compounds (e.g., cis-pinonic acid) have been found to be more CCN active than the predictions based on water soluble organic compounds (e.g., cis-pinonic acid) have been found to be more CCN active than the predictions based on their limited solubilities (3). In this study, the phase transition and hygroscopic properties of deposited ammonium sulfate-adipic acid (AS-AA) particles on a hydrophobic substrate with AA wt fractions (f$_{(AA)}$) ranging from 0.03 to 0.90 were studied. Phase transitions were observed under an optical microscope, enabling larger than 50 particles (10 to 30 micron) to be examined at each composition simultaneously. Upon evaporation, over 50% of particles crystallized at RH 34% to 39% for all compositions, consistent with the CRH of pure AS reported in the literature. For 0.03 < f$_{(AA)}$ < 0.90, AA solids were formed at the highest achievable RH (93%), leading to the formation of mixed phase particles between 40%RH and 93% RH. On the other hand, complete deliquescence was observed at 90%RH for f$_{(AA)}$ = 0.03. This indicates that AA dissolved in AS solutions below the DRH of pure near 100%RH. Furthermore, substantial water uptake (molwater/molAS > 1.3) was detected at ~ 70%RH for f$_{(AA)}$ = 0.03 and 0.10. More significant (molwater/molAS > 9.1) water absorption occurred at ~ 80%RH which was attributed to the deliquescence of AS. The amounts of water uptake of the particles (0.03 < f$_{(AA)}$ < 0.50) were determined from the Raman peaks and they agreed well with that of pure AS. However, the amount of water content prior to 80%RH could not be quantified from the spectra due to instrumental limitation. Additional electrodynamic balance measurements were made to determine the mass of water absorbed before AS deliquescence.

References

Acknowledgement
This work was funded by an Earmarked Grant (610805) from the Research Grants Council of the Hong Kong Special

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14E.03
Single-particle Oxidation State and Morphology of Atmospheric Iron Aerosols from Spectromicroscopy Analysis. SATOSHI TAKAHAMA(1), Stefania Gilardoni (2), Lynn Russell (1), (1) Scripps Institution of Oceanography, La Jolla, CA (2) Climate Change Unit, Institute for Environment and Sustainability, JRC, Ispra, Italy.

Sixty-three iron-containing particles from five field campaigns [PELTI, ACE-Asia, MILAGRO (urban location and aloft on NCAR C-130), INTEX-B] were studied with Scanning Transmission X-Ray Microscopy and Near-Edge X-Ray Absorption Fine Structure L-edge spectroscopy. Particle sizes ranged from 0.2-4.5 micrometers and were found in many types of morphologies. Iron was found to exist in many different oxidation states with average Fe(II) to Fe(II)+Fe(III) ratios ranging from 0.0 to 0.73. Twenty-two inclusions and six agglomerations were found. For 29 particles, concurrent (spatially-resolved) carbon K-edge absorption spectra were collected; x-ray images suggest that in some instances there are clear phase barriers between iron and carbonaceous regions in agglomerations and irregular particles. The relationship between iron oxidation state and organic functional group abundance is also discussed. Reduced form of iron on particle surfaces was observed in some particles, suggesting evidence of atmospheric processing. In general, neither inferred particle source nor any metric of surface processing was by itself a strong predictor of overall Fe(II) fraction, indicating that both source and processing may be important contributors to the observed Fe(II) fraction in the atmosphere. In addition, seven spherical particles from the ACE-Asia campaign showed an iron shell with an absence of iron toward the core. These particles have characteristics consistent with tarballs described by Posfai et al. (2004), Hand et al. (2005), and Tivanski et al. (2007).


14E.04
Heterogeneous Chemistry of Mineral Dust Particles and its Effects on their Ability to Nucleate Clouds. RYAN SULLIVAN (1), Meagan Moore (1), Markus Petters (2), Sonia Kreidenweis (2), Greg Roberts (1), Alexander Laskin (3), Kimberly Prather (1), (1) University of California, San Diego (2) Colorado State University, Fort Collins (3) Pacific Northwest National Laboratory.

Our laboratory investigations of mineral dust particle reactions with acidic gases are motivated by field observations of the atmospheric processing of dust. During ACE-Asia we observed sulfate and nitrate to be strongly segregated from each other in individual aged Asian dust particles. Our recent laboratory results indicate that this mixing state would result in a large fraction of aged dust particles having low cloud formation potential, contrary to previous assumptions. CCN activation curves were measured for pure calcium salts and partially processed dust particles after reaction with acids in an aerosol flow tube. It is generally assumed that aged dust particles will have higher cloud nucleation ability than fresh dust due to the addition of secondary acids. However, calcium sulfate and oxalate had very low CCN activation potential, similar to that of calcite, while calcium chloride and nitrate were highly CCN active. Partially converting calcium carbonate to calcium nitrate through reaction with nitric acid rapidly increased the particle's hygroscopicity. The degree of conversion was determined by single-particle mass spectrometry. A conversion of less than 5% decreases the critical supersaturation by ~35%, with a corresponding increase in hygroscopicity from k = 0.002 to 0.01. This can be achieved in the atmosphere by exposure to ~50 ppt HNO3(g) for less than 5 minutes. The reaction kinetics are strongly dependent on relative humidity, with high RH producing larger reactive uptake coefficients and nitrate conversion. Reactions performed at very low RH can produce particles with an insoluble carbonate core and soluble nitrate shell, to which nitric acid can continue to partition to. The cloud formation potential of aged dust particles therefore depends on both the quantity and form of the acidic species that have reacted with the dust. These results have important implications for the treatment of mineral dust particles in global climate models.
Understanding the important mechanisms of Br₂ production from NaBr aerosols. PAUL NISSENSON (1), Donald Dabdub (1), Daniel Packwood (2), Barbara Finlayson-Pitts (3), Jennie Thomas (4), (1) Department of Mechanical and Aerospace Engineering, University of California, Irvine, (2) Department of Chemistry, University of Canterbury, New Zealand, (3) Department of Chemistry, University of California, Irvine, (4) Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles

A first-order sensitivity and uncertainty analysis is conducted on the Model of Aqueous, Gaseous and Interfacial Chemistry (MAGIC). Uncertainty ranges are established for input parameters related to chemical and physical processes involving brominated species and are used in conjunction with latin hypercube sampling and multiple linear regression to determine (1) the correlation between each input parameter and the model output and (2) the contribution of each input parameter to the uncertainty in the model output. In this study, the output parameter of interest is the production of molecular bromine since MAGIC has previously demonstrated the importance of an interfacial reaction between O₃ and Br⁻_aq, surf in the production of Br₂. An additional interfacial reaction between OH and Br⁻_aq, surf also is considered in this study.

The sensitivity analysis reveals that the interface reaction rates are the input parameters most strongly correlated with the production of Br₂. The uncertainty analysis shows that the interface reaction rates also are responsible for most of the uncertainty in MAGIC's ability to precisely calculate the production of Br₂. Results from this study establish priorities for refining estimates of input parameters.
Aerosol Physics

9J.01
Transport And Deposition Of Submicrometer Particles In A Human Nasal-Laryngeal Model During Expiration. Jinxiang Xi (1), Xiuhua Si (2), Worth P. Longest (3,4), (1) Department of Systems Engineering University of Arkansas, Little Rock, AR, (2) Department of Engineering Calvin College, Grand Rapids, MI, (3) Department of Mechanical Engineering Virginia Commonwealth University, Richmond, VA, (4) Department of Pharmaceutics Virginia Commonwealth University, Richmond, VA

A significant fraction of submicrometer aerosols that enter the respiratory tract do not deposit during inhalation. As a result, it is important to quantify the deposition characteristics of these aerosols during exhalation. However, simulating the transport and deposition of submicrometer aerosols in the range of 100 to 1000 nm is challenging due to low deposition rates and the concurrent action of inertial and diffusional effects. In this study, a well-tested Lagrangian transport model and a newly-proposed drift-flux model have been implemented to characterize the regional and local depositions of submicrometer particles in a nasal-laryngeal geometry. Both the Lagrangian particle tracking model and the continuous field drift-flux model with near-wall velocity corrections (DF-VC) accounted for the concurrent effects of particle inertia and diffusion. The nasal-laryngeal model was constructed from available MRI and CT data, which was used in previous numerical and experimental studies. Particle sizes ranging from 1 nm through 1000 nm and exhalation flow rates from 4 through 43.5 L/min were examined. Under these conditions, turbulence only appeared significant in the laryngeal and pharyngeal regions. Both the Lagrangian particle tracking model and the continuous field drift-flux model with near-wall velocity corrections (DF-VC) accounted for the concurrent effects of particle inertia and diffusion. The nasal-laryngeal model was constructed from available MRI and CT data, which was used in previous numerical and experimental studies. Particle sizes ranging from 1 nm through 1000 nm and exhalation flow rates from 4 through 43.5 L/min were examined. Under these conditions, turbulence only appeared significant in the laryngeal and pharyngeal regions. Both the Lagrangian particle tracking model and the continuous field drift-flux model with near-wall velocity corrections (DF-VC) accounted for the concurrent effects of particle inertia and diffusion. The nasal-laryngeal model was constructed from available MRI and CT data, which was used in previous numerical and experimental studies. Particle sizes ranging from 1 nm through 1000 nm and exhalation flow rates from 4 through 43.5 L/min were examined. Under these conditions, turbulence only appeared significant in the laryngeal and pharyngeal regions.

Simulation results of both the Lagrangian and DF-VC models provided a good match to experimental deposition data from similar nasal replica casts. The computational predictions of total deposition were also in good agreement with an existing empirical correlation for in vivo nasal deposition during expiration. Local deposition characteristics predicted by the Lagrangian and DF-VC models were similar. Results of this study indicate that the continuous phase DF-VC model is effective in capturing the finite inertial and diffusional transport mechanisms of fine respiratory aerosols and produces results that are comparable to Lagrangian particle tracking.

9J.02
Optical Properties of Size-resolved Aerosol Observed in the Mega-city of Seoul and the National Park Area of Gyeongju, Korea. KYUNGWON KIM (1), Young J. Kim (2), Jinsang Jung (2), (1) Gyeongju University, Korea, (2) Kwangju Institute of Science and Technology, Korea

Optical properties of airborne particles affect visibility impairment in the atmosphere. Light attenuation by aerosol depends on aerosol size distribution, chemical composition, and relative humidity. Aerosol size distribution and chemical composition can vary with measurement area. Size-resolved aerosols were measured in the mega-city of Seoul and the national park area of Gyeongju, Korea. In order to investigate the relationship between optical properties and aerosol chemistry, semi-continuous measurements were made at the visibility monitoring station of Yonsei University in the urban area of Seoul and at the aerosol monitoring site of Gyeongju University in the national park area of Gyeongju, Korea. Light extinction, light scattering, and light absorption coefficients were measured simultaneously with a transmissometer, a nephelometer, and an aethalometer, respectively. Elemental, ionic, and carbonaceous analyses were conducted by a proton induced X-ray emission (PIXE) method, an ion chromatography (IC) method, and a thermal optical transmittance (TOT) method, respectively. During the intensive monitoring periods, the average light extinction coefficient was measured to be 406±211 Mm⁻¹ for Seoul and 279±163 Mm⁻¹ for Gyeongju. Mass extinction efficiencies of PM₁₀, PM₂.₅, and PM₁ were estimated to be 12 ~ 14, 5 ~ 7, 2 ~ 4 m²/g.

Chemical compositions of size-resolved aerosols showed difference characteristics between the mega-city and the national park areas.
J.04
Charging State of Submicron Aerosol in Relation to Rain Droplets Size Evolution. JAN HOVORKA and Devraj Thimmaiah, Charles University in Prague

The presence of charge on water droplets or aerosol particles significantly increases aerosol scavenging by rain droplets and may enhance new particle formation via ion-induced nucleation mechanism. Aerosol nucleation and following condensational growth usually come after the rain periods, when number of accumulation mode particles has dropped down. We hypothesized, that convective precipitation brings more charge to submicron aerosol particles than the stratiform precipitation, and therefore nucleation bursts will be more frequent after the convective precipitation events. Stratiform and convective precipitations were distinguished by rain droplet size evolution. Stratiform precipitation is characteristic by very small rain droplets (<0.125 mm) which may gradually increase during the rain event, while larger rain drops right from the beginning the event are characteristic for convective rain. Mid latitudes is a typical region of stratiform precipitations, but several episodes of convective rain events was also registered. Rain droplets size evolution was analyzed in conjunction with long-term measurements of aerosol charge size distributions within the size range of 3-700 nm. Yearly measurements were conducted at roof-top station in Prague city center. We did not find remarkable difference in aerosol charging between stratiform or convective events, but typically higher aerosol charging appeared on aerosol approximately an hour before the nucleation burst.

J.05
Collective Protection Airflow Mapping. KENT REDWINE (1), Mark Hanning-Lee (1), Daryl Ward (2), Darren Jolley (2), (1) Jacobs Technology Advanced Systems Group (2) U.S. Government

It is important to measure the infiltration rate and the permeation rate of a Collective Protection (ColPro) structure, in order to determine mission performance. Such structures can be designed to protect personnel while moving or stationary structures may be deployed outdoors. Infiltration and permeation rate measurements can validate the design operating pressure and define the effect of wind-driven flow on a structure.

In this work, airflow was measured outside of a ColPro structure. To leverage the test opportunity, the airflow test was combined with a wind-driven challenge test in which an aerosol was introduced into the airflow. The aerosol introduced was in the 15 um range and served as both a simulant for bio particles and as a filterable tracer for airflow. Airflow vectors, challenge concentrations, challenge particle size distributions, optical data, and environmental data were measured outside the structure. Air speed at a rate of 0-6 m/s. and wind direction were also controlled. A lined tent was used as the first structure to test. For more realistic internal flow, materiel will be placed inside the tent in a mission configuration for future testing. Future testing will also be done with the airlock open and closed and at different operating pressures. Testing occurred at Dugway Proving Ground in 2008.

The test plan included flow modeling using a computational fluid dynamics package and test results were combined with the results of modeling to yield a fuller understanding of airflow and aerosol distribution.
Aerosol Physics

9J.06
Aircraft-Based Aerosol Cloud Sampler Design. ARASH MOHARRERI, Kevin J. Gucwa and Suresh Dhaniyala, Clarkson University, Potsdam, NY

Improved modeling of aerosol-cloud interactions is central to accurate estimation of the role of aerosol particles in global climate change. To develop and validate accurate aerosol-cloud system models, experimental data on the physical and chemical characteristics of activated and nonactivated aerosol over a range of cloud systems is required. Such data must often be acquired from aircraft platforms in order to achieve desired information about temporal and spatial variation of these parameters. A particular challenge for such aerosol-cloud characterization studies is to sample particles without contamination and at known enhancement efficiency, accounting for aircraft and sampler body influence on particle trajectories in the vicinity of the sampling inlet. An analysis of particle concentration around a blunt body has been performed to facilitate the interpretation of data taken from samplers. Also, these results will help determine the ideal locations for inlets on blunt body samplers. Measurements in cloud systems with blunt body samplers will be affected by cloud droplet impaction on the body and the consequent generation of splattered particles. This phenomenon can create a very large number of small drops/particles that can cause substantial bias in measurements. Available results from literature as well as recent experimental data are being utilized to model and characterize the droplet-wall impaction in terms of governing non-dimensional numbers. This model will be used to design and optimize the sampler for aerosol-cloud sampling, considering particle concentration variation, flow separation around the sampler body, and droplet splattering.

9J.07
A Web-Based Course for Particle Transport, Deposition and Removal. GOODARZ AHMADI (1), Suresh Dhaniyala (1), Cetin Cetinkaya (1), John McLaughlin (1), Stephen Doheny-Farina (1), Kambiz Nazridoust (1), David J, Schmidt (1), Xinli Jia (1), and Xiangwei Liu (1), Jeffrey Taylor (1), Mark Glauser (2) Syracuse University, Fa-Gung Fan (3), and Ahmed Busnaina (4) , (1) Clarkson University (2) Syracuse University (3) Xerox Corporation (4) Northeastern University

A sequence of courses on particle transport, deposition and removal was developed. In these courses, the fundamentals of particle transport, deposition and removal and re-entrainment were described. An extensive web for the course materials was developed and the courses materials were made available on the web. The course sequence was also taught simultaneously at Clarkson University and Syracuse University couple of years ago. These combined research and curriculum development (CRCD) courses are composed of four modules. The models are:

- 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

The details of the course lectures and computational modules are posted on the web at http://www.clarkson.edu/projects/crcd/.
9J.08
Change of the particle extinction coefficient during the aerosol dynamic processes. C. H. Jung (1), Y. P. Kim (2), (1) Kyungin Women's College, Incheon, Korea (2) Ewha Womans University, Seoul, Korea

The aerosols in the atmosphere change their particle size and composition continuously and, thus, optical properties. In order to quantify the effect of particle size distribution change on the optical properties of aerosols, the change of overall extinction coefficient and visibility during coagulation and condensation process should be simulated.

Jung and Kim (2006) approximated the single particle extinction efficiency with 6 order polynomials in the particle diameter range of 0.01-2.5 micrometer in three kinds of aerosols and applied the moment method in estimating optical properties change. Later, Jung and Kim (2007) developed general expressions for single particle extinction efficiency and overall extinction coefficient without the limitation of specific refractive indices or applicable particle size range. These are based on the harmonic mean between the Rayleigh scattering region and geometric scattering region.

In the present study, the effects of aerosol dynamics to aerosol optical properties were investigated analytically using an approximated expression for the overall extinction coefficient that is valid for a wide range of particle size. Both coagulation and condensation processes in the continuum region were considered using the moment method with the overall extinction coefficient from the harmonic mean between overall particle extinction coefficient of the Rayleigh scattering and geometric scattering regions. The derived analytic solutions were compared with asymptotic solutions of extinction coefficient and showed that the obtained solutions approach to asymptotic solutions ultimately.


9J.09
Large Eddy Simulation of Particle Transport and Deposition in a Turbulent Channel Flow. Mazyar Salmanzadeh (1,2) Mohammad Rahnama (1,2) and Goodarz Ahmadi (1), (1) Clarkson University, Potsdam (2) Shahid Bahonar University of Kerman, Kerman

Transport and deposition of particles in a turbulent channel flow were presented. A computational model using the Large-eddy simulations (LES) was used to simulate the instantaneous airflow condition in the duct. The code uses a finite volume method as well as the selective structure function model to account for the subgrid-scale Reynolds stresses. The Lagrangian particle tracking approach was used and the transport and deposition of particles in the channel were analyzed. The Stokes drag, lift, Brownian and gravity forces were included in the particle equation of motion. The Brownian force was simulated using a white noise stochastic process model. The simulation results showed that computational model captured the turbulence near wall coherent eddy structures, and predicted initial location of deposited particles was concentrated in certain bands for the short duration of simulations.
9J.10 Quantum Mechanical Investigation of New Particle Formation. HUA DU, Fangqun Yu, State University of New York, Albany

Atmospheric aerosols have continuously been of interests to many scientists due to their health and climatic impacts. Nucleation, which is the source of secondary aerosols in the atmosphere, therefore needs to be fully understood. Recent nucleation laboratory studies mimicking atmospheric conditions indicate some yet to be identified nucleation processes. In one set of experiments, the required H2SO4 concentrations to initiate binary nucleation in the cases producing H2SO4 via SO2 + OH are a factor of 10 to 100 lower than those generating H2SO4 via vaporization or SO3 + H2O. One possible explanation is that free radicals produced during the course of chemical conversion of SO2 into SO3 participate in the nucleation, which lowers the required H2SO4 concentration needed to form new particles. In the other set of experiments, experimental data suggested that the electron on the cluster not only enhances the collision rates but also acts as a catalyst to oxidize and stabilize the existing clusters. Since the electron may get detached from the existing stable cluster and get involved in the formation of many more stable clusters, the suggested ion nucleation pathways may imply the possibility of an ion-induced nucleation rate much higher than the ion production rate. In this study, we apply quantum-mechanical approaches to investigate the role of free radicals in the neutral binary nucleation and that of electron in the ion mediated nucleation. Stable ionic sulfur clusters have been identified in our preliminary study. The bonding of free radicals with binary clusters and their effects on cluster hydration and evaporation rate will be presented. A kinetic modeling study showing the enhancement of free radicals in the neutral binary nucleation and that of electron in the ion nucleation will be described. Further research needed to fully understand the new nucleation pathways will be discussed.

9J.11 Making Colloidal Suspensions of Initially Hydrophobic Black Carbon: Applications and Interference from Black Conductive Silicon Tubing. THOMAS W. KIRCHSTETTER (1), Odelle Hadley (2), Tami Bond (3), Chris Roden (3), Lawrence Berkeley National Laboratory, Berkeley, California (1) Scripps Institution of Oceanography, La Jolla, California (2) University of Illinois, Urbana-Champaign, Urbana, Illinois

Black carbon (BC) particles are generally hydrophobic directly after emission from combustion processes. We find that exposing BC to ozone transforms it from a hydrophobic to hydrophilic state. (We define hydrophilic as readily mixing with and forming a colloidal suspension in water and hydrophobic as clustering at the surface, i.e., non-wettable.) Not all BC exhibits this transformation, however. Whereas diffusion flame generated BC, which is essentially organic free, does, biomass soot does not, perhaps because the organic component of biomass soot prevents the transformation.

We find that black conductive silicon tubing (from TSI) alters aerosol water affinity. After passage through this tubing, the diffusion flame BC could no longer be transformed by oxidation to a hydrophilic state. Similarly, after equal exposures to ozone, biomass soot samples in significant prior contact with the silicon tubing were non-wettable whereas identical samples, except for the contact with the silicon tubing, were wettable. Since this type of tubing is widely used in aerosol research, further exploration and caution when using it in studies of aerosol hygroscopic properties is warranted.

The colloidal suspension of BC in water can be nebulized and dried to produce a BC-laden air stream for laboratory experiments. Mixing in water soluble substances, such as ammonium sulfate, offers a means of producing internally mixed BC particles. Additionally, the BC suspension can be turned into mist and cooled to make BC-contaminated snow. We can measure the mass concentration of BC in suspension and in snow down to ~5ppb using a spectrometer equipped with a liquid waveguide capillary cell.
**9J.12**

Fast-response particle sizers open a pathway for studying short-term new particle formation events in the atmosphere.

Xiaohong Yao, Cheol-Heon Jeong, Greg J. Evans, *University of Toronto*

Recently, several fast-response particle sizers have been developed for measuring real-time number concentrations of different sizes of particles in relation to primary combustion emissions. These instruments also allow for the investigation of short-term formation events of new particles, varying from dozens of seconds to several minutes, in the atmosphere. Short-term formation of new particles has been reported in the last decade, but has not been well discussed and understood due to the time-response limitations of past generation particle sizers. In this study, a Fast Mobility Particle Sizer (FMPS, TSI inc.), operating in 1 s time resolution, as well as a complementary suite of gas and particle analyzers were used to investigate short-term formation of new particles in the atmosphere. Several strong, short-term new particle formation events, characterized by the total concentration of <100 nm particles (with diameter less than 100 nm) > 105 cm-3 and < 10 nm particles >104 cm-3, were detected and these events were found to be not related to primary combustion emissions. These strong short-term new particle formation events sometimes occurred concurrently with long-term (lasting several hours) new particle formation events, characterized by apparent particle growth, and sometimes they occurred alone. The particles formed during these short-term events sometimes exhibited a uni-modal size distribution with a mode of 10 nm while the particles exhibited a bi-modal size distribution with a minor mode at 10 nm and a dominant mode at about 30 nm. The 30 nm mode occurred in association with a high sulphate formation rate in the atmosphere.

**9J.13**

Simulation of in situ ultrafine particle formation in the Eastern United States using PMCAMx-UF.

JAEGUN JUNG (1), Peter J. Adams (1), Spyros N. Pandis (1, 2), (1) Carnegie Mellon University (2) University of Patras

A three dimensional chemical transport model (PMCAMx-UF) is developed incorporating TwO-Moment Aerosol Sectional (TOMAS) algorithm. The model can use a variety of nucleation theories and parameterizations. This study focuses on the PMCAMx-UF application in the Eastern and Central US in 2001-02 using a scaled ternary sulfuric acid-ammonia-water theory. The model predicts nucleation events that extend over scales of 100s to 1000 km especially in the midwest and northeastern US. The events are less frequent in the southern part of the country. The predictions of the model are compared to measurements in Pittsburgh, St. Louis and Atlanta. The contributions of nucleation to particle number concentrations and the sensitivity of these concentrations to emissions of sulfur dioxide, ammonia, and primary particles are quantified.
9J.14
Experimental Estimation for Ion Induced-Nucleation. Eriko Nakatani Natsuko Yokoyama Motoaki Adachi, Osaka Prefecture University

The growth of ion to particle in atmosphere is one of important mechanisms to generate an atmospheric aerosol. We need a new method to measure directly the growth process from ions to particles because existing equipments could not measure it continuously. We have proposed a new method using Cluster-Differential Mobility Analyzer(C-DMA) as a nucleation chamber. When the humidity of sheath air is higher than that of the sampling flow in which ions are contained, sizes of initial ions can be bigger by the condensation of water molecules. On the other hand, when the humidity is lower, sizes of initial ions can reduce to smaller by the evaporation (Yokoyama and Adachi, Abs. 7th IAC, p.1617, 2006 ).

In this study, species, sizes and polarity of initial ions are changed. And, their electrical mobility distributions are measured at various humidity. Results obtained show the peak of electrical mobility distribution of initial ions shifts to lower mobility with increasing humidity. In order to calculate the growth rate of ions from the shift of mobility, the data reduction method is developed. Growth rates are evaluated from experimental results by the data reduction method.

9J.15
Aerodynamic Properties of Test Aerosols. SHANNA RATNESAR-SHUMATE, Joshua L. Santarpia, Jason Quizon, Neal Baker, Christopher Bare, Jerome Gilberry, Johns Hopkins University Applied Physics Laboratory

In order to accurately challenge biological and chemical detection sensors with realistic environmental backgrounds it is often necessary to generate a broad range of compositionally diverse aerosols. Understanding the properties of these aerosols is important for rating sensor performance in a laboratory setting and relating it to future performance in the field. Near real-time characterization of polydisperse fine and coarse-mode aerosol populations, that may be generated in these laboratory studies requires measurement with multiple instrument technologies (e.g. differential mobility analysis and optical light scattering). In order to present a complete size distribution, the aerodynamic properties of the aerosol need to be understood and quantified in order to convert and merge data sets obtained from multiple types of instruments. The JHU/APL Dynamic Concentration Aerosol Generator (DyCAG) will be used to generate and deliver a broad range of aerosols of interest including combustion products (e.g. diesel exhaust), aerosolized industrial chemicals, dusts, and salts to several commercially available instruments. A comparison of mobility based measurement using a Scanning Mobility Particle Size Spectrometer (SMPS) with mass based measurements using a cascade impactor, aerodynamic based measurements using a UVAPS, and geometric diameter based measurements using a Grimm Portable Aerosol Spectrometer will be used to calculate the effective densities and the shape factors of the different test aerosols. This data set will serve as a tool for testing and evaluation of future technologies that may be challenged by the presence of aerosol interferents.
Effects of Particle-Particle Collisions and Two-Way Coupling on Dispersed and Carrier Phase Fluctuations in DNS Channel Flow.

Hojjat Nasr (1), Goodarz Ahmadi (1) and John B. McLaughlin (2), (1) Department of Mechanical and Aeronautical Engineering (2) Department of Chemical and Biomolecular Engineering, Clarkson University, Potsdam, NY

This study was concerned with the effects of particle-particle collisions and two-way coupling on the dispersed and carrier phase turbulence fluctuations in a channel flow. The time history of the instantaneous turbulent velocity vector was generated by the two-way coupled direct numerical simulation (DNS) of the Navier-Stokes equation via a pseudospectral method. The particle equation of motion included the drag and the shear induced lift forces. The effect of particles on the flow was included in the analysis via a feedback force that acted on the computational grid points. Several simulations for different particle relaxation times and particle mass loadings were performed, and the effects of the inter-particle collisions and two-way coupling on the particle deposition velocity, fluid and particle fluctuating velocities, particle normal mean velocity, and particle concentration profiles were determined. It was found that, when particle-particle collisions were included in the computation but two-way coupling effects were ignored, the particle normal fluctuating velocity increased in the wall region causing an increase in the particle deposition velocity. When the particle collisions were neglected but the particle-fluid two-way coupling effects were accounted for, the particle normal fluctuating velocity decreased near the wall causing a decrease in the particle deposition velocity. For the physical case that both inter-particle collisions and two-way coupling effects are present, a series of four-way coupling simulations was performed. It was found that the particle deposition velocity increased with mass loading. The results for the particle concentration profile indicated that the inclusion of either two-way coupling or inter-particle collisions into the computation reduces the accumulation of particles near the wall. Comparisons of the present simulation results with the available experimental data and earlier numerical results are also presented.

The Nucleation Rate Experimental Data Inconsistencies.

MICHAEL P. ANISIMOV (1) Philip K. Hopke (2), (1) Institute of Chemical Kinetics and Combustion, Siberian Division of the Russian Academy of Sciences, Novosibirsk (2) Clarkson University, Potsdam, NY

Several research groups [1-4, etc] have made comparative measurements of nucleation rates. For these similar experiments, the slopes of the nucleation rate isotherms for different measurement systems should be nearly the same. However, the data illustrate inconsistency with each other. For example, recent data [1] reveal disagreements of nucleation rates for the same chemical systems measured using a static diffusion chamber and a flow diffusion chamber (FDC). FDC data are located around three-four orders of magnitude higher than the static diffusion chamber results. These examples illustrate the internal inconsistence of the experimental measurements, which are originated from the different experimental settings. Multiple inconsistencies suggest the assumption that the present nucleation vapor-gas experiments include an unknown, and uncontrollable parameter.

Inconsistency among experimentally measured values from different research groups and different experimental schemes is the main problem of the current generation vapor-gas nucleation experiments. In the most cases, the carrier gas is treated currently as an inert media to absorb a heat released by the phase transition. Consideration of a vapor-gas nucleation as binary system is the plausible way to solve the problem of data inconsistencies. It is very reasonable to think that different experimental systems have the different trajectories across the nucleation rate surface for vapor-gas systems. This idea can be proved experimentally using high pressure measuring techniques that are designed for vapour-gas nucleation studies. Several results illustrating the gas effects on nucleation will be presented.

10E.02
Case studies of particle formation events observed in boreal forests: Implications for nucleation mechanisms. FANGQUN YU (1), Richard Turco (2), (1) State University of New York, Albany (2) University of California, Los Angeles

Aerosol nucleation events observed worldwide may have significant climatic and health implications. However, the specific nucleation mechanisms remain ambiguous. Here, we report case studies of six nucleation events observed during an intensive field campaign at a boreal forest site (Hyytiala, Finland) in spring 2005. The present analysis is based on comprehensive kinetic simulations using an ion-mediated nucleation (IMN) model in which the key physical and chemical parameters are constrained by a variety of recent measurements. Out of roughly 30 days sampled during the campaign, four were initially selected on the basis of indications that the observed air masses were relatively homogeneous. It happens that all four of these days exhibited medium to high electrical overcharging of the nucleated nanoparticles. In each of these well-defined cases, reasonable agreement is found between the predictions and field data for a range of variables, including size-dependent overcharging ratios, the concentrations of 1.8-3 nm stable clusters and 3-6 nm particles, and their diurnal variations. However, to extend the scope of the study, one case of weak electrical overcharging, and one of clear undercharging, of the nucleated particles were also selected. These electrical states represented less than ~20% of the total event-days recorded, and the consistency between model simulations and measurements was less satisfying. We tentatively conclude that the outcomes in these cases were influenced by the significant variability in the sampled air masses and the possible role of species other than sulfuric acid in the nucleation process. Statistically, roughly 80% of the nucleation events recorded during the Hyytiala campaign exhibited mean size-dependent overcharging ratios within the range, or exceeding, those predicted by the IMN model, suggesting that ion nucleation processes are significant. The nucleation rates calculated using the IMN model are contrasted with those predicted by other theories/models, and key differences between the results are discussed.

10E.03
Homogeneous nucleation rates of aluminum, based on atomistic simulations of cluster free energies and condensation rate constants. STEVEN L. GIRSHICK (1), Zhen Hua Li (2), Donald G. Truhlar (1), (1) University of Minnesota, (2) Fudan University, Shanghai

Recently data were reported for the free energies of aluminum clusters, Aln [1], and for the rate constants of the condensation reaction Aln-1 + Al = Aln [2], in both cases up to n = 60. We have used these data to calculate transient and steady-state homogeneous nucleation rates of aluminum at 2000 K, for a range of saturation ratios S, and have compared these results to the predictions of self-consistent classical nucleation theory [3].

Classical theory predicts that the cluster free energy has a single peak at the critical nucleus, whose size depends on the value of S. In contrast the atomistic data exhibit a number of local maxima and minima and show a particularly pronounced maximum at n = 55 over a wide range of saturation ratios. In addition the atomistic simulations predict a higher condensation rate constant than does classical theory, because the atomistic simulations predict a larger cross section for monomer-cluster collisions compared to the hard sphere model of classical theory.

Steady-state nucleation rates predicted using the atomistic data are quite different than in classical theory, except for S > 35, for which nucleation becomes collision-controlled. Moreover the dependence of nucleation rate on saturation ratio is qualitatively different according to whether the atomistic data or classical theory are used. At S = 10 the predicted nucleation rates differ by over 20 orders of magnitude.

10E.04
On the role of sulfuric acid and organics in the first steps of atmospheric particle formation and growth. ILONA RIIPINEN (1), Hanna E. Manninen (1), Tuomo Nieminen (1), Mikko Sipila (1), Heikki Junninen (1), Mikael Ehn (1), Sanna-Liisa Sihto (1), Tuukka Petaja (1, 2), Miikka Dal Maso (1, 3), Taina Yli-Juuti (1), Frank Arnold (4), Veli-Matti Kerminen (5), Ari Laaksonen (5), Kari E.J. Lehtinen (5,6), Markku Kulmala (1), (1) University of Helsinki, Finland, (2) NCAR, Boulder, USA, (3) Julich Forschungszentrum, Germany, (4) Max Planck Institute for Nuclear Physics, Germany, (5) Finnish Meteorological Institute, Finland, (6) University of Kuopio, Finland

To better estimate the climatic importance of secondary aerosol particles, detailed information on atmospheric particle formation mechanisms and the vapors forming the aerosol is required. Sulfuric acid has been identified both theoretically and experimentally as a key component in atmospheric particle formation. On the other hand, a close link between particle formation and the emissions of biogenic organics has also been reported. In this work we studied the relative role of sulfuric acid and organics in the first steps of atmospheric nanoparticle formation and growth.

We applied versatile instrumentation at the SMEAR II station at a boreal forest site in Hyytiälä, Finland. The used data sets included 0.8-1000 nm particle and air ion size distributions and concentrations recorded with mobility spectrometers, CPC-Batteries, as well as hygroscopicity and volatility DMA setups. The particle data were compared to ambient concentrations of sulfuric acid and VOCs.

From our analysis we can conclude that in boreal forest conditions, both sulfuric acid and organics are needed for regional particle formation and growth events, the previous contributing mainly to particle formation and latter to growth. Ambient sulfuric acid concentrations showed a strong correlation with particle formation rates, whereas the particle growth rates, particularly those of over 7 nm particles, seemed to be correlated with the emissions of biogenic organics. However, sulfuric acid is not likely to be the only component of the freshly formed particles. Firstly, the ambient sulfuric acid concentrations were not enough to explain the observed particle growth rates. Secondly, even close to 2 nm, the atmospheric particles seemed to be less hygroscopic than pure ammonium sulfate of sulfuric acid would be. This suggests that the atmospheric organics participated even in the very first steps of particle formation and growth, although their importance significantly increased with particle size.

10E.05
Can cosmic rays possibly affect clouds by altering new particle formation rates? JEFFREY PIERCE, Peter Adams, Carnegie Mellon University

Proposed correlations between the atmospheric cosmic ray flux and global cloud cover, although highly controversial, may be important in determining natural sources of climate change (Carslaw et al., 2002). However, a physical link between cosmic rays and cloud cover has yet to be fully understood. One proposed link, the ion-aerosol clear-air mechanism, involves increases in the ion-induced new particle formation rates due to increases in the cosmic-ray atmospheric flux. The additional new particles may then grow to CCN sizes and modify cloud properties. We simulate the changes in CCN due to changes in the cosmic ray flux globally using the GISS GCM II-prime (Hansen et al, 1983) with online aerosol microphysics (Adams and Seinfeld, 2002). We test two different assumptions for the ion-induced nucleation rate: 1) the parameterization of Modgil, et al., 2005 and 2) the limit in which every atmospheric ion forms a new particle.

Using either ion-induced nucleation assumption, the proposed ion-aerosol clear-air mechanism cannot explain trends in cosmic ray/cloud correlations. Between the periods maximum and minimum solar activity, the ion-induced nucleation rate changed by 20-100% globally. However, in both cases, the change in CCN (at 0.2% supersaturation) between the solar maximum and minimum was less than 0.1%, likely too small to make noticeable changes in cloud properties.

13C.01  
Deliquescence and Water Uptake of Salt Nanoparticles from MD Simulations. LYNN RUSSELL and Ranjit Bahadur, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, USA

Salt nanoparticles constitute a significant fraction of marine and some continental atmospheric aerosols. We have used pure NaCl particles as a proxy for the behaviour of these particles in humid conditions simulated by Molecular Dynamics (MD). We find that the increase in deliquescence relative humidity at sizes smaller than 20 nm is well predicted by MD simulations, showing a good correspondence with measurements. The dynamics of this process reveal significant size dependence of the simulated uptake coefficients for water, with simulated values within the range predicted by atmospheric modelling studies (0.1 to 0.4). The uptake coefficient decreases with the fraction of particle surface already covered by water, and increases with decreasing particle size. The former effect is the result of the reduced solvation effect, and the latter effect is caused by the increased fraction of edges in the surface area of smaller particles.

13C.02  
Advantages Of A Semiempirical Design Of The Nucleation Rate Surfaces Over Phase Equilibria Diagram. MICHAEL P. ANISIMOV (1) Philip K. Hopke (2), (1) Institute of Chemical Kinetics and Combustion, Siberian Division of the Russian Academy of Sciences, Novosibirsk, Russia, (2) Clarkson University, Potsdam, New York.

A promising approach to provide a commonly applicable description of nucleation rates is the semiempirical nucleation rate surface displayed over the applicable phase equilibria diagram [1]. The nucleation rate surfaces arise from lines of phase equilibria. Lines of interface equilibria can be drawn through any triple point to areas of unstable equilibria. In these areas, one gets multiple nucleation rate surfaces. Multiple nucleation rate surfaces are likely to be present more often than we usually think [2]. It is important to avoid the interpretation of what are actually multiple nucleation rate data using the conventional one-surface approximation. Appropriate multiple rate surfaces will provide a much more reliable basis for the comparison of the experimental results with nucleation theory. Reliable nucleation rate surfaces play a key role in the identification of the nucleation conditions required to obtain a specific phase or composition. Thus, nucleation rate surfaces are widely applicable in technology development such as the production of nanosize materials.

2. M. P. Anisimov, Russian Chemical Reviews 2003, 72 (7), 591-628.
13C.03
The effects of porosity and surface concentration on condensation mass-transfer. Michael Buhlmann, Sean Garrick, University of Minnesota, Minneapolis, MN

Gas-particle mass transfer via condensation is studied analytically as well as numerically. Porous particles are modeled as a homogeneous assembly of sorbent material, forming a spherical, macroporous structure. The concentration in the macropores and in the solid is obtained as a function of time and space. The Langmuir theory is used to model sorption kinetics. Results show that, over a wide time range, the concentration in the solid is negligible and the macropore concentration reaches a pseudo steady-state. For that case an analytical expression is derived for the macropore concentration inside the particle and at the particle surface in particular. It is shown that the surface concentration decreases with decreasing mass Biot numbers and increasing Thiele numbers. The analytical model discussed in this work can be utilized in computational mass transfer studies in lieu of the "perfect sink" assumption, in which the surface concentration is identically zero. Moreover, it captures the effects of enhanced mass transfer due to convection at the gas/particle interface.

13C.04
Grouping of Aerosol Particles in Oscillating Flows. DAVID KATOSHEVSKI, TAL SHAKKED, Ben-Gurion University, Israel

Grouping of particles/droplets in an oscillating flow will be addressed. This has ramifications to various environmental processes such as: atmospheric aerosols, air pollution particulates emitted from vehicles and plants, fuel sprays, as well as particle motion in water. The prediction of grouping tendency and the associated characteristic time can be incorporated in aerosol/spray models, for example to estimate the effect of grouping on the overall vapor production of a multi-sized spray. It is shown, by our model, that the relatively small droplets tend to form groups and are thus expected to undergo a decrease in their evaporation rate. On the other hand, the larger droplets tend not to group, thus their rate of evaporation is maximized. Therefore, such travel-grouping may bring the evaporation rates of different droplet size ranges closer together. The tendency for non-grouping behavior is characterized by a new non-dimensional parameter designated NG. The mathematical model, although relatively simple, has shown a good qualitative agreement with two entirely different two-phase systems: 1) droplet grouping within a Diesel engine, and 2) grouping of particles in water. We will elucidate the stable and non-stable grouping modes and the parameters which govern each mode. Controlling aerosol particle grouping has important and useful applications, ranging from the control of air pollution to the optimization of medical aerosol delivery.
13C.05
Modeling Polydisperse Soil Particle Resuspension accounting for Saltation and Aerodynamic Entrainment.
Allison Harris (1), Cliff Davidson (2), (1) Cleveland Executive Fellowship, Cleveland (2) Carnegie Mellon University

Most models characterizing the mass flux of resuspending grains are empirical and hold only for the range of field and meteorological conditions under which experiments were run. Furthermore, most of these models are based on monodisperse particle sizes; there is inadequate knowledge about the movement of polydisperse beds. In addition to the mass flux, little is known about the number flux of crustal grains, which is a significant source of uncertainty in global climate models.

This paper describes a stochastic model for resuspension based on a Monte Carlo simulation that includes both aerodynamic entrainment and momentum transfer from saltating particles. Two case studies are performed based on conditions for the topmost layer of soil in Los Angeles County, CA, and Allegheny County, PA. Under a broad range of wind conditions, the predicted mass and number fluxes are in rough agreement with empirical results from other sites reported in the literature. Plots of particle mass flux versus height show concentration peaks at two different heights; the same is true for plots of particle number flux. Wind shear altered by saltating particles is quantitatively addressed, and steady-state conditions are achieved after \(~0.01\) seconds. The probability of resuspension for a range of particle diameters is estimated and appears to favor particles that are less than \(10\) um in diameter and particles that are greater than \(100\) um in diameter. The mean particle diameter of resuspended material is shown to increase with height up to \(0.4\) m.

14C.01
Spray Current and Droplet Size in a Dual-capillary Electrospray System.
FAN MEI (1), Da-Ren Chen (2), (1) Washington University in St. Louis, (2) Washington University in St. Louis

Dual-capillary electrospray (ES) systems have been proposed to overcome the limits of single capillary electrospray systems. The limits include (1) it is desirable to have spray solutions in a suitable electrical conductivity range to operate the cone-jet mode in a single-capillary ES system. It is often difficult to identify a proper additive to control the electrical conductivity of spray solutions with the solvents of low dielectric constants; (2) the encapsulation of particles is limited for single-capillary ES systems. Applications of dual-capillary ES technique have been demonstrated among the literature. However, the fundamental understanding on the spray current and droplet size produced in dual-capillary ES systems is largely unclear. In this study experiments were carried out to systematically investigate the correlation of spray current and droplet size, with the operational parameters and solution properties in a dual-capillary ES system operated at the compound cone-jet mode. Two groups of solvents were selected in this study based on the dielectric constant of spray solvents. Different combinations of the electrical conductivities, flowrates for inner and outer liquids were tested. The results show that the spray characteristics of the first solvent group (i.e., for outer-liquid driving cases) can be represented by that of EG/TBP pair and that for the second group (i.e., for inner-liquid driving cases) by those for the ethanol/ mineral-oil and ethanol/ olive-oil pairs. The detail of experimental results will be presented in this talk.
14C.02

A new, miniature flow reactor has been developed which converts small (<1 micron) particles into simple molecular gases such as carbon monoxide, hydrogen, carbon dioxide and water for subsequent stable isotope analysis by an isotope ratio mass spectrometer (IRMS). Samples were introduced into the flow reactor by the ultra-violet (UV) laser ablation (LA) of organic samples including polymers and biological samples such as hair. UV laser ablation is a proven technique for the generation of small aerosols from refractory solids such as minerals but has not widely been used for organic samples. An Aerodyne aerosol mass spectrometer (AMS) was used to help understand the physical and chemical processes of aerosol production by LA of organic solids and to quantify the effectiveness of LA as a sample introduction technique for quantitative analysis. Laser parameters were optimized to produce particles in the range of 100 - 200 microns for optimal particle transport and the AMS was used to measure both the size and composition of the ablated particles to ensure that the aerosols delivered to the flow reactor are representative of the bulk organic sample. The quantitative measurements from the AMS were used to ensure that all ablated material was transported to the flow reactor from the ablation cell and the IRMS was used to demonstrate that isotopic biases were not introduced by the ablation process. Applications of this technology to the real-time analysis of atmospheric organic aerosols are also presented.

14C.05
Complex-valued variable and solutions for boundary layers with a discrete phase. RO'EE ORLAND (1), David Broday (2), David Katoshevski (1), (1) Ben Gurion University of the Negev, Israel, (2) Technion - Israel Institute of Technology, Israel

Aerosol concentrations in a boundary layer with downstream velocity variation reveal a bifurcational behavior. The solution of both the flow and concentration fields involves the use of similarity transformations. The similarity solution of the flow field has 3 bifurcating branches: for accelerating flow, for decelerating flow, and a previously unexplored solution for high-rate deceleration which involves complex values of the similarity solution. Although the latter solution involves complex values of the similarity variable, it still leads to an acceptable solution in the physical variables. The bifurcation in the downstream distribution of the aerosol concentration stems from the bifurcation characteristics of the flow, with a further third branch stemming from downstream behavior outside the boundary layer. These results have ramifications to aerosol dynamics (transport, deposition) in boundary layers developed in industrial facilities and sizing instrumentation, over airfoil, as well as in the human respiratory system and spray-based cooling systems.
3D.01
Effects of Electrostatic and Capillary Forces and Surface Deformation on Particle Detachment in Turbulent Flows.
XINYU ZHANG and Goodarz Ahmadi, Clarkson University

Rolling detachment of particles from surfaces in the presence of electrostatic and capillary forces based on the maximum adhesion resistance was studied. The effective thermodynamic work of adhesion including the effects of electrostatic and capillary forces was used in the analysis. The JKR and DMT models for elastic interface deformations and the Maugis-Pollock model for the plastic deformation were extended to include the effect of electrostatic and capillary forces. Under turbulent flow conditions, the criteria for incipient rolling detachments were evaluated. The turbulence burst model was used to evaluate the airflow velocity near the substrate. The critical shear velocities for removal of particles of different sizes were evaluated and the results were compared with those without electrostatic and capillary forces. The model predictions were compared with the available experimental data and good agreement was observed.

3D.02
Morphology Control of Particles Produced by a Dual-capillary Electrospraying System.
FAN MEI (1), Da-Ren Chen (2), (1) Washington University in St. Louis, (2) Washington University in St. Louis

The generation of particles in different shapes using a dual-capillary electrospray (ES) system was investigated in this study. It has been demonstrated that the dual-capillary ES technique can produce particles in various shapes, i.e., spherical and fibrous ones. The control of the microstructure of produced capsules is also feasible with the ES technique. In this experiment we focused our study on the effect of the outer liquid to the change of particle morphology.

We chose polymer solutions as the inner liquid and 95 wt.% ethanol (or acetone) as outer liquids. The polymer solutions used in this study were prepared by dissolving PVA (polyvinyl acetate) polymers of three different molecular weights in two solvents, i.e., 95 wt % ethanol and acetone (HPLC grade). The morphology of produced particles was characterized by SEM/TEM. The result shows that the morphology of particles can be varied from the spherical shape to fibrous one by simply increasing the concentration of the polymer solution while keeping the outer-liquid flowrate the same. Our experiment also demonstrated that the advantage of using dual-capillary ES systems over single-capillary systems is that the morphology transition can occur at a much lower inner flowrate with an inner capillary of smaller ID. It is because the sheathing of polymer solution with outer liquid prevents the inner capillary from the clogging or polymer accumulation at the capillary tips, resulting in the cease of the cone-jet mode operation. Meanwhile, with the increase of the outer-liquid flowrate while keeping the inner-liquid flowrate and polymer concentration the same, it is feasible to convert the particle morphology from the fibrous shape back to the spherical one. We further found that the morphology transition range for a given polymer can be varied by changing the properties and flowrate of outer liquids.
3D.03
Electrospray Deposition Characteristics of Titanium Dioxide Nanoparticles Suspensions for Thin Film Fabrication For Use in Solar Cells.

LUIS MODESTO, Elijah Thimsen, Pratim Biswas, Aerosol and Air Quality Research Laboratory, Washington University in St. Louis

Suspensions containing varying concentrations of nanoparticles were electrospayed to obtain agglomerates of different characteristics, which were then deposited to produce films with varying morphology, thickness, total surface area, and porosity. The role of the effective electrical conductivity and mass fraction of TiO₂ nanoparticles in suspension on the size of agglomerates produced by electrospray was investigated. Precise control of agglomerates of TiO₂ nanoparticles was achieved by electrospaying suspensions with electrical conductivity on the order of $10^{-3}$ S/m and varying particles mass fraction in the suspension. The size of the agglomerates ranged from around 29 nm (primary particles, mass fraction = 0.0002) to 300 nm (mass fraction = 0.02). Mobility based real time particle size measurements showed monodisperse size distribution for all the suspensions except for the one with mass fraction of particles of 0.001 (trimodal distribution). Addition of nanoparticles to the solution resulted in a significant change in the overall electrical conductivity in the range of $10^{-4}$ to $10^{-3}$ S/m, increasing with increasing mass fraction of particles. In the range of $10^{-3}$ to $10^{-2}$ S/m, however, addition of particles did not have any significant effect on the effective electrical conductivity. The resultant TiO₂ films were then used to prepare solar cells and the performance characteristics established as a function of the film parameters.


1D.02

Hee Dong Jang (1), Hankwon Chang (1), Kuk Cho (1), Sun-Kyung Kim (2), Kikuo Okuyama (3), (1) Nano-Materials Group, Korea Institute of Geoscience and Mineral Resources, Daejeon, Korea (2) Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima, Japan

Porous nanostructured materials have attracted great attention from many researchers due to their potential applications in catalysts, separations, coatings, chromatography, low dielectric constant fillers, pigments, microelectronics, and electro-optics. In this study, we prepared porous nanostructured TiO₂-SiO₂ particles for photocatalytic application via aerosol spray method from a solution which contained TiO₂ and SiO₂ nanoparticles and polystyrene latex (PSL) particles. We investigated the effects of experimental variables such as the mixing ratio of PSL to the nanoparticles, and that of TiO₂ to SiO₂ nanoparticles on the properties of as-prepared particles. The product particles were a spherical shape having a well-ordered meso/macro porous nanostructure after PSL in the nanostructured particles was effectively removed. As the mixing ratio of PSL to the nanoparticles increased, the larger pores were shown in the particles and the specific surface area decreased. As the mixing ratio of TiO₂/SiO₂ increased, higher intensity of UV-absorption spectrum was observed. The higher decomposition of methyleneblue was observed at the higher porosity of particles and mixing ratio of TiO₂/SiO₂.
1D.03
SiO₂ coating of silver nanoparticles by photoinduced chemical vapor deposition. ADAM BOIES, Jeffrey Roberts, Steven Girshick, University of Minnesota, Twin Cities

Gas-phase silver nanoparticles were coated with silicon dioxide (SiO₂) by photoinduced chemical vapor deposition. Silver nanoparticles, produced by inert gas condensation, and a SiO₂ precursor, tetraethylorthosilicate (TEOS), were exposed to vacuum ultraviolet light (VUV) in a chamber at atmospheric pressure and room temperature. The high energy VUV photons dissociated the TEOS molecules, thereby promoting the formation of SiO₂ coatings on particle surfaces. Coating thicknesses ranging from subnanometer to 11 nm were measured by tandem differential mobility analysis for variations in precursor flow rate, particle residence time, VUV intensity, and chamber geometry. Coated particles were imaged by transmission electron microscopy and coatings were shown to be SiO₂ by energy dispersive X-ray spectrometry and Fourier transform infrared spectroscopy. Studies were conducted to clarify the relative contributions of gas-phase versus surface processes in growth of the coatings.

3D.04
Preparation of Unsintered BaFe₁₂O₁₉ fine particles using an Alcohol Assisted Spray Pyrolysis Method. Hye Moon Lee, Ji-Hun Yu, Yong-Jin Kim, Korea Institute of Materials Science

BaFe₁₂O₁₉ particles are considered attractive candidate materials for the preparation of magnetic recording media due to their high uniaxial magnetic anisotropy and Curie temperature, large saturation magnetization and coercivity, and excellent chemical stability and corrosion resistivity. Various BaFe₁₂O₁₉ preparation methods, such as chemical coprecipitation, sol-gel, glass crystallization, hydrothermal, citrate precursor, and aerosol methods have been developed and are widely used for the synthesis of particles with good magnetic properties. However, since these methods consist of 2 steps, i.e., synthesis of amorphous magnetic particles from a precursor and a post-annealing process for enhancing crystallization into hexagonal phase, some inconveniences are inevitable. The post-annealing process is performed at temperature higher than 900 degrees C and for more than 5h, leading to severe sintering problems among the magnetic particles. Moreover, the prepared particles are very large and irregular in size and morphology, respectively.

The aim of this study is to prepare unsintered spherical BaFe₁₂O₁₉ nanoparticles via a spray-pyrolysis method without any post-annealing processes. For this purpose, it is necessary to decrease the sprayed droplet size, which is proportional to the final particle size, and to supply sufficient energy for enhancing the crystallization of barium ferrite into hexagonal phase. Since Ethyl alcohol (EtOH) has not only very small surface tension value, but also very high caloric value, its addition to the precursor solution for preparing BaFe₁₂O₁₉ particles is expected to be very useful in the preparation of unsintered BaFe₁₂O₁₉ nanoparticles without any post-annealing processes. Thus, we applied EtOH to the precursor solution for the preparation of unsintered spherical BaFe₁₂O₁₉ nanoparticles with good crystallinity of hexagonal phase. The effects of EtOH on BaFe₁₂O₁₉ particle size and crystallinity were experimentally investigated in detail, and the morphology and magnetic properties of the particles, such as magnetic intrinsic coercivity, remanent magnetization, and saturation magnetization, were also analyzed.
1D.01
Structural Evolution of Hydrogen-Capped Silicon Nanoparticles: Coalescence, Sintering, and Morphological Behavior as a Function of Temperature.

JASON HOLM, Jeffrey Roberts, University of Minnesota

Hydrogen-capped silicon nanoparticles are synthesized via gas-to-particle conversion in a non-thermal RF plasma. Particles are thermally processed up to 900 degrees C using several techniques. In addition to characterizing particle size changes, structural evolution of both discrete particles and agglomerates is characterized as a function of particle size and temperature using TEM, XRD, TGA/DSC, and differential mobility analysis. In the first heating technique, particles flow directly from the plasma through a tube furnace. Samples are collected at various processing temperatures, and particle size and structure are characterized by TEM and XRD. In the second technique, powder samples are collected downstream from the plasma, and are characterized by TGA/DSC and XRD. Powder samples are heated in situ to ~900 degrees C in inert environments. In XRD the FWHM of the (111) peak is monitored as a function of temperature, and in the DSC/TGA the calorimetric behavior is examined as a function of temperature. In the third technique, particles are extracted immediately downstream from the RF plasma and then size selected based on their electrical mobility. Discrete primary particles ranging in size from ~5-12 nm and agglomerates comprised of similarly sized primary particles are collected on grids for in situ heating in a TEM where structural morphology, coalescence, and sintering behavior are monitored as a function of temperature.

Particles undergo several transitions with heating. At ~350 degrees C particles exhibit hydrogen desorption, and at ~500 degrees C crystallinity loss is apparent. Smaller particles become amorphous while larger particles exhibit core-shell structures comprised of an amorphous silicon outer layer and a crystalline silicon core. We conjecture that surface hydrogen on hydrogen-capped particles plays a strong role in the crystalline nanoparticle structural stability. As samples are heated above ~700 degrees C, coalescence and sintering behavior are observed resulting in polycrystalline nanoparticles structures. Transition to single crystal structure is observed at higher temperatures.

11E.01
Coagulation in a Nanodusty Plasma.

Lavanya Ravi, STEVEN L. GIRSHICK, University of Minnesota

Nanodusty plasmas - plasmas containing nanoparticles - display a number of phenomena not observed in neutral-gas aerosols. As particles nucleate and grow, they become increasingly charged, and this in turn has a profound effect on the plasma. We previously developed a numerical model for the spatiotemporal evolution of a nanodusty plasma, that self-consistently couples the equations describing the plasma dynamics to the equations describing the aerosol behavior, for a parallel-plate radio frequency discharge [1]. Here we focus on the nature of coagulation in such a plasma. Experimental evidence from several groups indicates that coagulation plays an important role in the rapid growth of particles from a few nm to several tens of nm in diameter. However, once they grow beyond a few nm almost all particles become negatively charged, suppressing coagulation. Moreover, while very small neutral particles can exist in high concentration, the time scales for neutral-neutral coagulation are much longer than the time scale for diffusional loss to the walls in the low-pressure (100 mTorr) plasma. Simulations run with our numerical model indicate that coagulation is indeed important, but that it exists almost entirely as coagulation between very small neutral particles, continuously generated by fresh nucleation, and much larger charged particles, where coagulation is enhanced by the induced dipole (image potential) in the neutral particle. This further explains experimental observations that particle growth rates are much higher than can be explained by ordinary Brownian coagulation.

3D.05
Synthesis of TiO2 nanoparticles and Films in Stagnation-point Swirl Flames. Junjing. Wang, Shuqing Li*, Bin Ma, Qiang Song, Qiang Yao, Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing, 100084, CHINA

In this paper, a new method was proposed to fabricate nanocrystalline titania (TiO2) particles and films. Firstly, the low swirl burner (LSB) with a swirl number of 0.2-0.3 was developed for the synthesis of titania nanoparticles. The swirler section is comprised of an annular vane section along the inside wall of the tubular burner (i.d. 12mm) and a central bypass into a smaller vertical tube with a perforated screen. The LSB can reduce the lean flammability limit by 16-33% compared to the laminar flame without the swirler. TEM results indicated that, the sizes of TiO2 particles from low-swirl flame are about 20 nm and less aggregated, while those from laminar flame without the swirler are 50nm and more aggregated. Secondly, a temperature-controlled substrate was further placed above the LSB, which can not only form stagnation-point flow in front of substrate, but also serve as the surface for film deposition. The growth rate of particle film in this kind of stagnation-point swirl (SPS) flame were discussed.

2D.01
Micropattern Deposition of Semiconductor Nanocrystals by Aerodynamic Focusing. LEJUN QI, Peter H. McMurry, David J. Norris, Steven L. Girshick , University of Minnesota

The deposition of patterned assemblies of semiconductor nanocrystals (NCs) with controlled feature size and thickness is an essential step in the manufacture of optoelectronic devices based on these materials. For colloidal semiconductor NCs, patterning methods reported so far include dry casting, spin coating, inkjet printing, and electrophoretic deposition. We here report an alternative approach, which utilizes aerodynamic lenses to produce beams of focused NCs, and then creates micropatterns by rastering a substrate across the beam. Compared with other techniques, aerodynamically focused nanoparticle beam deposition utilizes easily manufactured thin metal plates with mm orifices, and is able to deposit patterns rapidly. It can also be easily incorporated into high vacuum systems used in microelectronics fabrication and can take advantage of the pressure drop from the ambient to the chamber to drive the NC pattern deposition.

To demonstrate this approach we used an aerodynamic lens assembly to deposit micropatterns of colloidal semiconductor nanocrystals. CdSe and CdSe/ZnS core/shell NCs, with core diameters of 4-5 nm, were dispersed in hexane and then nebulized to generate droplets consisting of multiple NC clusters, where each droplet was a few tens of nm in diameter. These droplets were then focused aerodynamically by a lens system. Microscale towers, lines and patterns were deposited on thin sapphire plates and silicon wafers. Upon exposure to near-UV illumination, these deposits exhibited robust fluorescence in the visual, with the color depending on the diameter on the individual NC cores. The heights and widths of the deposits were adjustable by varying the experimental parameters. The deposits were shown to consist of closely packed nanocrystals embedded in the organic matrices from the aerosolized solution. A red shift of the photoluminescence peaks from the NC dispersion to the glassy solid deposits was also observed.
3D.06
Aerosol-Gel Synthesis and Characterization of Pt-SiO₂ Catalysts for Hydrocarbon Selective Catalytic Reduction of Gaseous Nitrogen Oxides, JAE-WOOK JUNG, Donggeun Lee, Pusan National University, South Korea

Recently nitrogen oxides (NOx) which have been considered one of the most serious and environmentally-regulated species have been of increasing interest over the past decades. In this work, we performed one-step synthesis of platinum-silica nano-composite catalyst and tested the catalytic particles for hydrocarbon selective catalytic reduction (HC-SCR). The Platinum-silica catalysts were prepared by aerosol-gel method using tetraethylorthosilicate (TEOS) and Platinum acetylacetonate (Pt(acac)₂). This aerosol-based method has several advantages over liquid phase methods, e.g., easier scale up to large scale production and relatively easy control of particle evolution. Characteristics of the catalytic particles are attempted to control by changing reaction temperature, reaction time and Pt-to-Si molar ratio of the mixed precursors. A series of such experiments revealed that size, morphology and dispersion of Pt dots on SiO₂ were controllable. At the condition of 600°C of reaction temperature, 4 hour pre-sol-gel reaction prior to atomization, 1 : 0.02 of molar ratio between TEOS and Pt(acac)₂, we obtained best-dispersed Pt dots of about 3nm on silica particles. TEM (Transmission Electron Microscope) and EDS (Energy Dispersive Spectroscopy) are used for the characterization of their size, morphology and composition. XPS (X-Ray photoelectron spectroscopy) confirms that platinum exists primarily in its metallic state on the functionalized silica surfaces. The actual loading of Pt-SiO₂ is measured using inductively coupled plasma (ICP). In addition, the samples are also characterized by UV (Ultraviolet)-Visible spectroscopy, FT-IR (Fourier transformation infrared spectroscopy) and XRD (X-Ray Diffraction).

3D.07
Pt Coating on Flame-Generated Carbon Particles and Their Application for a Catalytic Electrode of Proton Exchange Membrane Fuel Cell (PEMFC), IN DAE CHOI, Donggeun Lee, Pusan National University, South Korea

Carbon black, activated carbon and carbon nanotube have been used as supporting materials for precious metal catalysts used in fuel cell electrodes. One-step flame synthesis method is used to coat 2-5nm Pt dots on flame-generated carbon particles. By adjusting flame temperature, gas flow rates and resident time of particles in flame, we can obtain Pt/C nano catalyst-support composite particles. Additional injection of hydrogen gas facilitates pyrolysis of Pt precursor in flame. The size of as-incepted Pt dots increases along the flame due to longer resident time and sintering in high temperature flame. Surface coverage and dispersion of the Pt dots is varied at different sampling heights and confirmed by Transmission electron microscopy (TEM), Energy-dispersive spectra (EDS) and X-ray diffraction (XRD). Crystalinity and surface bonding groups of carbon are investigated through X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The electro-catalytic property of Pt/C composites for the application to catalytic electrode PEMFC are also investigated by Cyclic voltammetry (CV).
Insights into the formation and the structure of nanoparticle aggregates are essential in many fields of science and engineering. Especially, controllability of aggregate structure with adjusting the experimental conditions is very important in fabricating nanoparticle catalysts which can be applied to energy systems like nanofluids, fuel cell and solar cell. In this work, 3D off lattice Monte Carlo simulation was implemented to irreversible cluster-cluster aggregations in the diluted system for different sticking probabilities which determine aggregation kinetics and structure. Firstly, DLCA regime (Pij=1) and RLCA regime (Pij=0.03) were simulated to validate the code, and the fractal dimensions for two regimes were obtained 1.8 and 2.11 respectively, which are in good agreement to the previous researches. The kinetics and structure of the aggregates were studied for different sticking probabilities. CMD (cluster mass distribution) and weight averaged cluster mass transitions were investigated to study the kinetics, and fractal dimensions, pair correlation function, g(r), and morphology of the final clusters for the structure.

Finally, the simulation was applied to the diluted aqueous systems of CuO(I) and Silica(SiO2), respectively. Based on DLVO theory, interactions were obtained with measured zeta potential to different pH conditions. Sticking probabilities for the simulation were obtained with the maximum interaction energy barriers. The kinetics and structure investigations were also conducted to the different pH conditions and interaction ranges. It was found that DLCA regime dominated the aggregation kinetics near p.z.c (point of zero charge) and an abrupt change from DLCA to RLCA regime occurs at specific pHs in both systems of CuO(I) and SiO2. Physical parameters related to interactions were interpreted to reveal this phenomenon.

A hygroscopicity or volatility tandem differential mobility analyzer (HTDMA or VTDMA) technique was used to determine hygroscopicity and volatility of nano/ultrafine particles (Rader and McMurry, 1986) in real time at urban Gwangju and coastal Yeosu sites in Korea. The burst of nanoparticles was continuously monitored by a scanning mobility particle sizer (SMPS) and the TDMA system was triggered when nanoparticle or ultrafine particle events occurred (Sakurai et al., 2005; Park et al., 2008). The TDMA system uses a combination of two nano DMAs and two regular DMAs to measure particle size change in a wide dynamic particle size range under increased relative humidity (RH) or temperature. Hygroscopicity and volatility database for various nanoparticles (ammonium sulfate, ammonium nitrate, sulfuric acid, sodium chloride, black carbon, and dicarboxylic acid) that can be possible candidates for constituents of atmospheric nanoparticles was constructed by measuring their hygroscopic growth factors (GF) at 85% RH and shrinkage factors (SF) at 100℃; at a heater temperature of 100 oC to be compared with those of atmospheric nanoparticles. Data for atmospheric aerosol particles showed that organic compounds with low GFs are dominant constituents for the newly formed and growing particles at Gwangju site, while at costal Yeosu site, sulfate and salts with high GFs are dominant, although nanoparticles formed at both sites are internally mixed. Nano/ultrafine particles observed at combustion events (traffic and residential heating events) showed little hygroscopic growth. To examine the matrix effect of mixing components on hygroscopicity and volatility, we are carrying out GF and SF measurements of laboratory-generated particles that are internally mixed.
3D.08
Generation of Zinc and Zinc Oxide Nanoparticles with an Aerosol Flow Reactor. HungMin Chein, Sheng-Chang Tsai, Yu-Du Hsu, Energy and Environment Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu, Taiwan

We have developed an aerosol flow reactor including Zn/ZnO furnace-tube reactor and a dilution chamber. The Zn powder was evaporated from a quartz boat (open diameter = 5, 8, 10 mm) inside the tube. The Zn vapour was mixed with reaction air to form ZnO nanoparticles and diluted in the chamber subsequently. The system was able to generate size-selectable aerosols of count median diameter (CMD) with stable number concentration (N) measured with scanning mobility particle sizer (SMPS). The CMDs of ZnO aerosols changes with operation time as quartz boat diameter increases. After the evaporation, reaction and coagulation process, the CMD can be maintained at a stable value for four hours. The CMD value decreases from around 23 nm to 10 nm as the boat open diameter increases from 5 mm to 8 mm. Submicron aerosols of CMD larger than 200 nm could also be generated using the same system.

3D.09
Film Formation Using Atmospheric Aerosol Spray Method. Hoomi Choi(1), Kwangsu Kim(1), Heesung Choi(2), Hyunho Shin(2), Miyang Kim(2), Taesung Kim(1), (1) Sungkyunkwan University, Suwon (2) Samsung Electro Mechanics Corporation, Suwon

Coating is one of the material processing technologies that can enable recent downsizing and high performance trend of digital products. Coatings are often applied via a spray process, in which powder feedstock is accelerated by a high velocity gas. We developed a spray process, in which the powder feedstock is neither melted nor softened prior to impingement onto the substrate. This process operates under atmospheric pressure and temperature so we named it as atmospheric aerosol spray method. The atmospheric aerosol spray method is a film deposition technology that utilizes an impact solidification phenomenon of particles in an operating gas flow. This process enables a highly functional film to be formed onto any type of substrate using metal or non metal powders. The phase of the powdered material can be kept in the coating. Film formation depends on several parameters including the distance between nozzle exit and substrate, exit gas velocity, spray time and particle diameter. In this paper, we studied on film properties such as thickness and area as a function of these parameters. We performed experiments to understand the different results by controlling these factors and observed analysis results. Moreover the relative theory about particle motion during film formation time was studied and compared with experimental results. This process is expected to be applied to integration and embedment of various passive components like resistor, capacitor, and, inductor.
Charging Efficiency of a Nanoparticle Charger. Chuen-Jinn Tsai, Guan-Yu Lin, Huei-Lin Chen, Sheng-Chieh Chen, National Chiao Tung University, Hsinchu, Taiwan

In a unipolar charger, charged nanoparticles can deposit in the charger due to electrostatic and diffusional mechanism, resulting in the decrease of the extrinsic charging efficiency. In this study, a unipolar charger was developed to enhance the extrinsic charging efficiency of nanoparticles by using sheath air near the wall of the charger to reduce the electrostatic loss of nanoparticles. The charger has a cylinder of 50 mm in diameter in which four gold corona wires of 25 µm in diameter and 15 mm in length were used to generate unipolar ions. Monodisperse sodium chloride (NaCl) particles of different diameters were generated to test the charging efficiency at an aerosol flow rate of 10 L/min. The intrinsic and extrinsic charging efficiencies and the diffusion and electrostatic loss of NaCl particles at different corona voltages and sheath flow rates were examined. When the operating voltage is increased from +4.0 KV to +10 KV, the ion number concentration is increased from 2.96 x 10^8 to 3.89 x 10^9. The intrinsic charging efficiency of 20 nm particles is increased from 58 % to 95 % with increasing supplied voltage from +5 KV to +10 KV when the sheath air flow rate is 20 L/min. The extrinsic charging efficiency is seen to increase with the sheath flow rate for 20 nm particles, with the highest extrinsic charging efficiency of 62 % occurs at the discharging voltage of +8.0 KV, aerosol flow rate of 10 L/min and sheath flow rate of 20 L/min. The electrostatic loss increases with the applied voltage and is reduced with an increasing sheath flow rate. Compared to the case without using sheath air flow, as much as 30 % of electrostatic loss is reduced by using sheath air flow rate of 20 L/min. Future work is to increase the sheath air velocity near the wall to reduce the electrostatic loss further. Nanoparticles of different diameters will be tested.

Controlled synthesis of ZnO nanoparticles by gas phase reaction. HISASHI YAMAMOTO(1), T. Charinpanitkul(2), P. Nartpochananon(2), T. Seto(1), Y. Otani(1), (1)Kanazawa University, kanazawa JAPAN (2)Chulalongkorn University, Bangkok Thai

Zinc oxide (ZnO) is one of the important industrial materials used as a transparent pigment for absorbing ultraviolet light. ZnO particles synthesized by the oxidation of zinc vapor are known to have unique shape like a tetra pod. The shape of ZnO was altered by the mixing condition of zinc vapor and oxygen, reaction temperature, and vapor concentration, however the growth mechanism of ZnO is not fully understood. In order to investigate growth mechanism of ZnO, we carried out experiments under well-controlled temperature and mixing conditions. The reactor was composed of two heating zone tubular furnaces which can control reaction temperature and vaporization temperature independently. An orifice was employed to enhance the mixing between zinc vapor and oxygen. From the results of the SEM observation, two types (spherical and needle-like) of ZnO nanoparticles were generated depending on the temperature and mixing condition. The crystalline structure and the particle size distribution have been investigated by XRD and ELPI, respectively. The flow, temperature and concentration profile in the reactor was analyzed by solving the energy and momentum equation using the computational fluid dynamics code (CFD, FLUENT ver. 6.3). As a result, it was shown that the needle-like zinc oxide particles were selectively formed when zinc vapor is uniformly mixed with oxygen using an orifice. Possible formation mechanisms of needle-like ZnO particles were proposed according to the experimental results.
11E.02
Nanoparticle deposition on inverse surfaces under low pressure. CHRISTOF ASBACH (1), Burkhard Stahlmecke (1), Heinz Fissan (1), Thomas A. J. Kuhlbusch (1), Jing Wang (2), David Y. H. Pui (2), (1) Institute of Energy and Environmental Technology (IUTA), Duisburg, Germany (2) University of Minnesota, Minneapolis

The deposition of even nanoparticles is a major concern in clean manufacturing processes. Extreme ultraviolet lithography (EUVL) is a prominent candidate for the production of the next generation of computer chips. EUVL photomasks need to be kept nanoparticle free to assure accurate printing of the structures. EUVL systems operate at a low pressure level of 10 Pa or below which makes particles particularly prone to inertial and diffusional deposition.

We have developed a complete model that estimates the contamination probability for particles with or without initial velocity under the influence of gravity, drag force, thermophoresis and diffusion. The model is designed to be solvable without major computational resources. The inertial motion is covered purely analytically, whereas the diffusional motion follows an analytical-statistical approach. The model distinguishes cases where the deterministic particle stopping distance is larger and smaller than the initial distance between particle and critical surface. The calculations show that, depending on their initial distance, particles <30 nm may be deposited even under the protective influence of thermophoresis due to their high diffusivity. With a temperature gradient of 10 K/cm, the deposition of particles between 30 and 200 nm is very unlikely, even at relatively high initial velocity. The deposition probability for particles larger than 200 nm increases drastically with increasing initial velocity, due to inertia. For instance with a temperature gradient of 10 K/cm and an initial distance of 1 mm, the contamination probability is approximately 9% for 10 nm, 1.4% for 20 nm and near 0% for 30-200 nm, more or less independent of initial velocity. While for an initial velocity of 10 cm/s it remains at 0%, it increases to 28% for 250 nm and 100% for 300 nm for 10 m/s.

This research is supported by Deutsche Forschungsgemeinschaft (DFG) under grant number AS291/1-1.

9K.03
Agglomerate Stability in Orifices. Burkhard Stahlmecke, Sandra Wagener, CHRISTOF ASBACH, Heinz Kaminski, Heinz Fissan, Thomas A. J. Kuhlbusch , Institute of Energy and Environmental Technology (IUTA), Division Air Quality and Sustainable Nanotechnology, Duisburg, Germany

Depending on their mobility agglomerates described by an appropriate equivalent diameter are deposited in different compartments within the human respiratory tract. The size may also determine the mobility after deposition in the lung. Therefore, in industrial hygiene the (aerodynamic) size of agglomerates is an important measure. During handling of agglomerated nanopowders, agglomerates may break up into smaller aggregates / primary particles when the effect of applied shear forces exceeds the binding energy. The case studied here to quantify the binding energy uses intermediate shear forces which are higher than those occurring in the lung.

To study the stability of agglomerates we performed measurements of aerosolized nanopowders passing a (critical) orifice. The aerosol is prepared in a beaker under different pressure conditions ranging from 20 kPa up to 140 kPa above ambient pressure. After generation the aerosol passes an orifice and the resulting particle size distribution is measured by a scanning mobility particle sizer. Due to shear forces within the orifice agglomerates may break up when passing the orifice. The obtained size distribution is compared to that measured directly after generation, i.e. without passing the orifice. This allows the calculation of the relative increase or decrease of particle number for a given size channel.

We present results for agglomerates from different well characterized nanopowders. The number of smaller particles (particles below 300 nm) increases with increasing pressure difference, whereas the number of larger particles (particles above 300 nm) is decreased due to deagglomeration. Additionally, scanning electron microscopy was applied to study the morphology of the agglomerates with and without passing the orifice.

This work is supported by the German Federal Ministry of Education and Research (BMBF) as part of the NanoCare project.
3D.11
Particles generation in laser ablation plasma. Shun Kuroda,
Shinishi Kaihara, Motoaki Adachi, Osaka Prefecture University

Pulsed laser deposition (PLD) method is one of important fabrication processes to form thin films or synthesize nanoparticles. However, particle generation mechanisms in laser ablation plasma have not been clarified well. In this study, we develop the pulsed laser deposition system using YAG laser to investigate experimentally effects of operation conditions, that is, a gas pressure and a kind of gas in the deposition chamber on a particle generation. The particles generated at various pressures of He, Ar, and O2 gases are collected on the substrate and observed by SEM. We try also theoretical investigation. The simple model based on Brownian coagulation theory and diffusion charging theory is proposed and the population balance equations for the model are solved numerically. Following assumptions are used in the model; (1) Primary species in the plasma are electron, positive ion (A+), source atom (A), (2) Particle formation processes are collisions between neutral atoms, between neutral clusters, between neutral clusters and neutral atoms, between charged atoms, between charged clusters, between charged clusters and charged atoms, between charged clusters and neutral clusters etc., and (3) Ion-electron-particle interaction are collisions between positive ions and electrons, between positive ions and neutral atoms, between positive ions and neutral clusters, between electrons and neutral atoms, and between electrons and neutral clusters.

11E.03
Langevin Dynamics for a Nanorod in an Electric Field.
CHARLES HAGWOOD (1), George Mulholland (2), (1) National Institute of Standards and Technology (2) University of Maryland and NIST

Recently the length of carbon nanotubes has been determined from electrical mobility measurements. In one approach, the data have been analyzed assuming a Boltzmann form for the orientation probability for the charged nanorod. It is of interest to study the dynamics of this charged nanorod in an electric field. Our approach is to solve the Langevin equation. In this case, we characterize both the rotational and translational motion, because the friction coefficient is dependent on the orientation of the rod relative to the electric field. As a first step in this analysis, we consider the model problem of a nanorod constrained to diffuse in only the x and y direction and rotate only about the z axis. The force and torque acting on the nanorod are computed assuming a singly charged nanorod. The friction coefficient is taken to be the free molecular value for a rod and the rotational resistance is also based on free molecular dynamics. We have used the Ermak - Buckholz methodology for the numerical integration of Langevin equations (J. Comp. Physics 35: 169-182, 1980). The time for the nanorod to rotate on the order of Pi/90 sets the time increment for the integration. The basic quantity of interest is the time evolution of the probability distribution of the nanorod as a function x, y, and angle. We are interested in the small time behavior where the Brownian motion has a significant effect as well as the long time behavior where the distribution is expected to approach a Boltzmann distribution. We study the effect of the nanorod length, diameter, and the field strength on the time dependent electrical mobility. We consider an absorbing boundary condition at one electrode with a gap to compute the time dependent flux through the gap as a prototype transfer function.
Modeling Low Energy VUV-Induced Photoelectron Emission from NaCl Nanoparticles. Matthew J. Berg(1), Kevin R. Wilson(2), Christopher M. Sorensen(1), and Amit Chakrabarti(1), (1) Kansas State University, Department of Physics, Manhattan, KS (2) Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

Photoelectron emission can be used to study the electronic structure of nanoparticles. For many materials, this emission can be initiated by Vacuum Ultraviolet (VUV) light of wavelength in the 100-nanometer range with corresponding energy range around 10 eV. The distribution of VUV light within the nanoparticles determines the internal location and rate of photoelectron emission. The subsequent interaction of the ionized electrons with the nanoparticle material modifies the electrons trajectory and energy. In this work, the angular distribution of the photoelectron emission from NaCl nanoparticles is studied. The discrete dipole approximation is used to find the internal distribution of VUV light in the nanoparticle. A simple Monte Carlo-based random walk model of the low energy electron transport through the NaCl material is developed to simulate the angular photoelectron emission. The simulation results are compared to measurements of the angular emission conducted with the Advanced Light Source at the Lawrence Berkeley National Laboratory [1].


Mass-Mobility Relationship for Silica Agglomerates: Implications for Transport and Morphological Properties. Jacob H. Scheckman (1), Peter H. McMurry (1), Sotiris E. Pratsinis (2), (1) University of Minnesota, (2) ETH Zurich

Transport and physical/chemical properties of nanoparticle agglomerates depend on primary particle size, fractal dimension, and the number of primary particles in the agglomerate. The objective of this research is to measure such properties. We are especially interested in the effects of agglomerate structure on lung deposition, and in future work will measure deposition efficiencies in realistic models of the human respiratory system. We are determining agglomerate properties by tandem measurements of mobility (DMA), mass (APM) and morphology (TEM). The first step of this research involved developing methods to produce agglomerates with controlled and known properties.

Agglomerates of silica were generated by oxidizing hexamethyldisiloxane in a methane/oxygen diffusion flame burner (1). The measured relationship between mass and mobility was used to determine the fractal dimension. The effects of oxygen flow rate and precursor delivery rate on the mass-mobility relationship were characterized. Electron microscopy was used to determine primary particle size and give qualitative information on particle morphology.

The generated particles were chain agglomerates with clearly defined primary particles. Primary size ranged from 22 to 65nm. Fractal dimensions ranged from 1.76 to 2.34. Increasing the oxygen flow rate was shown to decrease the primary particle size and the fractal dimension. Increasing the precursor delivery rate was shown to increase the primary particle size mass of the product particles without affecting the fractal dimension. The effects of oxygen flow rate and precursor delivery rate on primary particle size were in agreement with literature (1,2). The mass increase was equal to the increase in the primary particle diameter cubed, implying that the primary particle size increased without a change in the number of primary particles.

Bionano Antenna-Reaction Center (ARC) Hybrid Solar Cells Facilitated by Aerosol Processing. Elijah Thimsen(1), Aaron Collins(2), Luis Modesto-Lopez(1), Robert Blankenship (2) and Pratim Biswas(1), (1) Aerosol and Air Quality Research Laboratory, Department of Energy, Environmental and Chemical Engineering, Washington University, Saint Louis, MO 63130 (2) Blankenship Laboratory, Department of Chemistry and Department of Biology, Washington University, Saint Louis, MO 63130

Nature is fueled by solar energy. To enhance light capture, extend photoresponse to longer wavelengths and improve electron transport in low cost oxide solar cells, we seek to mimic nature by designing solar cells based on the photosynthetic apparatus of green bacteria. Chlorosomes, the organism's light-harvesting antenna complex, are one of the key elements of its photosynthetic system. The chlorosomes used in this study have an ellipsoidal shape, approximately 170 nm x 50 nm x 24 nm. Chlorosomes were extracted from a culture of Chlorofexus aurantiacus and then integrated into nanostructured inorganic-polymer Gratzel type devices, to form antenna-reaction center (ARC) solar cells. Aerosol processing is used in the fabrication of these cells. Specifically, n-type TiO2 semiconducting layers with a nanocolumnar morphology were synthesized by a flame aerosol reactor. The nanocolumns have superior electronic properties relative to conventional nanoparticulate layers. The TiO2 layer was functionalized using a Ru-based dye which acts as a reaction center by injecting electrons into the semiconductor. Chlorosomes were next deposited onto the functionalized TiO2 by spin-coating. To finish the device, a continuous p-type polymer (P3OT) layer was deposited by electrospray deposition such that no solvent contacted the device. This is a key processing step because the chlorosomes become denatured if they come into contact with the organic solvents typically used to deposit conducting polymers. The performance of the ARC cells under simulated solar illumination will be discussed along with the implications for industrial implementation.

Density Measurement of Size Selected Multiwalled Carbon Nanotubes. Soo H. Kim (1), GEORGE W. MULHOLLAND (2), Michael R. Zachariah (2), (1) Pusan National University, Busan, (2) University of Maryland, College Park

We describe the combination of tandem differential mobility analyzer (DMA) and aerosol particle mass analyzer (APM) technique to measure absolute material density of gas-phase grown carbon nanotubes (CNTs). This methodology employs two steps of electrical mobility classifications. In the first mobility classification step combined with in-situ sintering process, a stream of monodisperse catalytic particles was produced by pulsed laser ablation (PLA). With the assistance of thermal CVD process under atmospheric pressure, these mobility-classified particles were subsequently seeded to grow the CNTs with diameter close to that of catalytic particles. Then, the second electrical mobility classification step allows us to classify the diameter-controlled CNTs in length. These diameter-and length-classified CNTs were finally introduced into the aerosol particle mass analyzer (APM) to measure their mass distribution. The volume of the CNTs was determined from TEM measurements of the diameter together with the electrical mobility. We found that the condensed phase density of CNTs was nearly constant, standard deviation of 4 %, with an average value of 1.70g/cm³ for two different groups of CNTs with diameters of ~15 and ~22 nm, respectively. In each group, the density was measured for mobility diameters of 50 nm, 100 nm, and 150 nm. The corresponding range in the CNT length is from about 100 nm to 1500 nm. The combined uncertainty of the measurement is +/- 9 % with the projected area having the largest uncertainty. The measured density is slightly less than densities measured for carbon black, (1.84 - 2.06) g/cm³, and significantly less than for graphite, 2.22 g/cm³. The tandem DMA-APM technique described in this work will enable one to make real-time measurements of the density of nanoscale elongated non-spherical materials with high aspect ratio (e.g. nanowires, nanofibers, or nanotubes), which have masses down to sub-femtogram level.
Synthesis of silicon nanoparticles is of great interest because of their unique optical and electronic properties. Fundamental understanding of the various interconnected mechanisms involved in the particle formation, such as gas phase and gas-surface phase chemical kinetics and particle size/morphology evolution through nucleation, growth, coagulation and coalescence, would be of great value in designing and optimizing processes for producing silicon nanoparticles. In this work, we modeled silicon nanoparticle synthesis by silane decomposition in a six-way cross laser driven aerosol reactor. This corresponds to a reactor system used in our laboratory. Because of the complexity of the problem at hand, the simulation was carried out via several sub-models. First, the chemically reacting flow inside the reactor was simulated in three dimensions in full geometric detail, but with no aerosol dynamics and with highly simplified chemistry. This was done using MPSalsa, a finite element program developed by Sandia National Laboratories. Second, the reaction zone was simulated using an axisymmetric 2-D MPSalsa model, whose boundary conditions were obtained from the first step. Last, a quasi-2-D aerosol dynamics model was used to study the silicon nanoparticle formation using more complete silane decomposition chemistry, together with the temperature and velocities extracted from the reaction zone simulation. Both moment-based and sectional models were used to describe the aerosol dynamics, and results will be compared. In addition, a bivariate moment model that models finite rate coalescence was applied, allowing realistic predictions of primary particle size at high particle number concentration.

TiO₂-based photocatalysts have been applied for the decomposition of organic compounds in polluted air and wastewaters because of their high photocatalytic activities, commercial availability, and good stability against chemical and photochemical corrosion. Here, we report the synthesis of Fe-doped TiO₂ nanoparticles from a mixed precursor solution of titanium (IV) isopropoxide (TTIP) and iron nitrate by flame spray pyrolysis. We analyzed the properties of as-prepared nanoparticles, such as morphology, crystal structure, composition, and light-absorption using TEM, XRD, EDS, and UV-Vis spectrophotometer. In addition, the decomposition of NOx by the Fe-doped TiO₂ nanoparticles was investigated using an analytical system for the estimation of photocatalytic activities, which consisted of UV lamps and a NOx analyzer. Crystalline Fe-doped TiO₂ nanoparticles less than 20 nm in diameter for photocatalysts were successfully synthesized by flame spray pyrolysis. The Fe-doped TiO₂ nanoparticles were found to be an effective photocatalyst for the decomposition of NOx.
3D.13  
**Carbon-Nanotube-Assisted Transmission Electron Microscopy Characterization of Aerosol Nanoparticles.**  
SHUN MAO, Ganhua Lu, Junhong Chen, *University of Wisconsin-Milwaukee*

Aerosol nanoparticles are important for both environmental science in which nanoparticles are contaminants and materials science in which unique properties of nanoparticles can be harnessed for innovative applications. Detailed microscopic characterization of aerosol nanoparticles is critical to both fields as health effects and unique properties of nanoparticles significantly depend on the nanoparticle structure. Transmission electron microscopy (TEM) has been widely used for the nanoparticle characterization. Here we report on a simple and efficient method for the TEM analysis of aerosol nanoparticles using carbon nanotubes (CNTs) as the nanoparticle support. Aerosol nanoparticles from various generation techniques are first assembled onto the external surface of CNTs and then analyzed using TEM and high resolution TEM (HRTEM). The CNT support provides significantly improved contrast in HRTEM imaging mode since nanoparticles lying on CNTs can be observed easily under vacuum, unlike on conventional TEM grids with amorphous carbon film as the background. For nanoparticles with an amorphous shell, the shell can be easily identified in comparison with that on a carbon-film-coated TEM grid. The reported method can be used to facilitate the TEM analysis for aerosol nanoparticles of various compositions.

3D.14  
**Dustiness Testing of Nanoparticles.** PATRICK O’SHAUGHNESSY, Mitchell Kang, *University of Iowa*

The exposure of workers in nanoparticle production facilities to airborne nanoparticles is a concern. The ability of the nanoparticles to form an aerosol is related to its dustiness - the propensity of the bulk powder to generate airborne dust during handling or as a consequence of a fugitive emission. Two dustiness methods were developed and tested: (1) one which allows a bolus of the powder to fall through a tube with a photometer at the bottom to record dust concentrations over time; and (2) a method that employed a pulse of air to suspend the powder resting on a filter support pad up to a photometer. The photometer output was read every 0.20 seconds to typically produce a curve representing a sharp rise then gradual decay over a 2 min period. The peak concentration, area under the curve, and decay residence time on a per bolus-mass basis were used as indicators of the magnitude and duration of the dust cloud produced and therefore of the dustiness of the powders. Four nanoparticle powders were tested in each device: two titanium dioxide powders (5-nm and 20-nm primary particle size), silicon dioxide and iron oxide (both with 20-nm primary particle size), and single-walled carbon nanotubes. Both methods were capable of producing reproducible response curves. In general, the more densely structured powders, such as titanium dioxide, produced an aerosol that was less dusty on a per mass basis but took longer to clear once aerosolized using method 2 compared with the loosely-structured silicon dioxide powder. The opposite effect was seen when the powders were dropped because the denser powders did not break up into a fine aerosol while falling. These methods proved to be useful for predicting the relative dustiness of nanoparticle powders given their production by handling or as a fugitive emission.
Data on mobility Z and mass m recently reported for clusters of a diversity of materials, are now reinterpreted with the aim of determining the relation between electrical mobility and mass diameter \[d_m = (6m/(\pi*rho))^{1/3}\], where rho is bulk particle density. The clusters were generated by electrospraying solutions of ionic liquids (ILs), tetra-alkyl ammonium salts, cyclodextrin, bradykinin, etc., in acetonitrile, ethanol, water or formamide (~ 0.001 up to 1.0 mol/l). Z was measured directly with a differential mobility analyzer (DMA) of high resolution, and m was in most cases assigned indirectly by first distinguishing singly (z = 1) and doubly (z = 2) charged clusters, and then identifying monomers, dimers, ...n-mers, etc., from their ordering in the mobility spectrum. Provided that \(d_m > 1.5\) nm, \(Z(d_m)\) data yield a single curve for nanodrops of ILs for which rho is known. Using an effective diameter for gas molecules of 0.31 nm, this curve is also in good agreement with the accepted drag law for spheres. Particles of solid materials for which also m is measured (by mass spectrometry) fit well the same curve when their (unknown) bulk density is assigned such that one point falls on the line. The same holds for a wider group of \(Z(d_m)\) data from clusters of unknown density for which m is inferred from the ordering of peaks in the mobility spectrum. It was found that for pure Y2O3 the monoclinic phase is only formed when the particles are smaller than a certain critical diameter.

In this study, we investigated the crystal structure of Y2O3:Eu fluorescent particles as a function of particle size and dopant concentrations, in an effort to identify a method of phase control. Polydispersy Y2O3:Eu particles were synthesized by flame spray pyrolysis using a H2/O2 flame and ultrasonic atomization. An additional dopant was added to the Y2O3:Eu particles. X-ray diffraction, fluorescence spectroscopy and electron microscopy were used to determine the crystal structure of the particles. It was found that the additional dopant had a significant effect on the phase-size relationship and a phase control strategy could be developed based on this phenomenon.

References
1D.05
New Flame Pyrolysis Reactor for Probing Carbon Black Yield: The Role of Soot Oxidation and Surface Growth.
ANSHUMAN AMIT LALL, Xiaofei Ma, Dale Hsien-Yi Huang and Michael R. Zachariah, University of Maryland, College Park

A new relatively large-scale laboratory reactor (~100 g/hr) for studying carbon black synthesis has been developed. The reactor consists of a flame on which the heated fuel/liquid precursor is sprayed in gas/droplet form with nitrogen as carrier gas. The sprayed fuel gets partially pyrolyzed to carbonaceous soot particles and other gaseous byproducts. The resulting soot aerosol is maintained at a high temperature for a certain time to allow soot surface growth onto previously formed seed soot particles. However, the overall soot yield is a complex interplay of competing soot surface growth [Yozgatligil, A. and Zachariah, M. R. (2008) Measurement of soot surface growth kinetics. Combust. Sci. and Tech., 180: 941-949] and oxidation kinetics. Our goal is to optimize soot yield by improving the soot surface growth. In our preliminary measurements, it is found that a higher reactor temperature leads to lower yield due to higher soot oxidation rate. The results are supported by the increase in total CO and CO2 concentrations.

The soot yield measurements are made by using a novel online aerosol method of measuring soot yield in the gas phase. The online method enabled us to measure soot yield for a number of process parameters and operating conditions such as the overall and burner equivalence ratio, and the time-temperature history. Our preliminary measurements indicate that the soot yield increases with the overall equivalence ratio at a given burner equivalence ratio. The CO and CO2 emissions from the reactor are monitored and suggestions are made to reduce emissions of the green-house gases.

2D.03
Copper Oxide Nanoparticles via Flame Spray Pyrolysis for Photoelectrochemical Hydrogen Generation.
Ranjan Pati (1), Joshua Emmanuel (1), SHERYL EHRMAN (1), Aadesh Singh (2), Monica Gupta (2), Vibha Satsanghi (2), Rohit Srivastav (2), Sahab Dass (2), (1) University of Maryland, College Park, (2) Dayalbagh Educational Institute, Agra

Many countries face challenges with respect to energy utilization, specifically reliance on imported and ever costlier sources of energy and thus many are looking towards conversion to a hydrogen-based economy. In the rush to new solutions, however, it is important to consider the long-term impact of any technology. One class of hydrogen generation materials receiving renewed attention is earth abundant transition metal oxides, used for photoelectrochemical hydrogen generation. These materials are of interest because of their potential for low life cycle cost as compared to higher efficiency compound semiconductor heterostructures, once raw material costs, manufacturing, lifetime and disposal considerations are taken into account. Here, a flame spray pyrolysis process is described for preparation of undoped and chromium doped copper oxide (CuO) nanoparticles from copper nitrate and chromium nitrate precursors. Addition of the Cr dopant was expected to increase conductivity of the powder. The particles were crystalline and consisted of aggregates of primary particles with diameters of 13 nm, as measured via nitrogen absorption (BET), for powders prepared at a flame temperature of 1500 C. The powders were pressed into a pellet and current voltage characteristics were obtained under dark and illuminated conditions using a 300 W solar simulator. Interestingly, undoped CuO, which has a band gap in the visible light range, was not photoactive, while 5% Cr doped CuO was found to be photoactive. Results of additional characterization and performance testing will be presented with the goal of developing a better understanding of photoactivity in these materials.
9K.07
Dynamic shape factor of silver nanoparticle agglomerates.
Weon Gyu Shin (1), Seong Chan Kim (1), George W. Mulholland (2), Jing Wang (1), Mark S. Emery (1), and David Y. H. Pui (1). (1)Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN (2)Department of Mechanical Engineering, University of Maryland, College Park, MD

Nanoparticle agglomerates are produced by combustion and include diesel particulate, soot from building fires, and combustion synthesized fumed silica, titanium dioxide, and carbon black. The particle structure affects particle transport such as diffusion, sedimentation, and electrical mobility. Dynamic shape factor is a correction factor which can account for the effect of shape on the particle motion if sphere volume equivalent diameter of the agglomerate is known.

In this paper, we have chosen to measure the dynamic shape factor of silver agglomerates using a combination of a DMA and an Aerosol Particle Mass analyzer (APM) - (Ehara et al., 1996). The use of an aerosol composed of one material allows us to determine the volume of the particles from their mass and the density of silver. The motivation for our study was to obtain accurate measurements of the dynamic shape factor for agglomerates with up to several hundred primary particles and to compare with theoretical predictions (Chan and Dahneke, 1981; Meakin et al., 1989). Our experiments include agglomerates over the mobility diameter range from 50 nm to 300 nm compared to a range of about 25 nm to 90 nm in the Schmidt-Ott study (1988).

The Dynamic shape factor obtained from theoretical derivation is larger than that from DMA-APM measurement. We carried out multiple charge corrections for experimental data and estimated the effects of necking between particles, polydispersity of primary particles, and the electrical alignment of agglomerates in DMA on the theoretical predictions. Modified predictions based on the Meakin et al. (1989) method reduces the difference between theory and experiment but it is still significantly greater than the uncertainty range of the measurements. Results from this study demonstrate the capability of quantitative measurements of dynamic shape factor using the large throughput DMA-APM method.

References

11E.05
Friction coefficient of silver nanoparticle agglomerates.
Weon Gyu Shin (1), George W. Mulholland (2), Seong Chan Kim (1), Jing Wang (1), Mark S. Emery (1), and David Y. H. Pui (1). (1)Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN (2)Department of Mechanical Engineering, University of Maryland, College Park, MD

Combustion and furnace generated aerosol particles generally consist of individual primary particles forming a fractal agglomerate structure. This agglomerate structure affects the friction coefficient, which is a key quantity in computing properties such as diffusion, sedimentation, electrical mobility, thermophoresis, and coagulation.

The objective of this study is to obtain quantitative data on the friction coefficient of nanoparticle agglomerates as a function of the agglomerate size for agglomerates with fractal dimension less than 2 and primary sphere size in the free molecular regime. We measured the mass of silver agglomerates using a tandem Differential Mobility Analyzer (DMA) - Aerosol Particle Mass analyzer (APM). The use of an aerosol composed of one material allows us to estimate the number of primary particles on agglomerates from their mass, primary particle size, and the density of silver. Our experiments include agglomerates over the mobility diameter range from 50 nm to 300 nm. The average primary particle diameter is 16.2 nm. From our experimental data, the friction coefficient has a dependence on N^0.75 for N between 10 and 600 compared to N^0.995 by Chan and Dahneke and on N^0.898 by Meakin et al. From a detailed analysis, the uncertainty in the exponent was found to be +/- 2.7 %, which is small compared to the difference between experiment and theory. For the small agglomerates in the range of N between 12 and 52, we obtain a value of N^0.87. This value is similar to N^0.85 for small agglomerates in the range of N between 2 and 40 obtained by Schmidt-Ott (1988) for silver agglomerates and to N^0.86 by Cai and Sorensen, for small agglomerates in the range of N between 5 and 50, for soot agglomerates. The model predictions decrease by only 2 % to 3 % for small vs large agglomerates while the measured results indicate a 12 % to 14 % change. This shows that the Knudsen number based on the length of the agglomerate affects the friction coefficient for agglomerates in the free molecular regime in terms of the primary sphere size.

References
2D.04
Array Formation of 3-D Nanostructure of Nanoparticle via Electrodynamic Focusing of Charged Aerosols. Mansoo Choi, HEECHUL LEE, Sukbeom You, Changkyu Woo, Seoul National University

We report the formation of 3-dimensional nanoparticle structures in atmospheric condition. Effects of particle size, applied electric field and surface charge on nanoparticle structure formation were examined and numerical simulation confirmed the experimental results.

Spark discharge method and condensation and evaporation method were used for the generation of nanoparticles and electric field was utilized for the buildup of nanoparticle. By utilizing electrostatic lens effect, the arrays of nanoparticles structure can be realized onto desired area with small size compared to original PR (photoresist) prepattern. We fabricated various 3-dimensional nanoparticle structures such as pillar, mushroom, flower, circle and wall shapes from nanoscale to microscale with controllability of structure dimensions. The height of nanoparticle structure could be controlled with that of PR prepattern and applied potential on substrate. Additionally, various shapes of nanoparticle structures in same PR prepattern could be made just by changing deosition time.

9K.08
The Crystalline Phase Transition Following Morphology Exchange Of Copper (I) Oxide Nanoparticles During Spray Pyrolysis. DUDI ADI FIRMANSYAH, Taeil Kim, and Donggeun Lee, Pusan National University, Busan, South Korea

A more economical and continual manufacturing process of copper nanoparticles via spray pyrolysis has been developed recently. Metallic copper nanoparticles were produced by spray pyrolysis of copper nitrates with ethanol as co-solvent at 450-600oC. During spray pyrolysis, copper nitrates involve the solid-state reaction to produce Cu2O and subsequently Cu2O particles were reduced to metallic copper under the strong reducing atmosphere resulted from ethanol decomposition. It was observed that this reduction caused the shift of particle size distribution to smaller particle size and particle morphology exchange from shell-like particle to solid-like particle. The X-ray Diffraction (XRD) patterns showed two Cu2O reduction pathways i.e. (i) Cu2O were directly reduced to metallic copper, and (ii) Cu2O were oxidized to CuO which subsequently reduced to metallic copper. This may be implied that copper are produced through the homogenous conversion of Cu2O as single reactant in the system with the strain energy as the driving force induced by microstrain effect inside the Cu2O particle. The kinetics of this reduction fits linearly with the first order model and yields straight line in the Arrhenius plot, with an activation energy of $E_a = 127.15$ kJ/mol which agrees with the activation energy for Cu2O reduction. The HR-TEM images of the center area of particle also confirmed the formation of Cu which induced the strain to the lattice distance of Cu2O at inner particle.
3D.16

As a way to improve the environment, continuous efforts are being made to degrade contaminants completely by the activation of light as eco-friendly energy of photocatalyst. In order to develop enhanced photo activity of titanium dioxide, we studied TiO$_2$ synthesized high efficiency photocatalysts doping Zr and N , Zr and precursor concentrations of N source were set differently in turn to characterized the particle properties also influence of the degradation of NO was considered.

As a result TEM were found to be around as average particle size between 20 and 30 nano-meter, also polyhedral singular powders were shaped. The result of TiO$_2$:Zr, N measured by XRD showed that increasing mixed ratio of rutile crystallite was caused by precursor concentrations of N source. For TiO$_2$:Zr, N, another result improved by UV-Vis light reflectance spectra was shown that compared with commercial P25 under both UV and visible light within entire wavelength range. Under UV and fluorescent lamps, the photocatalytic degradation of NO in the prepared powders and commercial P25 were showed. After 90 minutes under UV lamps, the highest degradation is up to 80 percent, and the lowest degradation is 77 percent, the corresponding values are 37 percent and 23 percent under fluorescent lamps while photocatalytic degradation of commercial P25 was observed as 18 percent and 4 percent under UV and fluorescent lamps respectively.

In this study, the increases in precursor concentrations of N source raised heats of combustion and sintering between nanosized powders in turn. Effects of prepared TiO$_2$:Zr, N were improved 4 to 5 times more than commercial P25 under UV and fluorescent lamps, according to this result, the remarkably photocatalytic activity can be demonstrated. However, mechanism for of added Zr and N are needed. Further studies about how mechanism exerts an influence on the improvement of photocatalytic characteristics are needed.
4B.01
On the link between carbon dioxide and particulate matter mortality. MARK Z. JACOBSON, Stanford University

Global warming due to greenhouse gases and soot aerosol particles has been linked to enhanced sea-level, snowmelt, disease, heat stress, severe weather, and ocean acidification, but the effect of carbon dioxide (CO2) alone on air pollution mortality was only recently examined. Results from the study are reported here. It is shown that increased temperatures and water vapor from higher CO2 increase particulate matter and ozone and their resulting health effects. A high-resolution global-regional nested model found that CO2 may increase U.S. annual air pollution deaths by at around 1000 (350-1800) and cancers by 20-30 per 1 K rise in CO2-induced temperature. About 40% of the additional deaths may be due to ozone and the rest, to particles, which increase due to CO2-enhanced stability, humidity, and biogenic particle mass. An extrapolation by population could render 21,600 (7400-39,000) excess CO2-caused annual pollution deaths worldwide, more than those from CO2-enhanced storminess. It was found that the effects of carbon dioxide on air pollution are greatest where the pollution is already bad. Thus, for example, although it has only 12% of the U.S. population, more than 30% of the increased deaths found in the U.S. occurred in California, which has 6 of the top 10 polluted U.S. cities. The results here provide a basis for regulators to control carbon dioxide based on air pollution health grounds.

4B.02
Variable Moment General Dynamic Equations for Global and Regional Aerosol Modeling. Boris Grits (1) and Anthony Wexler (1,2,3), (1) Department of Mechanical and Aeronautical Engineering, (2) Department of Civil and Environmental Engineering, (3) Department of Land, Air and Water Resources

Particles influence a wide range of atmospheric processes such as cloud and fog formation, light scattering and absorption, visibility, and health effects. Each of these processes depends on one or more moments of the particle size distribution and composition. Most atmospheric particle dynamics models simulate one moment of the distribution, typically mass or number, and may infer other moments by making uncertain but computationally necessary assumptions about particle morphology, density, and composition. Substantial uncertainties may also be introduced moving from mass to number or vice versa since these moments are related by the cube of the particle diameter, thereby amplifying diameter uncertainty substantially. Finally, uncertainties may be introduced due to sharp gradients in the particle size distribution due to numerical artifacts introduced during integration of these equations.

In the present study we propose a novel form of the multicomponent general dynamic equation that simulates arbitrary moments of the distribution. In previous work, an equation for the evolution of a general function of aerosol size distribution due to a pure condensation/evaporation processes was derived. This function may describe any distribution moment (both integer and non-integer) or arbitrary combination of such moments. It was found that this scheme reducing significantly numerical errors if appropriate function is employed. In the current work, we generalized our algorithm for the case where coagulation influences the size distribution in addition to condensation and evaporation. To test our algorithm we perform simulations of aerosol population growth in several cases and compare these results with those obtained using existing schemes.
**4B.03**
**Studying Climate-Chemistry-Aerosol-Cloud-Radiation Feedbacks in North America and Asia using Online-Coupled WRF/Chem.**

YANG ZHANG, Xin-Yu Wen, Yao-Sheng Chen, Ying Pan and Xiao-Ming Hu, North Carolina State University, Raleigh, NC

The feedback mechanisms among climate-chemistry-aerosol-cloud-radiation represent one of the most uncertain research areas in understanding climate change and its potential impact on atmosphere. For example, the feedbacks of aerosols include a reduction of downward solar/thermal-IR radiation (direct effect); a decrease in surface temperature and wind speed but an increase in relative humidity and atmospheric stability (semi-direct effect), a decrease in cloud drop size but an increase in cloud drop number via serving as cloud condensation nuclei (first indirect effect), as well as an increase in liquid water content, cloud coverage, and lifetime of low level clouds but a suppression of precipitation (the second indirect effect). Accurately simulating these feedbacks requires the use of online-coupled meteorology-chemistry models; among which the Weather Research and Forecast Model with Chemistry (WRF/Chem) represents a state-of-the-science online model.

In this work, the climate-chemistry-aerosol-cloud-radiation feedbacks are studied using WRF/Chem. Model simulations have been conducted at a horizontal grid spacing of 36-km for January and July 2001 episode over North America and January and July 2005 episode over Asia to examine important climate-chemistry-aerosol-cloud-radiation feedbacks. Seasonal variations in aerosol direct, semi-direct, and indirect feedbacks are analyzed and contrasted for North America and Asia. Major challenges in accurately representing such feedbacks along with recommendations for future online model development and improvement will be discussed.

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**4B.04**
**Development of a Framework for the Parameterization of Aerosol Indirect Effects on Cirrus Formation in Large-Scale Simulations.**

DONIFAN BARAHONA (1), ATHANASIOS NENES (1), (2), (1) School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA (2) School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta

This work presents a new physically-based framework for parameterization of cirrus cloud formation in large-scale models, which is robust, computationally efficient, and accounts for chemical effects (e.g., water activity and water vapor deposition effects) on ice nucleation. Using this framework the ice crystal size distribution and the crystal number concentration can be calculated, explicitly considering the effects of aerosol size and number, updraft velocity, and deposition coefficient. The formulation is based on parcel model theory and includes homogeneous and heterogeneous freezing mechanisms. Calculation of the rate of crystal nucleation is achieved using either empirical correlations or classical nucleation theory without affecting the accuracy of the formulation. Interaction between homogeneous and heterogeneous nucleation is accomplished by allowing the latter to deplete water vapor before the homogeneous nucleation pulse. The parameterized framework is evaluated against a detailed numerical cirrus cloud parcel model where the solution of equations is obtained using a novel Lagrangian Particle Tracking scheme. Over a broad range of cloud forming conditions, the parameterized framework showed less than 10% average discrepancy with respect to the parcel model predictions.
5K.01
Effect of climate and emission changes on particle number concentration over the US. Tagaris Efthimios (1), Kuo-Jen Liao (1), Kasemsan Manomaiphiboon (1), Jung-Hun Woo (2), Shan He (2), Praveen Amar (2) and Armistead G. Russell (1), (1) School of Civil & Environmental Engineering, Georgia Institute of Technology, Atlanta, GA (2) Northeast States for Coordinated Air Use Management (NESCAUM), Boston, MA

The objective of this study is to assess the impacts of global climate and emissions changes on ambient particle number concentration. Particle number concentrations for a historic period (i.e. summers 2000-2002) are compared to a future period (i.e. summers 2049-2051). Meteorological fields are derived from the GISS GCM and have been regional downscaled using the Penn State/NCAR Mesoscale Model (MM5). CMAQ with SAPRC-99 chemical mechanism is used for the regional air quality modeling using a binary nucleation approach. The effect of climate change alone is less important than the combined effect of climate and emission changes. Small size particles appear to have the maximum reduction in number concentration. However the reduction in number concentration is less compared to the reduction in mass concentration. Due to the significant role of particle number concentration on the earth energy balance (e.g. CCN) as well as on human health a sensitivity analysis using different nucleation theories is necessary.

5K.02
On the Structure of Organic Coated Water Droplets or what causes an \textit{Oily} Drop to Process Water. Purnendu Chakraborty, Michael R. Zachariah, University of Maryland and NIST

Organic coated aerosols may play an extremely important role in atmospheric processes and can influence global climate and perhaps climate change. In this paper, we report the results of molecular dynamics studies on the effect of fatty acid chain length, chain branching, and terminal group on the morphology, internal pressure profile, surface tension and water processing properties of water droplets coated with organics. In our earlier works, we had seen that the particles coated with fatty acids with smaller chains maintain their overall spherical shape leading to a negative surface tension effect and consequently are net water attractors despite an apparent hydrophobic surface. On the other hand, for particles coated with longer/branched surfactants, as a result of much stronger interactions in the coating, the fatty acid chains were seen to align parallel to each other, forcing local flattening of the underlying water substrate. Sticking coefficient calculations, of water vapor on such particles, showed that these newly formed particles behave in a manner that is consistent with an \textit{oily} surface as opposed to the ones with shorter chains that can process water despite their apparent hydrophobic surface.
Influence Of Altitudinal Distribution Of Gaseous Absorbate On Gas Absorption By Falling Liquid Droplets.  

BORIS KRASOVITOV, Tov Elperin, Andrew Fominykh, Ben-Gurion University of the Negev

Concentration measurements of soluble trace gases in the atmosphere revealed altitudinal dependence of the concentrations. In this study we analyze mass transfer during absorption of soluble atmospheric gases by falling rain droplets with internal circulation taking into account altitudinal dependence of concentrations of soluble trace gases in the atmosphere. Concentration of soluble gases in a droplet is governed by a system of unsteady convective diffusion equations with time-dependent boundary conditions (Elperin et al. 2007; 2008). It is shown that gas absorption by falling droplets is governed by Volterra integral equation (Elperin & Fominykh 2005) that is solved numerically. We compare the results obtained using the model of gas absorption in the case of uniform distribution of soluble gases with those obtained when concentration of soluble gases varies with altitude. The comparison showed that vertical concentration profile of a soluble gas in atmosphere has a profound effect on mass transfer during gas absorption by a falling rain droplet. When concentration of soluble trace gases in the atmosphere is assumed constant, their content in the droplet attains saturation after a certain time elapsed, and at the final stage of their fall droplets do not absorb soluble trace gases. When concentration of soluble gases in the atmosphere decreases with altitude, droplets absorb trace gases during all the fall period. Consequently, concentration of soluble gases inside droplets at the ground which fall in the atmosphere with a homogeneous distribution of trace gases is lower than the concentration inside the droplet falling in the atmosphere with altitude dependent concentrations. When concentration of soluble gases increases with altitude, after a certain time interval droplets begin to release the dissolved gases. Consequently droplets have a lower concentration of trace gases at the ground level as compared with droplets falling in an atmosphere with a homogeneous distribution of trace gases.

**5K.05**

Effect of temperature on atmospheric particle formation: A positive climate feedback mechanism? FANGQUN YU, State University of New York, Albany

The abundance of cloud condensation nuclei (CCN) is a key factor determining the indirect radiative forcing of aerosols, a major source of uncertainty in climate change predictions. New particle formation observed frequently in the atmosphere contributes significantly to CCN abundance. Temperature is well known to strongly influence the nucleation rate of atmospheric aerosols. The percentage change in the nucleation rate per degree increase of temperature is a non-linear function of several parameters, and has an average value of around -80 to -20 % per degree C based on existing binary, ternary, and ion-mediated nucleation theories. To assess the potential impact of future climate change on global new particle production, we employ the GEOS-Chem global chemical transport model with the ion-mediated nucleation (IMN) mechanism integrated. Here we focus on IMN because it appears to be the only physically-based mechanism currently available to explain most of the nucleation events observed in boreal forests, and to predict global nucleation distributions in reasonable consistency (in terms of both spatial patterns and absolute magnitude) with land-, ship-, and aircraft-based observations. We show that global warming could lead to substantial reductions in new particle formation rates (~3-15% per degree C) over large parts of the troposphere. Based on well-constrained case and sensitivity studies of two nucleation events in boreal forests, we find that a one degree C temperature increase could lead to a reduction of ~6-11.5% in the number concentrations of total particles (> 3 nm), and a 2.5-7.5% reduction of climate effective particles (> ~50-80 nm). Since atmospheric aerosols have a net cooling effect, the reduction of particle production and hence CCN abundance associated with global warming defines a potentially significant positive nucleation/climate feedback. Observations indicating the existence of the proposed positive feedback process and the implications of such feedback on climate change will be discussed.

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**5K.06**

Examining the Effect of Future Sulfate Emissions Controls in the U.S. on Photolysis Rates. CHRISTOPHER G. NOLTE (1), Shawn J. Roselle (1), Francis S. Binkowski (2), (1) EPA, RTP, (2) University of North Carolina

An online photolysis module has been developed and implemented within the Community Multiscale Air Quality (CMAQ) model. The module uses clouds predicted by the meteorological model and modeled nitrogen dioxide (NO₂), ozone (O₃), and aerosol concentrations to calculate actinic fluxes and photolysis rates at every vertical level in each of seven wavelength intervals from 291 to 850 nm, as well as the total surface irradiance and aerosol optical depth within each interval. The module is computationally efficient, requiring approximately 7.5% additional runtime compared to the offline lookup table method employed in standard CMAQ. The vertical profiles of summertime photolysis rates and ozone concentrations computed by the online and offline modules will be compared. Preliminary results indicate significant decreases in ozone over urban areas due to either enhanced absorption by NO₂ and O₃ or increased aerosol scattering. We will also present a sensitivity study with emission controls mandated by the U.S. Environmental Protection Agency's Clean Air Interstate Rule (CAIR) to examine the effect of reduced sulfate emissions on predicted photolysis rates and ozone concentrations.
Parameterization of Cloud Droplet Formation for large-scale models: Including the effects of Hydrophilic Insoluble particles.

PRASHANT KUMAR (1), Irina Sokolik (2), Athanasios Nenes (1,2),
(1) School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA
(2) School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA

Dust and black carbon aerosol has long been known to have potentially important and diverse impacts on cloud droplet formation. Most studies to date focus on the soluble fraction of such particles, and ignore interactions of the insoluble fraction with water vapor (even if known to be hydrophilic). We address this gap, and present a new parameterization framework that considers cloud droplet formation within an ascending air parcel containing insoluble (but wettable) particles mixed with aerosol containing an appreciable soluble fraction. Activation of particles with a soluble fraction is described through well-established Kohler Theory, while the activation of hydrophilic insoluble particles is treated by adsorption-activation theory. In the latter, water vapor is adsorbed onto the insoluble particles, the activity of which is described by a multilayer Frankel-Halsey-Hill (FHH) adsorption isotherm modified to account for particle curvature. The condensation rate of water vapor onto both types of particles, required for determination of the maximum supersaturation and droplet number, is calculated using the population splitting concept of Nenes and Seinfeld (JGR, 2003). Formulations are presented for sectional and lognormal aerosol size distribution functions.

The new parameterization is evaluated by comparing the parameterized cloud droplet number concentration against predictions with a detailed numerical cloud model, for a wide range of particle populations, cloud updraft conditions, water vapor condensation coefficient and FHH adsorption isotherm characteristics. The agreement between parameterization and parcel model is excellent, with an average error of 10% and $R^2 \sim 0.98$. This work offers for the first time a comprehensive parameterization framework which from first principles links chemical effects and aerosol heterogeneity within the frameworks of cloud droplet activation.

Aerosol cloud drop concentration closure for clouds sampled during MASE.

WEI-CHUN HSIEH(1), Athanasios Nenes(1,2), Rebecca Ugalde(2), Purvi Patel(2), Roya Bahreini(3,6), William C. Conant(3,7), Hafidi Jonsson(4), Shane Murphy(5), Armin Sorooshian(5), Varuntida Varutbangkul(5), Fred Brechtel(4), Richard C. Flagan(3,5), and John H. Seinfeld(3,5),
(1)School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, (2)School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, (3)Environmental Science and Engineering, California Institute of Technology, Pasadena, (4)CIRPAS, Naval Postgraduate School, Monterey, (5)Chemical Engineering, California Institute of Technology, Pasadena, (6)National Oceanic and Atmospheric Administration, Boulder (7)Atmospheric Sciences, University of Arizona, Tucson, Arizona, Tucson

This study analyzes stratocumulus clouds sampled aboard the CIRPAS Twin Otter during the 2005 Marine Stratus Experiment to access cloud droplet closure using a detailed adiabatic cloud parcel model, and, a state-of-the-art cloud droplet activation parameterization. A distinguishing feature of this dataset was the sampling of marine stratocumulus clouds influenced by emissions from ships. Observed droplet number was found to correlate much higher with accumulation mode aerosol concentration than with updraft velocity. In agreement with previous studies, the average updraft velocity yields optimum cloud droplet closure, and, is consistent with a Gaussian distribution of vertical velocity with a zero mean. Overall, good closure was achieved using both cloud parcel model and parameterization, the average error of which was 0.14 % with the parcel model, and, 5.01 % with the parameterization. The optimum value of water vapor uptake coefficient (defined as that which gave average error and standard deviation within measurement uncertainty) was equal to 0.1. We explore the sensitivity of cloud droplet closure to water vapor uptake coefficient and the assumption used for size-dependent chemical composition; droplet error was found to mostly correlate with water vapor uptake coefficient.
9B.01
Formation of Secondary Organic Aerosol through Cloud Processing of Anthropogenic VOCs. JAMES W. HUTCHINGS III, Pierre Herckes, Arizona State University

Cloud processing of gas phase species and their transformation into non-volatile species is a potential mechanism for the formation of secondary organic aerosol (SOA) material. Recent research efforts focused largely on heterogeneous chemistry as well as aqueous phase chemistry of species from predominately biogenic precursors. Few studies have focused on the volatile, anthropogenic species including benzene, toluene, ethylbenzene, and xylenes (BTEX) and their processing by clouds.

We present data on field measurements of the occurrence of these VOCs in clouds collected at Mt. Elden in Flagstaff, Arizona. While the species are only a small fraction of the Total Organic Carbon in cloud droplets (<1%), their concentrations are orders of magnitude higher than expected from equilibrium partitioning using standard Henry's law. The ambient vapor phase concentrations of TEX (0.02-1.0 micro-gram*meter\(^{-3}\)) are lower than typical concentrations found at many other sites. Based on the measured gas phase concentrations at Mt. Elden, the theoretical Henry's law concentration of toluene would be ~2 nano-gram*liter\(^{-1}\) compared to measured concentrations of ~1 micro-gram*liter\(^{-1}\).

In a second step, laboratory experiments have been performed to investigate the aqueous phase reactivity of BTEX species in simulated and authentic cloudwater under controlled conditions. Results of these experiments in terms of products formed and reaction kinetics will be presented. Identified reaction products include aldehydes and acids that are less volatile than the BTEX precursors, hence evidence for the cloud processing pathway to SOA generation.

9B.02
Cluster Analysis of UV Laser Induced Fluorescence Spectra of Ambient Aerosols. HERMES HUANG (1), Yong-Le Pan (1), Steven Hill (2), Ronald Pinnick (2), Richard Chang (1), (1) Yale University, (2) Army Research Laboratory, Adelphi, MD

Cluster analysis is a method by which we are able to classify and summarize the many thousands of spectra which we acquire when we monitor the air using our ultraviolet laser induced fluorescence (UV-LIF) single-particle fluorescence spectrometer, capable of measuring the fluorescence spectrum of single particles (1 to 10 micrometers in diameter) [1]. We have used it as an initial step toward understanding what these LIF spectra indicate.

Cluster analysis is used in biology, image analysis, and other fields to determine if natural classes exist in data, how well these classes separate or overlap, and which characteristics are most useful in separating classes. We have looked at two different methods of clustering data: (a) In hierarchical clustering, each data point starts in its own cluster, and most similar are then combined. The combining continues until a threshold is reached. (b) In disjoint clustering, one starts with a number of clusters and some initial assignment of clusters, and the clusters are adjusted to optimize similarity within a cluster and minimize similarity between clusters [2]. These algorithms and their results will be illustrated.

While clustering cannot identify specific aerosol species, it does allow us to summarize and classify our spectral data. By doing so, we are now able to compare spectral data taken at different times, at different sites, and under different conditions much more effectively then if just looking at the raw spectral data. Understanding the ambient background is a key step to development of instrumentation which allows us to monitor the air effectively.

9B.03  
Measuring Homogeneous Freezing with a Continuous Flow Diffusion Chamber. MATHEWS RICHARDSON, Paul DeMott, Sonia Kreidenweis, Department of Atmospheric Science, Colorado State University

The field-ready version of Colorado State University's (CSU) continuous-flow diffusion chamber (CFDC-1H) is one of the few instruments capable of measuring atmospheric ice nuclei (IN) concentrations in real time. Researchers from CSU have operated this chamber in several field campaigns, typically measuring IN concentrations at conditions warmer than those required for homogeneous freezing (> -35°C). During the few periods in which the CFDC-1H has been operated at low temperatures, analysis of the data indicates that there may be inherent limitations to the ability of the CFDC-1H to detect the onset of homogeneous freezing consistent with accepted theory. These results are consistent with previous exploratory lab studies.

Homogeneous freezing theory and parameterizations have never been rigorously validated by observing nucleation of real atmospheric particles. This fact also complicates clear recognition of other potential aerosol chemical impacts on freezing. To investigate the capability of the CFDC-1H to accurately capture the onset of homogeneous freezing we have simulated the fluid dynamic and thermodynamic fields in the chamber using computational fluid dynamics and run a microphysical model along particle trajectories produced from these simulations for a variety of operating conditions. Through these simulations, we have developed a methodology for sampling with the CFDC-1H under which we will be able to reliably capture the onset of homogeneous freezing. We have validated these results in a controlled laboratory setting using size-selected ammonium sulfate.

This presentation examines the results from these experiments. We take an in-depth look at the sources of these limitations, rooted primarily in residence time limitations in an aircraft-based instrument package and the impact on diffusional growth rates of water and ice, as well as what operating parameters we are able to adjust to overcome these limitations. In addition, we present findings from further studies in which we directly sampled from the atmosphere, demonstrating the CFDC-1H's ability to capture the onset of homogeneous freezing in a population of ambient particles.

9B.04  
Oceanic Trace Gases: Quantification and Climate Impact. BRETT GANTT, Nicholas Meskhidze, Daniel Kamynkowski, North Carolina State University

Volatile organic compound (VOC) emissions from phytoplankton have been shown to have considerable impacts on the oxidative capacity of the atmosphere, new particle formation at a coastal site, and influence cloud properties over the remote ocean. The factors influencing VOC emission rates from the ocean are not well understood, but seem to strongly depend on environmental parameters such as phytoplankton abundance, light, temperature, and wind speed. Using gas chromatography, we have made laboratory measurements of headspace concentrations of several VOCs including isoprene (C_5 H_8), bromoform (CHBr_3), methyl iodide (CH_3 I), and dimethylsulfide (DMS). To test the impact of environmental stresses to VOC production, species from several phytoplankton classes including diatoms, coccolithophores, and dinoflagellates were exposed to intense light, mechanical damage, and nutrient deprivation. The stressed phytoplankton show very high emission rates of VOCs compared to the non-stressed control group. We have observed hourly emission rates of some VOCs to be higher than previously published daily emission rates.

These new, phytoplankton-dependent emission rates were implemented in three different global models containing phytoplankton speciation to determine a total magnitude of different VOC fluxes from the oceans. The calculated oceanic fluxes of VOC (e.g. isoprene) are higher than previous studies, although still far less compared to the terrestrial source. On a local scale, in regions of high biological activity this increased VOC production could be of importance to local photochemistry, aerosol concentration, and properties of warm marine clouds.
New Approach for Inversion of Tandem Differential Mobility Analyser Measurements. M. Gysel (1), G. B. McFiggans (2), H. Coe (2), (1) Paul Scherrer Institut, Villigen, Switzerland, (2) SEAES, The University of Manchester, UK

The tandem differential mobility analyser (TDMA) technique is used to detect size changes of submicron particles after a treatment such as exposure to high relative humidity. Measured growth factor distribution functions (MDF) must be inverted, because they are only a skewed and smoothed image of the actual growth factor probability density function (GF-PDF). The TDMAfit algorithm is the most widespread inversion approach. It describes the GF-PDF as a superposition of multiple Gaussians, whereas the mean GF, standard deviation and number fraction in each Gaussian mode are varied until the MDF is reproduced by sending the resulting GF-PDF through the forward function of the TDMA. However, convergence of fitting multiple modes is not robust in cases with largely overlapping modes or shoulders, and successful convergence may depend on the initial guess. This makes automated data analysis of large data sets difficult.

We introduce a new approach, TDMAinv, representing the inverted GF-PDF as a piecewise linear function, whereas the values of the GF-PDF at given support points are varied until the MDF is reproduced by sending the resulting GF-PDF through the forward function of the TDMA. Computer exercises are used to demonstrate that the proposed algorithm is able to recover the key features of the GF-PDF. Laboratory measurements of an aerosol with a bimodal GF-PDF show that inversion with the TDMAinv algorithm allows to recover two nearby narrow modes from an apparently monomodal MDF. Furthermore, TDMAinv provides equivalent information to TDMAfit. The major advantage of TDMAinv is that convergence of the inversion is robust and independent of the initial guess, thus making TDMAinv suitable to analyse large TDMA data sets. However, quantification of measurement uncertainties and careful choice of the resolution for the inversion remains inevitable, when it comes to recovering fine details of the GF-PDF.

Morphological Analysis of Mobility Classified Submicron Atmospheric Particles by Transmission electron Microscopy (TEM) and Atomic Force Microscopy (AFM). LAARNIE TUMOLVA, Kihong Park, Gwangju Institute of Science and Technology

Morphological property of atmospheric particles affects particle transport behaviors, atmospheric radiative transfer, and toxicity mechanisms in humans. A transmission electron microscopy (TEM) has been widely used to determine morphology of particles. However, the TEM method is limited for determination of three-dimensional shape of especially irregular particles, providing only projected images. In this study we combined particle mobility measured with a differential mobility analyzer (DMA), morphological property from TEM, and height information from atomic force microscopy (AFM) to estimate 3-D shapes of particles. The DMA (TSI 3080) was used to select particles of a certain size and then the mobility classified particles were collected onto a TEM grid using a filter holder for TEM analysis or onto a PET substrate for AFM analysis. We compare the current method using mobility-classified aerosol particles of known shapes such as PSL, NaCl, and agglomerated particles. Median values of shape parameters such as aspect ratio, circularity, and height to width ratio were used to infer 3-D shapes of PSL and NaCl particles, resulting in spherical and cubic shapes, respectively. Results for 3-D shapes of various types of atmospheric aerosol particles of known mobility sizes will be presented here.
9B.07
Hygroscopic Growth and Cloud Condensation Nuclei Activity of Secondary Organic Aerosol Formed Through Photo-Oxidation of Alpha-Pinene. Martin Gysel (1), Zs?fia Jur?nyi (1), Jonathan Duplissy (1), Torsten Tritscher, Joseph Dommen (1), Silvia Henning (2), Markus Ziese (2), Alexej Kiselev (2), Frank Stratmann (2), Ingrid George (3), Ernest Weingartner (1), Urs Baltensperger (1), (1) Paul Scherrer Institut, Villigen PSI, Switzerland, (2) Institute for Tropospheric Research, Leipzig, Germany, (3) Dept. of Chemistry, University of Toronto, Canada

Atmospheric aerosols play an important role in cloud formation because they act as cloud condensation nuclei (CCN). Secondary organic aerosol (SOA) is a major component of atmospheric aerosol particles and therefore influences their potential to act as CCN. The latter depends on their size, solubility, hygroscopicity and surface tension and is described by Kohler theory. We have simulated the photo-chemical formation of SOA from a biogenic precursor (alpha-pinene) and probed the Kohler curve in different RH ranges using different techniques. Hygroscopic diameter growth factors (GF) at RH=90-98% and RH=97-99% of SOA particles were measured using a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) and the Leipzig Aerosol Cloud Interaction Simulator (LACIS-field), respectively. Two cloud condensation nuclei counters (CCNC) were used to measure the CCN properties of the SOA particles.

Closure between HTDMA derived GFs and CCNC derived critical supersaturation ($S_{cr}$) can be achieved within measurement uncertainty, when constant hygroscopicity and surface tension of pure water is assumed. However, HTDMA derived GFs are systematically lower at high precursor concentrations compared to low precursor concentrations, which may be caused by different partitioning between particle and gas phase, while no precursor concentration dependence of the CCN properties was observed. Furthermore, the LACIS derived growth factors were lower than the HTDMA derived growth factors. Up to now we have no explanation for these differences, but we confidence in the results from both instruments.

The concentration dependence of the water activity largely determines the GFs at subsaturated RH, while the CCN properties are also very sensitive to the surface tension (Kelvin effect). Different Kohler models will be used in order to investigate, whether the observed different trends in GF and $S_{cr}$ with changing precursor concentration can be explained by changes in the solubility or the concentration dependence of water activity or surface tension.

9B.08
CCN Activity of SOA Mixed Organic-Sulfate Particles at Atmospheric Mass Loadings. SCOT T. MARTIN, Stephanie M. King, Thomas Rosenoern, John E. Shilling, Qi Chen, School of Engineering and Applied Sciences & Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

The effect of organic particle mass loading from 0.86 to 88.3 ug m$^{-3}$ on the cloud condensation nucleus (CCN) properties of SOA mixed organic-sulfate particles was investigated in the Harvard Environmental Chamber (HEC). The chamber was operated in a feedback-controlled continuous-flow mode, and the mixed particles were formed from the dark ozonolysis of alpha-pinene in the presence of 50-nm mobility-diameter ammonium sulfate seed particles. Chamber conditions were 40 (+/-2) % RH and 25 (+/-1) C. Ozone concentrations were set at either 50 or 300 ppbv. CCN activation was measured for 80- and 100-nm mobility-diameter particles. For organic mass loadings of 4.49 ug m$^{-3}$ and greater, the observed activation curves were well predicted by a two-component Kohler model using a constant set of physicochemical parameters for the organic mass. However, for mass loadings of 2.6 ug m$^{-3}$ and less, corresponding to the range of atmospheric organic mass loadings, the CCN activity was greater than predicted. The corresponding aerosol mass spectra indicate an increased fraction of polar and oxygenated components in the particle phase. The increased CCN activity at low mass loading implies changes in the physicochemical properties of the organic mass, such as surface tension, effective molecular weight, or density. A sensitivity analysis shows that a 10% drop in surface tension is the most consistent explanation of the observations.
9B.09
Ubiquitous Influences of CCN on Small Cumulus Microphysics. JAMES G. HUDSON Stephen Noble Vandana Jha, Desert Research Institute

Measurements are presented from the NCAR C-130 airplane during the RICO field experiment in the eastern Caribbean in December-January (2004-05). CCN concentrations were averaged over two half hour circles at 100 m altitude. Since the CCN concentrations were consistent within and between each of these circles on each flight they provided representative inputs to the small cumulus clouds that were semirandomly penetrated during the intervening 4 hours. CCN concentrations for the 17 flights were all maritime (<200 per cubic centimeter), but the factor of four differences among the flights (50-200 per cubic centimeter) was sufficient to test correlations with flight-averaged cloud microphysics.

Correlation coefficients \( R \) between flight-averaged CCN concentrations and flight-averaged total cloud droplet concentrations exceeded 0.80 not only for unmixed (nearly adiabatic) cloud parcels but for cloud parcels with a wide range of liquid water contents (LWC) down to a few percent of adiabatic LWC. The high \( R \) was also consistent over altitude bands from cloud base at 600 m to at least 3000 m. When various cloud droplet threshold sizes were considered (i.e., cumulative cloud droplet concentrations greater than various sizes) \( R \) abruptly flipped from positive to negative at sizes that increased with altitude. The negative \( R \) for the larger cloud droplets (40 micrometers diameter) was similar to the positive \( R \) for all cloud droplets (0.8). Again this was true for all LWC and altitude bands but especially for higher altitudes where droplets are larger. \( R \) between CCN and cumulative concentrations of small drizzle drops (up to at least 100 micrometers diameter) increased with altitude to 0.8 above 2000 meters.

These results show the ubiquitous influence of CCN concentrations on cloud radiation and precipitation properties even over this rather narrow range of concentration variations. This upholds the viability of both the first and second indirect aerosol effects.

9B.10
Exploring the Differences in Aerosol and Cloud Properties Observed by the MODIS Twin Sensors. NICHOLAS MESKIDZE (1), Robinson Negr'n Ju?rez (2), Lorraine A. Remer (3), Steven Platnick (3) 1 Marine Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC, 27695 2 Ecology and Evolutionary Biology, Tulane University, New Orleans, LA 70118 3 NASA Goddard Space Flight Center, Greenbelt, MD, 20771 , (1) Marine Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC (2) Ecology and Evolutionary Biology, Tulane University, New Orleans, LA (3) NASA Goddard Space Flight Center, Greenbelt, MD

Twin Moderate Resolution Imaging Spectroradiometer (MODIS) sensors aboard Terra and Aqua satellites are used for characterization of cloud development and identification of processes affecting cloud formation. With 3 hr differences in equatorial crossing times, MODIS twin-sensors offer unprecedented opportunity to study the diurnal variability of cloud properties in different parts of the globe. The time window between the two times of MODIS overpass is small enough that observed differences in cloud and aerosol properties are primarily associated with the local events, making this technique ideal for exploring the effects of aerosols on clouds. We report significant morning-to-afternoon decrease in stratocumulus and trade-wind cumulus cloud coverage associated with the solar insulation. The year-round retrievals of aerosol and cloud properties by MODIS allow additional separation of aerosol effects on diurnal variation of clouds over the extensive areas of extratropical oceans. Drastic daytime reduction of cloud fraction for the episodes with elevated Aerosol Optical Thickness (AOT) suggests that despite seasonal variation, aerosols seem to always enhance afternoon 'burn-off' of marine clouds. Also discussed are diurnal variations of droplet effective radii (Re), optical depth and liquid water path (LWP).

Furthermore, we report strong diurnal variabilities in cloud properties over the land. By analyzing the data over the Amazon we find that the cloud fraction and Re observed in the afternoon by Aqua-MODIS is systematically higher than that observed in the morning by Terra-MODIS. The difference corresponds to the invigoration of convection in the afternoon with the corresponding growth of clouds. The overall pattern of the difference prevails throughout the Amazon, is repeated over other tropical rain forest regions globally, and is strikingly different from other types of cloud systems around the globe. We show large inter-annual variability in LWP above the Amazon forest during the dry-season and report strong correlation between cloud properties and biomass-burning aerosols.
Overview of Tropical Aerosol Properties Derived from NASA TC4 DC-8 Airborne Observations. G. Chen (1), B. E. Anderson (1), K. Lee Thornhill (1,2), M. M. Kleb (1), E. Winstead (1,2), J. Hair (1), C. Butler (1,2), J. E. Dibb (3), E. Scheuer (3), and Terry L. Lathem (4), (1) NASA Langley Research Center, (2) Science Systems and Applications, Inc., (3) University of New Hampshire, and (4) Georgia Institute of Technology

During the summer of 2007, NASA carried out a large-scale airborne field campaign: Tropical Composition, Cloud and Climate Coupling (TC4). The presented analysis is based on observations recorded during 11 NASA DC-8 research flights conducted from San Jose, Costa Rica. The DC-8 aircraft was equipped to make in-situ measurements of a comprehensive suite of trace gas as well as particle chemical composition, optical properties, and microphysical properties. In addition, the onboard DIAL lidar provided profiles of ozone simultaneous with multi-wavelength scattering and depolarization measurements from aerosols and clouds. The DC-8 boundary layer and lower troposphere observations allow us to characterize and contrast chemical, microphysical, and optical properties of the particles over the tropical Eastern Pacific and Caribbean regions. The preliminary analysis of filter-based chemical composition measurements along with particle scattering, absorption, size distribution, and loading measurements suggests: 1) Significantly larger particle loading was observed over the Caribbean, which is at least qualitatively consistent with model predictions; 2) Sea-salt appears to be the major component in both regions, contributing to about 65% of the total observed mass; and 3) Both Eastern Pacific and Caribbean particles showed indications of significant anthropogenic influences and impact of long-range transport of the Sahara dust. The DIAL observations also shows signature on Sahara dust on both side of isthmus, while the Caribbean side has higher levels of dust scattering and depolarization. In addition, volcanic plumes were sampled off the coast of South America, showing elevated levels of sulfate, particle scattering and volume. By contrast, the derived particulate organic matter is believed to be the dominant component of the particles strongly influenced by biogenic emissions which is identified by high levels of gas phase isoprene. The implications of the observed particle characteristics in different regions to cloud microphysics will also be discussed.

Using polydisperse CCN activity measurements to understand aerosol compositional impacts on droplet growth kinetics. ATHANASIOS NENES (1), Sara Lance (2), Akua Asa-Awuku (1), Luz Padro (1), Richard Moore (1), (1) Georgia Institute of Technology, Atlanta, GA (2) NOAA, Boulder, CO

The impact of aerosol composition on the water vapor mass transfer coefficient is a highly uncertain aspect of cloud droplet formation. Measurements of Cloud Condensation Nucleus (CCN) activity are ideally placed for resolving this, as they operate by nucleating droplets and subsequently growing them to a detectable size; if droplet detection is sensitive to size, one can then use this to constrain compositional impacts on growth kinetics. Ideally, the CCN instrument should activate CCN previously classified in a Differential Mobility Analyzer (DMA). Most CCN measurements however are not carried out in this way; instead, a polydisperse aerosol (e.g., ambient samples) is introduced, and CCN concentrations are counted as a function of instrument supersaturation. Droplet kinetic information can still be retrieved, and is the focus of this talk. The method, termed 'threshold droplet growth analysis' (TDGA), is based on comparing the droplet sizes measured during the activation of ambient aerosol, against those obtained from experiments using calibration aerosol. When this is done over a range of climatically-relevant supersaturations, one can clearly see the signature of delayed growth kinetics. We present examples of TDGA using CCN measurements obtained from a Droplet Measurement Technologies Continuous Flow Streamwise Thermal Gradient chamber deployed in six field campaigns during the period of 2004-2008.
**10B.01**

How accurately can CCN concentrations be calculated without measuring aerosol chemical composition?

BARBARA ERVENS (1,2), Mike Cubison (1), Elisabeth Andrews (1,2), Graham Feingold (2), Jose Jimenez (1,3), John Ogren (2), (1) CIRES, University of Colorado, Boulder (2) NOAA, Earth System Research Laboratory, Boulder (3) Dept. Chemistry and Biochemistry, University of Colorado, Boulder

Knowledge of the of cloud condensation nucleus (CCN) number concentration is crucial in order to describe the influence of aerosol on clouds. The ability of aerosol particles to act as CCN depends on their size, hygroscopicity, and, thus, chemical composition.

Many CCN closure studies have been performed in the past by using models of different complexity in order to explain measured CCN concentrations. The conclusions from these studies have been ambiguous in terms of key parameters that are essential for successful CCN closure.

We have used CCN data from a variety of field experiments at different locations where CCN concentrations, size distributions, chemical composition and/or other measures of hygroscopicity have been determined. The analyzed aerosol populations differ with respect to source region (marine, rural, urban), total aerosol loading, composition, age and mixing state.

Based on this overview, we conclude that under many conditions, measurements of hygroscopicity (e.g., RH-dependence of particle size, g(RH), or light scattering coefficient, f(RH)) are sufficient to predict CCN, and assumptions of chemical composition can be largely simplified. For the conditions studied, detailed information on size-resolved aerosol properties (composition, mixing state) is needed only in immediate proximity to sources when the aerosol is fresh and poorly mixed.

These conclusions will help to simplify the description of aerosols as CCN in large scale models as a function of location and sources.

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**10B.02**

Uncertainty in global CCN concentrations from aerosol nucleation, primary emissions and SOA.

JEFFREY PIERCE, Peter Adams, Carnegie Mellon University

Much of the uncertainty in the indirect effects of aerosols on climate stems from uncertainties in the prediction of pre-industrial or present-day Cloud Condensation Nuclei (CCN) concentrations. It is important to explore the causes of CCN uncertainty in order to focus on improving the understanding of the most important processes. We explore the contribution of present-day uncertainties in aerosol nucleation, primary emissions and Secondary Organic Aerosol (SOA) to uncertainties in CCN globally using the GISS GCM II-prime (Hansen et al, 1983) with online aerosol microphysics (Adams and Seinfeld, 2002). The sensitivity of CCN to the nucleation rate is found by using two nucleation parameterizations that give low (Vehkamaki, 2002) and high (Napari, 2002) nucleation rates. The difference in simulated nucleation rates between these two parameterizations is six orders of magnitude, globally. Primary emissions mass and number are varied by a factor of 3 to represent uncertainty in emissions estimates. The SOA condensation rates are varied by a factor of 3.5, consistent with Kanakidou et al. (2005).

The tropospheric-average CCN(0.2%) concentrations are 16% greater with the high nucleation parameterization than with the low nucleation parameterization, 16% greater with the high primary emissions than with the low primary emissions and 12% greater with the high SOA condensation than with the low SOA condensation. These results show roughly equal importance of each of these process uncertainties.

Models that estimate the formation of cloud condensation nuclei (CCN) from nucleated particles currently rely on growth rates based on sulfuric acid condensation. These growth rates are often at most 10% of the measured growth rate during a nucleation event and therefore lead to underestimations of the CCN production rate. The growth of nucleated particles from the lower detection limit (~3 nano-meter) to a representative size of CCN (100 nano-meter) has been modeled based on measured growth rates and size distributions from field campaigns in diverse atmospheric environments. The particle growth is simulated by solving the time-dependent general dynamic equation along a growth trajectory using the measured growth rate and accounting for particle production due to coagulation and particle loss through self-coagulation and scavenging by the pre-existing aerosol. The probability that a nucleated particle would survive to CCN size was calculated to be between 1 and 10%, several orders of magnitude larger than what would be predicted using particle growth rates based on sulfuric acid condensation alone.

The effects of aerosol composition (especially from organic species) on the cloud droplet formation process is highly variable and uncertain, but can be largely constrained by size-resolved measurements of Cloud Condensation Nucleus (CCN) activity (SRCM). A fast method for SRCM is Scanning Mobility CCN Analysis (SMCA; Nenes and Medina, in review), where the monodisperse aerosol output from a Differential Mobility Analyzer sampling ambient aerosol (and operated in scanning voltage mode) is concurrently introduced into a Streamwise Thermal Gradient CCN Chamber (STGC) and a Condensation particle counter; inversion of the concentration timeseries from both detectors yield the activation ratio (i.e., fraction of particles that act as CCN) and size of activated droplets, as a function of dry mobility diameter and supersaturation. From such measurements, Kohler Theory Analysis (e.g., Asa-Awuku et al., ACP, 2008; Moore et al., GRL, 2008; Padro et al., ACP, 2007) can be applied to infer the presence of surfactants, the average molecular weight of water-soluble organics and the impact of organics on droplet growth kinetics. In this study, we performed SMCA for aerosols sampled aboard the CIRPAS Twin Otter during the Marine Stratus/Stratocumulus Experiment II (MASE II) in Marina, CA in July 2007. We focus on two research flights, one carried out in marine air and one downwind of a large bovine source in the San Joaquin Valley, California; the differences seen in water-uptake properties, droplet growth kinetics as a function of organic content and character are presented.
10B.05
The Importance of Mixing and Ageing for the Evolution of CCN in Urban Plumes: Airborne CCN Measurements and Closure during TEXAQS 2006. AKUA ASA-AWUKU (1), Richard Moore (1), Chuck Brock (2), Roya Bahreini (2), Ann Middlebrook (2), Joshua Schwarz (2,3), Ryan Spackman (2,3), John Holloway (2,3), Dave Tanner (1), Greg Huey (1), Athanasios Nenes (2), (1) Georgia Institute of Technology, (2) NOAA, Boulder, (3) University of Colorado, Boulder

Predicting the concentration of particulate matter that can act as cloud condensation nuclei (CCN) is at the heart of quantifying the aerosol indirect effect. Although the theory of predicting CCN activity is well established, calculation of CCN concentration requires a substantial amount of information, being the aerosol size distribution, chemical composition and mixing state. Given the large uncertainty associated with predicting these aerosol properties, (especially for the highly heterogeneous aerosol close to source regions) it is very important to quantify the CCN prediction uncertainty associated with simplifying assumptions taken in aerosol models. In this study, airborne aerosol and CCN measurements collected aboard the NOAA WP-3D platform during the 2006 Texas Air Quality Study/Gulf of Mexico Atmospheric Composition and Climate Study (TexAQS/GoMACCS) are analyzed. Over a total of 10 flights (from September 20 to October 10, 2006), freshly emitted and aged aerosol was sampled in the vicinity of Houston, eastern/northeastern Texas and the northwestern Gulf of Mexico. The analysis focuses on the importance of chemical heterogeneity (size-dependant chemistry and mixing state) and aerosol size distribution function for achieving CCN closure, as a function of particle ageing. The relative contribution of particle ageing versus entrainment of background aerosol to the CCN concentration is also examined.

12B.01
Cloud chemistry in eastern China. Jeffrey L. Collett, Jr. (1), Xinhua Shen (1), Taehyoung Lee (1), Xinfeng Wang (2), Wenxing Wang (2), and Tao Wang (3), (1) Atmospheric Science Department, Colorado State University, Fort Collins, CO (2) Environment Research Institute, Shandong University, Jinan, China (3) Civil and Structural Engineering Department, Hong Kong Polytechnic University, Hong Kong

Clouds are important processors of atmospheric trace gases and particles. Clouds play a substantial role globally in the transformation of gas phase sulfur dioxide to particulate sulfate. Strong economic growth in China has been accompanied by large increases in emissions of sulfur dioxide. In order to assess the ability of regional clouds to oxidize sulfur dioxide to sulfate, spring and summer field studies of cloud chemistry were conducted in 2008 at Mt. Tai in eastern China. Mt. Tai is an isolated peak on the NE China plain that is frequently intercepted by clouds and experiences air pollution transport from a variety of source regions. Samples of cloud water were collected at Mt. Tai with single and multi-stage Caltech Active Strand Cloudwater Collectors and analyzed for pH and concentrations of major inorganic ions, total organic carbon, S(IV), hydrogen peroxide, Fe, Mn, and organic acids. The study also included measurements of PM2.5 composition and key trace gases including sulfur dioxide, ozone, hydrogen peroxide, ammonia, and nitric acid. This presentation will provide an overview of the composition of clouds measured in this region, will examine factors controlling cloud pH, and will examine the capacity of the atmosphere to support aqueous phase sulfur oxidation by hydrogen peroxide, ozone, and oxygen (catalyzed by Fe and Mn).
Previous research on multi-component organic mixtures containing up to 10 different compounds has provided interesting data on aerosol hygroscopic growth. For various mixtures of organics, some experiments have indicated continuous growth while other mixtures show restructuring and distinct deliquescence points. Research on super-micron particles has shown a relationship with phase state of the initial particles and deliquescence which may also extend to sub-micron particles and to cloud activity. This has important implications for the comparison of laboratory and field data on aerosol-water interactions and ultimately for understanding the aerosol indirect effect.

In this work, we will present results of experiments measuring hygroscopic growth (using HTDMA), cloud condensation nuclei activity (using CCNC), and phase state/morphology (using AFM) of various mixtures of up to 10 different common organic aerosol components. Additionally, we have analyzed the aerosol generation process typically used in laboratory studies (solution atomization and subsequent drying) to determine what parameters affect the resulting aerosol and its properties. We have investigated the influence of different types of atomizers, solvents, solution concentrations, drying rates and residence times, and temperatures on the resulting particles.

The results indicate that the particular method used to generate aerosols in the laboratory can have an important affect on aerosol morphology and phase state. The resulting aerosol hygroscopic properties are similarly altered with obvious relationships between hygroscopic growth and CCN activity.
12B.04

Real time measurements of atmospheric aerosols can be used to obtain new insights into the sources and processes producing them. On-line single particle mass spectrometry provides measurements of individual particle size and chemistry, detailing the specific associations or mixing state of chemical species within individual particles. Specifically, these instruments can be used to probe how secondary species including sulfate, nitrate, ammonium, and organics are distributed between various primary particles types such as dust, sea salt, organic carbon, and soot. High temporal resolution allows one to measure how individual particle size, chemistry, and optical properties evolve over time. This presentation will focus on field and lab studies and describe some unique aspects of aerosol chemistry that single particle mass spectrometers are being used to address. These include details on the mixing state of ambient particles in urban, rural, and marine environments at a number of locations around the world. A discussion will be presented, using recently acquired aircraft data, on how mixing state changes as a function of altitude. Finally, details on the mixing state of individual cloud and ice nuclei, as well as the optical properties as a function of size and mixing state will be discussed. The current focus involves integrating this newly acquired information on size-resolved mixing state and optical properties in atmospheric models in order to allow more accurate predictions to be made on our future climate.

12B.05
Closure-type Experiments Comparing Ice Nucleation by Atmospheric Aerosols and Ice Formation in Clouds. PAUL DEMOTT (1), Markus Petters (1), Anthony Prenni (1), Trude Eidhammer (1), Sonia Kreidenweis (1), Cynthia Twohy (2), Ottmar Moehler (3), Kerri Pratt (4), Kim Prather (4), David Rogers (5), Andrew Heymsfield (5), Daniel Cziczo (6,7) and Stephane Gallavardin (7), (1) Colorado State University (2) Oregon State University (3) Forschungszentrum Karlsruhe (4) University of California, San Diego (5) NCAR (6) Pacific Northwest National Laboratory (7) ETH-Zurich

To understand and predict potential impacts of changing atmospheric composition on the properties of clouds containing the ice phase, it is necessary to validate the ability to predict ice formation from the ice nucleating properties of atmospheric aerosol particles. We have conducted closure-type studies in the laboratory using known atmospheric ice nucleating aerosols (mineral dusts and bacteria) and in the atmosphere where the compositions are unknown a priori. Both studies utilized the Colorado State University continuous flow diffusion chamber (CFDC-1H) for ice nuclei (IN) measurements, exposing aerosol particles to a range of temperatures and water saturation ratios appropriate to the clouds examined. Laboratory measurements were conducted during the Fourth International Ice Nucleation Workshop (ICIS-2007), in which clouds were formed on aerosols during simulations in the AIDA cloud chamber at Forschungszentrum Karlsruhe. Field studies were performed in the Ice in Clouds Experiment - Layer clouds (ICE-L) where the particular focus was on orographic wave clouds with well-defined flow structure and limited depth, thereby allowing for isolating measurements in cloud entry air and in regions where ice is just forming. In both studies, aerosols were sampled directly by the ice nuclei instrument, from an aerosol chamber and from an ambient air inlet, respectively, or as residual nuclei of cloud particles using counterflow virtual impactors. Our results demonstrate the ability to explain ice formation in both laboratory and real clouds using detailed ice nuclei measurements. Based on the field data, we note that IN number concentrations are most closely associated with the concentrations of larger aerosol particles, and show contributions from primarily mineral dusts and biological ice nuclei. Aerosol processing and interaction with pollution may be associated with negative impacts on IN activation based on preliminary analysis.
The single particle soot photometer (SP2) measures black carbon (BC) using laser incandescence. During the Ice in Clouds Experiment (ICE-L) conducted over Colorado and Wyoming in November/December 2007, the SP2 was operated downstream of a counterflow virtual impactor (CVI) onboard the NCAR C-130 aircraft, when the plane passed through a cloud. The CVI collects cloud droplets and ice crystals larger than 5 micrometer and evaporates the water content, so that residual nuclei are sampled. The CVI also concentrates the incoming air-stream by as much as a factor of 30 or more. The combination enables measurements of BC lower than 1 ng/m$^3$. Preliminary results indicate that compared to aerosol in the surrounding air mass, black carbon concentrations (per unit volume air) were generally lower in cloud. During the November 16, 2007 flight, two wave clouds were sampled near Riverton and Wheatland, WY at altitudes between 6-8 km above sea level. While BC mass concentrations upwind of the clouds were less than 10 ng/m$^3$, in-cloud values were one to two orders of magnitude lower. BC mass concentrations in-cloud when normalized to cloud water content are on average between 19-64 ng/g-water in the Riverton cloud. In the cloud nearer Wheaton, BC averaged 15 ng/g-water, though concentrations varied from 1-100 ng/g; there does not appear to be a dependence on altitude within the cloud. These average values are in the range of previous literature results. Data on BC scavenging ratios and their relation to cloud water content will also be presented, as will BC measurements in upslope conditions.
1B.01
Worldwide Aerosol Chemistry: From Hemispheric Distributions to Megacity Sources. G. M. Hidy, Envair/Aerochem

A survey of more than 300 research results reported since the 1990s provides an up-to-date picture of bulk aerosol chemistry at surface levels across the earth's northern and southern hemispheres. On the average, the worldwide distribution of fine particles on a continental scale is generally dominated by non sea-salt sulfate and organic carbon, with lesser contributions of ammonium, nitrate, chloride and elemental carbon. The crustal elements and trace metals also contribute small amounts of fine particle mass, with much larger occasional contributions during certain events such as dust storms, wildfires or volcanic disturbances. Using a synthesis of disparate data, the continental scale geographical distributions of fine particles is deduced. The average particle distribution by mass depends on the proximity of major sources of particles and their precursors, most of which are continental in origin, with contributions from sea salt emissions in the marine environment. The highest concentrations are found downwind from the continents; megacities of population greater than 10 million people and coincident industry or transportation are particularly important sources for large scale aerosol concentration patterns. These giant communities are generally found in the mid-latitudes, creating a band of concentration gradients across the northern hemisphere, reflecting long-range transport with the westerly winds. The data from this survey complement contemporary estimates of aerosol distributions from global scale models.

1B.02
Aerosol Transport across the Arctic: Results from Alaska and Greenland. CATHERINE CAHILL (1), Thomas Cahill (2), (1) University of Alaska Fairbanks, (2) University of California, Davis

Aerosol measurements conducted at locations in the Arctic and sub-Arctic, such as Barrow and Denali National Park and Preserve, Alaska, and Summit Station, Greenland, demonstrate that aerosols capable of impacting the radiative balance of the Arctic regularly enter the Arctic from China and other mid-latitude sources. The aerosol measurements at Summit Station and associated backwards-trajectory modeling, show that in spring aerosols from China effectively transport in elevated layers across the North Pole and deposit in the Greenland ice sheet. This transport is similar to Arctic Haze, the transport of anthropogenic aerosols from Northern Europe and Russia around the Arctic, in its layered nature and effective transport of aerosols around the Arctic. In contrast to the Chinese aerosols, the sulfate and other aerosols from the United States are too fine to be deposited effectively to the Greenland ice sheet. In addition, the aerosols in the pristine, continental site of Denali National Park and Preserve contain higher concentrations but the same elemental ratios for major species as the aerosols reaching Summit. This implies that the aerosols are not being significantly transformed during their trans-pole transport.
1B.03
Ice Nuclei Measurements in the Amazon Basin. MARKUS PETTERS, Anthony Prenni, Paul DeMott, Sonia Kreidenweis, Colorado State University, Department of Atmospheric Science, Fort Collins, Colorado, USA

The Brazilian Amazon Basin is the largest intact tropical forest in the world, covering four million square kilometers. Interestingly, precipitation in the Amazon Basin exceeds that of its African counterpart, the Congo Basin, by roughly a factor of two and this difference is thought to be due to differences in the aerosols on which the clouds form. Tropical forests emit large numbers of particles directly to the atmosphere, including bacteria, pollen, spores, algae, protozoa, fungi, and leaf fragments. Secondary organic aerosol also forms from emissions and subsequent oxidation of biogenic gases. In their natural environment the ice nucleation ability of these particles has not been studied to date. In addition to surface sources, large quantities of wind-blown dust from North Africa reach the Amazon Basin during the wet season. Here we present ice nuclei measurements obtained over a one month period in February/March 2008 during the AMazonian Aerosol characteriZation Experiment (AMAZE-08). We focus on ice formation at temperatures relevant to mixed-phase cumulus clouds (-30 to -10 Celsius) characterizing ice nuclei number concentrations using the Colorado State University continuous flow diffusion chamber and their composition and using transmission electron microscopy.

1B.04
The Role of the Breakdown of the Nocturnal Boundary Layer in Particle Nucleation. R.J. BARTHELMIE (1,2) and S. C. Pryor (1) , (1) Atmospheric Science Program, Indiana University, Bloomington, IN 47405 (2) University of Edinburgh, Edinburgh, UK

Particle nucleation has been observed in most environments from remote to urban. As noted in many studies, nucleation events typically require a relatively clean atmosphere (low condensational sink) with relatively high net radiation levels (and hence possibly photochemical precursors). Nucleation frequently occurs during the early to mid-morning hours as the surface layer of the atmosphere that has become decoupled overnight is re-coupled to the overlying boundary-layer. This implies a critical role for vertical exchange and/or turbulence. There are several possible mechanisms at work e.g. the overlying boundary layer is relatively less polluted such that entrainment of this 'clean' (low condensational sink) air downward triggers particle nucleation when mixed into the near-surface layer or the overlying atmosphere contains key chemical ingredients such as sulfuric acid or lower humidity/higher temperatures, or the overlying air contains a high concentration of freshly nucleating particles. We present data to examine the structure and turbulence conditions of the boundary-layer as the nocturnal boundary-layer is eroded above a deciduous forest in southern Indiana. This is linked to an intensive field campaign (Nucleation In ForesTs: NIFTy) examining nucleation which is supported by extensive particle and atmospheric chemistry measurements. Our focus here is to examine the structure of the lower boundary-layer preceding and during nucleation events using data from an upward looking Doppler lidar that monitors wind speed components and turbulence with a high degree of both accuracy and precision in the first 200 meters and meteorological profiles obtained with a tethersonde up to 1 km. The aim is to determine whether nucleation events first observed above the canopy are associated with increased vertical exchange in the near-surface layer and to identify the role of different meteorological variables in triggering nucleation events.
1B.05  
**Nucleation and growth in/over a deciduous forest: How important are the trees?**  
S.C. Pryor (1) R.J. Barthelmie (1,2) A.M. Spaulding (1) A. Rossner (3) B. Crimmins (3) P.K. Hopke (3) L. Mauldin (4) T. Jobson (5), (1) Atmospheric Science Program, Indiana University, Bloomington, IN 47405 (2) University of Edinburgh, Edinburgh, UK (3) Clarkson University, Potsdam, NY (4) NCAR/ACD, Boulder, CO (5) Washington State University, Pullman, WA

We present 18 months of data from continuous measurements of particle size distributions (6 to 400 nm) at three-levels above and within a deciduous forest in southern Indiana (within the Ohio River Valley). These data are collected using two SMPS and one FMPS, and are supplemented with data concerning the spatial extent and the composition of ultra-fine particles using samples collected during May 2008 as part of the Nucleation In ForesTs (NIFTY) campaign. During this field experiment we will enhance the ongoing data collection at the forest site to include sulfuric acid, ammonia and VOC concentrations, and particle composition using two MOUDI-nano-MOUDI combinations. We will further instrument two additional sites - one directly south of the forest in a relatively rural setting, and one to the north in the city of Indianapolis.

The measurements presented herein are being collected in order to assess the frequency and characteristics of nucleation events and high ultra-fine particle concentrations in this rural (but regionally polluted) setting, including the chemical composition of the ultra-fine particles, the principal mechanisms of nucleation, limitations on nucleation and growth and the ultimate fate of the resulting ultra-fine particles.

The long-term data indicate; (i) nucleation is most frequently observed in spring, but occurs in all seasons, (ii) subsequent growth is more rapid during leaf-on, (iii) recently nucleated particles are always observed first at the upper-most sampling height. We present the data behind these assertions and also in terms of the classification of nucleation events developed by the University of Helsinki. We will then present observations along a north-south gradient in southern Indiana to identify the coincidence of nucleation in rural, forested and urban environments and contrast their growth patterns. We will further examine the relative importance of inorganic and organic species to the newly formed and aged particles.

3J.02  
**Cost Analysis of Impacts of Climate Change on Regional Ozone and PM2.5.**  
Kuo-Jen Liao (1) Efthimios Tagaris (1) Kasemsan Manomaiphiboon (1,3) Jung-Hun Woo (2,4) Praveen Amar (2) Shan He (2) Armistead G. Russell (1), (1) School of Civil & Environmental Engineering, Georgia Institute of Technology, Atlanta, GA, USA (2) Northeast States for Coordinated Air Use Management (NESCAUM), Boston, MA, USA (3) Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand (4) Department of Advanced Technology Fusion, Konkuk University, Seoul, Korea

Under the impacts of global climate change, it is important to quantify the economical impacts of climate change on regional air quality management if meteorological fields affect direction and magnitude of currently planned emission controls for improving future air quality. The objective of this study is to estimate the reductions required in precursor emissions and associated costs for offsetting the impacts of climate change on regional air quality. Here we use a United State Environmental Protection Agency's regional air quality model to investigate the impacts of climate change on regional ozone and PM2.5 and an economical model to estimate the associated costs of emission reductions for offsetting those impacts for five cities in the continental U. S. in the future. Future climate change is assumed to follow the IPCC A1B emission scenario, which assumes a future world of rapid economic growth with a balance between fossil and non-fossil energy sources. For the worst-case scenario and based on present emission control technologies, costs of emission reductions for offsetting impacts of climate change on regional peak fourth-highest daily maximum 8-h average ozone and yearly average PM2.5 are predicted to range from about $27 million to $5.9 billion of 1999 dollars in 2050s for the five examined in this study. Total costs of emission reductions for simultaneously offsetting climate impacts on ozone and PM2.5 for the five cities are predicted to be about $11 billion of 1999 dollars.
A Conceptual Model for PM-2.5 High Concentration Days over Southeast Michigan. 

JAY TURNER, Washington University in St. Louis

In 2006, the USEPA promulgated revisions to the National Ambient Air Quality Standard (NAAQS) for particulate matter (PM) which tightened the 24-hour (daily) PM-2.5 standard from 65 to 35 micrograms per cubic meter. This revision profoundly increased the frequency of exceedance days observed in Southeast Michigan with fourteen of the fifteen compliance monitors violating the standard for the period 2004-2006. An understanding of the drivers for high PM-2.5 days is needed to support the development of effective controls strategies and a study was undertaken to provide insights into such drivers. This analysis exploited PM-2.5 routine compliance monitoring data as supplemented by fine particle speciation data and surfaces winds. At most sites in Southeast Michigan, exceedances occur predominantly - and in some cases exclusively - on days when the entire Southeast Michigan network is exhibiting high PM. In most cases, exceedances were observed when the area was experiencing a multiday high PM episode. In contrast, two monitors - Dearborn and Wyandotte - frequently had exceedances on days when the entire network was not exhibiting high PM with 38% of the Dearborn exceedances and 27% of the Wyandotte exceedances occurring on such days. On these days, these sites are significantly influenced by nearby emission sources. A network-wide base concentration was defined for each day and the distribution of excess mass at each site, relative to the base concentration, was examined using nonparametric wind regression (NWR). This approach clearly identified the urban plume emanating from Detroit including a plume associated with a large industrial region west/southwest of the central business district. NWR was used to identify site-specific temporal changes in the expected excess mass concentration as a function of wind direction over the past nine years, and the observed decreases in expected concentrations are consistent with known point source emission reductions.

Measurement of SOA Precursor Compounds in the Nucleation In ForesTs (NIFTY) Campaign.

Alan Rossner (1), BERNARD CRIMMINS (1), Philip K. Hopke (1), Sara C. Pryor (2), (1) Clarkson University, Potsdam (2) Indiana University, Bloomington

As part of the Nucleation In ForesTs (NIFTY) campaign, volatile organic compounds (VOCs) were quantified in the Morgan-Monroe State Forest (MMSF) in southwestern Indiana in May 2008. This facet of the study was to assess the role of secondary organic aerosol (SOA) precursors (biogenic and anthropogenic) in particle nucleation. Two complementary sampling schemes were deployed in the deciduous forest. A series of multi-sorbant tubes and small canisters collected samples at two and six hour intervals, respectively. The resulting samples were analyzed by GC/MS for biogenic (alpha- and beta-pinene, isoprene) and anthropogenic (substituted aromatics) VOCs. The daily evolution and diurnal variation of VOC concentrations will be presented. The role of these VOCs in particle formation and growth will also be discussed.
5B.02 Measurement of Particle Concentrations above a Forest and Surrounding Farmland.

Daniel Valyou (1), Josh Butler (1), Erik Zito (1), Will Hull (1), Jon Hoffman (1), Pier Marzoceca (1), Suresh Dhaniyala (1), Philip K. Hopke (1), Rebecca Barthelmie (2), Steve Scott (2), Sara C. Pryor (2), (1) Clarkson University, Potsdam (2) Indiana University, Bloomington

Very little information is currently available regarding the spatial scales on which nucleation occurs in the near surface layer. As part of the May 2008 Nucleation In Forests (NIFTY) campaign, an unmanned aerial vehicle (UAV) system was flown across the study area of the Morgan-Monroe State Forest (MMSF). The Clarkson Vector-P UAV carried a TSI Model 3007 Condensation Particle Counter (CPC) and a Grimm Model 1.109 Universal Aerosol Spectrometer (UAS). The CPC provides the count of ultrafine particles while the UAS gives counts of large particles (0.25 to 20 µm). These measurements were designed to supplement the extensive measurements being made on the 46 m instrumented tower. Because of the FAA restrictions of line-of-sight observation of the UAV by ground observers, we were limited in the spatial extent and were limited to studying altitudes below 1200 feet. However, these restrictions still permitted us to make a series of measurements of the spatial and vertical extent of particle concentrations to support the ground level composition measurements to better understand nucleation and growth in this rural area of southwestern Indiana.

5B.03 Synoptic Scale Meteorological Controls on Particle Nucleation.

A.M. Spaulding (1), S.C. Pryor (1), R.J. Barthelmie (1,2), (1) Atmospheric Science Program, Indiana University, Bloomington, IN 47405, (2) University of Edinburgh, Edinburgh, UK

We present 18 months of data from continuous measurements of particle size distributions (6 to 400 nm) at three-levels above and within a deciduous forest in southern Indiana (within the Ohio River Valley). Data from two SMPS and one FMPS are being analyzed in terms of hypothesized links to large-scale (synoptic) meteorology. The occurrence of new particle formation, the persistence of nucleation and the subsequent growth behavior are thought to be strongly linked to physical parameters such as existing particle surface area, radiation, temperature and thermal structure of the atmosphere that in turn are products of the synoptic context. Here we classify the data using the classification derived by the University of Helsinki into nucleation class A, B and C and non-event days. The meteorological conditions that are associated with each class are then determined using surface synoptic charts in terms of the degree to which the different particle behaviors can be causally linked to synoptic scale conditions.
5B.04
Observations of Nucleation-Mode Particle Events and Size Distributions at a Rural New England Site. PHILIP PLACE, Robert Griffin, Luke Ziemba, University of New Hampshire

Particle number (PN) concentrations, particle size distributions, and particle compositions were measured continuously at the University of New Hampshire atmospheric observatory at Thompson Farm from 9 February to 4 April, 2007. A total of thirteen PN events were observed during this two month period, identified by PN concentration statistics. Events were subdivided into five different event types based on event duration and secondary measurements. Four of the five event types were observed, with the majority of events consisting of long-lived episodes, greater than five hours in duration, and associated with air mass backward trajectories from the clean northwest. Particle size distributions indicated increased number concentrations of nucleation-mode particles during event periods, along with particle growth of the nucleation-mode fraction. Particle diameter growth rates, determined from the geometric mean diameter of the 6-60 nm particle fraction ranged between 0.93 and 5.51 nm per hr. All events displayed steady particle growth rates, indicating the regional nature of PN events. Particle composition was measured with an Aerodyne quadrupole Aerosol Mass Spectrometer (Q-AMS), but particles during events did not grow past the lower limit of the Q-AMS. Also, preexisting aerosol concentrations, temperatures, and absolute humidities were found to be lower on PN event days; in contrast was solar radiation, which was increased on event days. Finally, theoretical particle growth rates from oxidation products of SO2, toluene, isoprene, and alpha-pinene were calculated and compared to measured growth rates.

5B.05

A 15-month ammonia air monitoring study was conducted at Boulder, Wyoming, in the Upper Green River Basin - a region experiencing rapid natural gas development with potential consequences of air quality and visibility impacts in the adjacent Class I Bridger Wilderness. The objective of this study is to characterize the local airborne nitrogen budget, specifically concentrations of ammonia and related gases and particles over one year. Samples were collected twice per week beginning December 15, 2006 and ending May 31, 2008, using coated annular denuders and stacked filters in a URG sampler, analyzed at Colorado State University's Atmospheric Science Department.

NH3 concentrations are variable throughout the year and below 1 ppbv for most of the monitoring period, peaking in August 2007 at 1.55 ppbv, with a yearly mean value of 0.24 ppbv. Concentrations are below or near detectable limits from December through February in 2007 and 2008. Elevated NH3 concentrations coincide with warmer summer months. A shift in ammonium nitrate equilibrium toward the gas phase might be responsible for some of this increase, although an increase in total reduced nitrogen (NH4+ plus NH3) during the summer suggests that changes in emissions and or transport patterns are likely also important contributors.

HYSPLIT back trajectories were used to identify the geographic source areas most likely to contribute to the highest measured ammonia days. Three back trajectories were generated per day, each hourly point along a 72-hour back trajectory path weighted with measured ammonia concentration at the end date of each trajectory. The ammonia values associated with each hourly point were summed and normalized into 1/4 degree horizontal grid cells. NH3 weighted residence time analysis indicates that much of the NH3 present is transported into the region from agriculture and urban areas to the West and Southwest.
5B.06
Phase Changes of Ambient Particles in the Southern Great Plains of Oklahoma, USA. SCOT T. MARTIN (1), Thomas Rosenoern (1), Qi Chen (1), and Donald R. Collins (2), (1) School of Engineering and Applied Sciences & Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA (2) Department of Atmospheric Sciences, Texas A&M University, College Station, Texas, USA

A new instrument, namely a 1x3 tandem differential mobility analyzer (1x3-TDMA), has been developed as purpose specific for the study of the phase of ambient particles. Its primary measurement is the irreversibility of the hygroscopic growth factor of aerosol particles, thereby taking advantage of the hysteresis of phase transitions to determine particle phase. The instrument, alongside an aerosol mass spectrometer, was deployed in June 2007 in the Southern Great Plains, Oklahoma, USA. In 101 runs, efflorescence occurred 70% of the time for particles sampled at ambient relative humidity, where an event is defined as at least 10% of the particles undergoing a phase transition. Deliquescence occurred in 11% of the runs. These percentages, however, are biased by the distribution of ambient RH values (67% median) because there was a strict correlation between occurrence of deliquescence or efflorescence and ambient RH. For example, deliquescence occurred only when the ambient RH was less than 40%, and this condition was met for only 20% of the 101 runs. For these cases, deliquescence was observed 65% of the time. Above 40% ambient RH, efflorescence occurred in 83% of the runs. The data set from the 1by3-TDMA regarding the phase and hence water content of ambient particles provides can be used for validating regional chemical transport models of particle phase.

5B.07
Volcanic Ash Collection and Characterization. PETER G. RINKLEFF, Catherine F. Cahill, University of Alaska, Fairbanks, Alaska Volcano Observatory

Volcanic ash poses a significant threat to aircraft safety, public health, and other human activities. However, little is known about the volcanological mechanisms responsible for forming fine primary volcanic ash, the reactions on ash surfaces that occur in volcanic plumes and the chemical reactions that occur as ash chemically ages during tropospheric transport. Volcanic ash from the 2006 eruption of Augustine volcano and the 2007 eruption of Pavlof Volcano have been collected with DRUM cascade impactors and analyzed for mass by β-gauge and elemental composition by synchrotron x-ray fluorescence. The aerosols collected during two different eruptive periods, the phreatomagmatic (the water and magma dominated, explosive phase) and magmatic (the magma only, continuous emission phase) eruptive phases, of Augustine Volcano show distinct size and compositional differences. Silicon-bearing aerosols collected during the phreatomagmatic eruption phase are mainly coarse mode (35-2.5 microns in aerodynamic diameter) while those during the magmatic phase are much smaller (< 2.5 microns). The measurements show that the shift in size and composition is due to different aerosol formation processes. Phreatomagmatic eruptions produce ash by mechanical fragmentation as magma comes in contact with water and rock grinds against rock in the vent. Magmatic eruptions form ash either by mechanical disintegration of magma from brittle fracture of a foamy, viscous liquid, or by gas-to-particle conversion of magmatic volatiles. Further analysis of aerosol morphology and composition by environmental scanning electron microscopy, atomic force microscopy, and electron microprobe are being conducted to confirm these volcanic ash formation processes, determine the degree of surface alteration ash particles experience, and identify the types of coatings formed on ash surfaces.
5B.08

Estimation of the contributions of long-range transport on high concentration events of PM10 in Seoul, Korea.

KYE SEON KIM, Jong Bae Huh, Hyun Sun Kim, Eun Mi Choi, Seung Muk Yi, Graduate school of public health, Seoul National University

Korea has been interested in the degradation of air quality by the long-range transport (LRT) since Korea is mostly downwind from China. The objective of this study was to investigate the contributions of long-range transport on high concentration events of PM10 by looking at the enhancement ratios such as \( \Delta \text{PM}_{10} / \Delta \text{CO} \) in Seoul, Korea. The concentrations of PM10, SO2, NO2, O3, and CO were obtained from real-time ambient air monitoring stations located in GwangHwa Island (one of national background sites) and in Seoul (27 stations) from January 2005 through December 2006.

In this study, there were many well-defined periods of enhancements in CO and PM10 concentrations. The high concentration events were defined when the average 24 hours PM10 concentration was more than 100 micro-gram per m\(^3\) and were observed totally 51 events during the study period. CO concentrations during those events were not similar to the typical patterns of CO concentrations that show high concentrations during the traffic rush hours indicating that those events were affected by the other sources rather than traffic source. Among 51 events, about a half of the events were associated with high \( \Delta \text{PM}_{10} / \Delta \text{CO} \) ratios above 0.04 indicating that LRT attributed to about 51% of high PM10 concentration events in Seoul, Korea. The previous studies also suggested that the CO enhancement ratios could be used to identify the source contributions from LRT compared to those from local sources.

5B.09

Aerosol organic and inorganic chemical composition at a high himalayan station (5079 m asl).

Claudio Carbone (1), M. CRISTINA FACCHINI (1), Stefano Decesari(1), Emanuela Finessi(1), Matteo Rinaldi(1), Lara Giulianielli(1), Paolo Bonasoni(1), Angela Marinoni(1), Paolo Cristofanelli(1), Francescapiere Calzolari(1), Rocco Duchi(1), Paolo Laj (2), Elisa Vuillermoz (3) and Sandro Fuzzi (1), (1) Institute of Atmospheric Sciences and Climate, CNR, Bologna Italy (2) Laboratoire de Meteorologie Physique Observatoire de Physique du Globe de Clermont-Ferrand Universite Blaise Pascal- CNRS (3) EV-K2-CNR Committee, Bergamo, Italy

High mountain stations, located far from direct anthropogenic emissions, are ideal sites for monitoring the atmospheric background conditions and can provide reliable information on pollution levels in the free troposphere as well as in studying regional and long range transport phenomena. The Himalayan ridge is located between China and India, two of the most rapidly developing countries and primary sources of pollution at the regional and global scale. In this region, the so-called ‘Asian Brown Cloud’ (ABC), a haze layer thick up to 3 km formed by the accumulation of pollution aerosol and trace gases has been seen extending from the Indian Ocean to the southern slopes of Himalayas. This phenomenon strongly impacts air quality, visibility and the energy budget of the atmosphere over the entire Indian sub-continental area. In the framework of the Ev-K2-CNR ‘SHARE’ and UNEP ‘ABC’ projects, a remote monitoring station, the Everest-Pyramid GAW Observatory, was installed in the Khumbu valley at 5079 m a.s.l. with the aim of investigating changes in atmospheric composition due to human influence at different spatial scales (local, regional and global).

Since March 2006, continuous measurements of aerosol particles (optical and physical properties), ozone and meteorological parameters as well as time-integrated samplings of particulate matter (for chemical analyses) and halogenated compounds have been carried out. These measurements provide data on the background atmospheric composition and its variations in the Himalayan area, including its dependence on the seasonal cycles (dry, pre-monsoon, monsoon, post-monsoon). Here we discuss aerosol chemical features during different regimes of pollution transport, showing correlations between inorganic ions and organic species, and aiming to identify fingerprints of local and remote natural and anthropogenic sources.
5B.10
Long-term measurement of aerosol at Cape Hedo, Japan using a Q-AMS. AKINORI TAKAMI (1), Takao Miyoshi (1), Xiaoxiu Lun(1), Shungo Kato (2), Naoki Kaneyasu(3), Akio Shimono(4), Yoshizumi Kajii (2), Shiro Hatakeyama(5), (1) NIES, (2) TMU, (3)AIST, (4)Sanyu Plant Service, (5)TUAT

East Asia has been rapidly developed recently and emissions are increasing. In order to monitor the aerosol concentration and its chemical compositions, we have set up an Aerodyne aerosol mass spectrometer (Q-AMS) at Cape Hedo, Okinawa, Japan since 2003. Okinawa is located at the southern part of East China Sea, and air masses were transported from China, Japan, Korea, South East Asia and Pacific Ocean.

The Q-AMS results were compared with filter sampling data. According to the comparison of the sulfate data, the collection efficiency of Q-AMS was found to be greater than 0.5. The data at Cape Hedo show that sulfate is the main component and the molar ratio of ammonium to sulfate was often to be between unity and 0.5. This means that sulfate is in the mixture of ammonium sulfate and ammonium bisulfate.

High sulfate was often observed when the air mass was transported from the continental area. The average sulfate concentration in the spring time was 5.18, 5.88, 6.18, 5.51 microgram m^{-3} for 2004, 2005, 2006 and 2007, respectively. The sulfate concentrations measured by a filter method in early 1990s were about 3 microgram m^{-3}. Sulfate concentrations seems to increase recently.

The SO4/SOy (SOy = SO2 + SO4) ratio is often to be more than 0.8. This ratio indicates that the sulfur compounds were well oxidized. The signal at m/z=44 is considered to be a fragment of oxidized organics. The signal at m/z=44 to total organics were 0.15-0.2. In the urban area, it is less than 0.1. The organics were also oxidized well. The chemical analysis shows that chemical component in the fine aerosol was oxidized during transport.

Chemical compositions were analyzed as a function of transport time, route and gas species.

5B.11
Summertime Aerosol Size Distributions at Summit, Greenland. LUKE ZIEMBA, Robert Griffin, Jack Dibb, and Pieter Beckman, University of New Hampshire

Aerosol size distributions were measured at Summit, Greenland (3100 m above sea level, 71.38 N and 31.98 W) during the summer of 2007. Measurements were made every five minutes from 15 May through 16 June, probing particles from 5 to 198 nm in diameter using a scanning mobility particle sizer (SMPS) which consisted of an ultrafine condensation particle counter (UCPC) and nano differential mobility analyzer (nano-DMA). Total aerosol number concentrations (with diameters between 15 and 3000 nm diameter) were measured using an additional CPC. Both instruments sampled from a common inlet approximately one meter above the snowpack.

Observed aerosol number concentrations were extremely low, with a median concentration of 218 cm^{-3} and 5th and 95th percentile concentrations of 72.7 and 734 cm^{-3}, respectively. Number size distributions were dominated by Aitken-mode aerosol with a diameter mode at 26 nm. An additional number-size mode frequently was observed at approximately 130 nm. No evidence for new particle formation was observed, as particles with diameters smaller than 10 nm were not observed, potentially indicating a lack of sufficient precursor gases to facilitate nucleation at the site. Several periods dominated by a consistent 20-40 nm diameter mode were observed. These events lasted up to four days, and particle growth was sometimes observed during these times. Meteorological conditions during these events were variable, and back trajectory analyses indicated that airmasses arrived at the site after several days of travel over Greenland ice, suggesting the snowpack as a potential source for condensable gases. Sources of the observed Aitken-mode aerosol events are discussed.
Relationship between Aerosol Optical Properties and Chromatic properties of Perceived Visual Air Quality.

KYUNGWON KIM (1), Young J. Kim (2), (1) Gyeongju University, Korea, (2) Gwangju Institute of Science and Technology, Korea

Human can perceive visibility that varies with optically attenuating aerosols and relative humidity in the atmosphere. Visibility refers to the clarity with which distant objects are perceived. Actually perceived scenic image can be affected by the viewing angle, cloud characteristics, and color contrast between objects as well. In order to investigate the relationship between aerosol optical properties and chromatic properties of visual air quality, semi-continuous measurements of chemical composition for visibility impairing aerosol were made at the visibility monitoring station of Yonsei university in the urban area of Seoul, Korea during the seasonal intensive periods of 19 ~ 30 May, 6 ~ 16 July, 29 Sep ~ 8 Oct., and 15 ~ 24 Dec. 2007. These included measurement of aerosol elemental composition by a proton induced X-ray emission (PIXE) method and aerosol ionic composition by a ion chromatography (IC) method, and aerosol carbonaceous composition by a thermal optical transmittance (TOT) method. Light extinction, scattering, and absorption coefficients were measured simultaneously with a transmissometer, a nephelometer, and an aethalometer, respectively. Documenting perceived visibility events were conducted with a Cannon EOS-10D self-contained automatic camera system installed at the scenic monitoring site of Seoul Tower at Nam Mountain. A photograph of visual air quality was taken every 10 minute all day during the intensive monitoring periods. The chromatic parameters were calculated from the scenic images using the HSI color difference method. It was revealed that perceived visibility varied with light attenuation coefficients. The aerosol optical properties showed non-linear relationship with chromatic parameters.

Hourly Sulfate and SO2 Impacts at Look Rock, Great Smoky Mountains National Park: Implications for PM$_{2.5}$ and Visibility Standards.

Roger L. Tanner (1) Solomon T. Bairai (1) Kenneth J. Olszyna (2), Tennessee Valley Authority, Muscle Shoals Tennessee Valley Authority, Muscle Shoals (retired)

Planned changes in point source emissions in the southeastern USA and the Tennessee Valley could affect the concentrations of secondary PM$_{2.5}$ sulfate at the Great Smoky Mountains National Park (GSMNP), a Class I area. Recent advances in instrumentation have made available hourly data for both aerosol sulfate and fine mass at Look Rock, a sampling site on the western edge of GSMNP, for the periods, April 2003-December, 2004, November, 2006-present, and selected other summer periods. The measurements show persistent diurnal and seasonal patterns in both sulfate and fine mass which permit a more dynamic evaluation of the effects of regional reductions in SO$_2$ emissions on sulfate and fine mass levels in GSMNP than could be obtained historically from IMPROVE network 24-h filter sampling. Since sulfate is a major source of visibility impairment in Class I areas including GSMNP, the potential for long-term monitoring in support of the Regional Haze regulation is very promising. An examination of observed short-term plume impacts of SO$_2$ and aerosol sulfate at Look Rock indicates that contributions from nearby point sources of SO$_2$, although modest, are much greater than the contribution of primary and secondary sulfate from those same nearby plumes. This work thus shows that the contribution of sulfate to visibility impairment in the GSMNP shows no significant trends over the period of these hourly data sets, and is related more closely to meteorological variability and regional changes in precursor SO$_2$ emissions than to nearby point source emissions in eastern TN or western NC.
6B.02  

Measurements of gaseous ammonia and PM$_{2.5}$ ammonium from the Southeastern Aerosol Research and Characterization (SEARCH) study monitoring network are presented. SEARCH was designed and implemented in 1998-1999 in an effort to provide extensive long-term data on the sources and chemical characteristics of atmospheric particulate matter (PM). Routine measurements at SEARCH sites include trace gases (O$_3$, SO$_2$, CO, NO, NO$_2$, HNO$_3$ and NO$_y$), surface meteorology, filter-based fine and coarse PM mass and composition, as well as semi-continuous PM$_{2.5}$ mass and composition. Ammonia (NH$_3$) is the dominant base in the troposphere and forms ammonium salts with sulfuric and nitric acids that comprise a significant portion of atmospheric particulate matter. Since 2004, ammonia has been measured on a 24-hr integrated sampling schedule by citric acid impregnated annular denuders at all eight sites in the SEARCH network. Additionally, since mid-2007, continuous measurements of NH$_3$ have been made at three SEARCH sites (one urban and two rural) down to a 1-minute temporal resolution. The paper will present analyses of both 24-hr integrated denuder-based NH$_3$ measurements collected since 2004, as well as investigations of data from the recently initiated continuous NH$_3$ instrument. Trends of NH$_3$ in the southeast U.S. since 2004 will be presented in addition to analyses of individual high NH$_3$ concentration episodes. SEARCH measurements have previously indicated the importance of local confined animal feeding operations (CAFOs) as sources of ammonia. Analyses will be presented to investigate the potential for the formation of ammonium nitrate aerosol when urban plumes containing nitric acid and other reactive nitrogen interact with plumes of NH$_3$ from CAFOs.

6B.03  
Weekly cycles in United States aerosols. DANIEL MURPHY (1), Shannon Capps (2), John Daniel (1), Gregory Frost (1), Warren White (3), (1) NOAA Earth System Research Laboratory, Chemical Sciences Division (2) Georgia Institute of Technology, (3) Crocker Laboratory, University of Colorado, Davis

Data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network of aerosol samplers and NOAA monitoring sites are examined for weekly cycles. At remote and rural sites, fine particle elemental carbon, crustal elements, and coarse particle mass had pronounced (up to 20%) weekly cycles with minima on Sunday or Monday. Fine particle organic carbon and mass had smaller amplitude cycles, also with Sunday or Monday minima. There was no statistically significant weekly cycle in fine particle sulfate. The only species found with a weekend maximum was Pb, probably from general aviation on weekends. Aerosol optical properties at NOAA monitoring sites were consistent with the IMPROVE chemical data, with significant weekly cycles in aerosol light absorption but not light scattering. These results support a large role of diesel emissions in elemental carbon aerosol over the entire United States and suggest that a large fraction of the airborne soil dust is anthropogenic. They also suggest that studies of weekly cycles in temperature, cloudiness, precipitation, or other meteorological variables should look for causes more in light-absorbing particles and possible ice nucleation by dust rather than sulfate or total aerosol. There are also implications for personal exposure and epidemiological studies of aerosol health effects.
An important aspect of understanding regional particulate matter source-receptor relationships and atmospheric processes is estimating the lifetimes (or ages) of the different particulate matter species in an area of interest. Knowledge of the age of the aerosols can give us insight into the impacts of a variety of processes on these aerosol populations including transport, emissions, removal and even chemical transformation.

In an effort to theoretically estimate the age of aerosols as a function of space and time, we have developed a computationally efficient scheme to allow tracking of aerosol age within a three-dimensional Chemical Transport Model, PMCAMx. The aerosol age is tracked by utilizing the Particulate Matter Source Apportionment Technology (PSAT) algorithm (Wagstrom et al., in press) which allows the tracking of different source contributions to both primary and secondary particulate matter concentrations in the domain. To our knowledge, this is the first study of this nature that has been carried out to estimate explicitly the age of each aerosol component.

This study looks specifically at aerosol age in the Eastern United States. The ages found have been on the order of a few days for aerosols near the surface, but they are highly variable in space and time. The ages of both primary and secondary species will be discussed including elemental carbon, secondary organic aerosol, nitrate and sulfate. We will also discuss the change of age within the aerosol size distribution, the aerosol age at particular locations within the domain with respect to time and seasonal impacts on aerosol age. These results are compared to the results of different observation-based approaches (often called chemical clocks) for the estimation of the 'age of an airmass'.


Aerosols can scatter and absorb visible radiation, and as such they play an important role in the Earth's radiative balance. Their optical properties also affect visibility or visual range, and issues as varied as air traffic safety and the preservation of natural vistas. We have collected a multi-year data set of continuous measurements related to aerosol optical properties at our Pinnacle State Park research site in Addison, NY, a rural location south of the Finger Lakes Region. Available data include PM2.5 mass from a TEOM monitor, PM2.5 sulfate from a Thermo 5020 analyzer, PM2.5 thermal EC/OC and optical BC from a Sunset Labs carbon aerosol analyzer, and dry PM2.5 scattering from an OPTEC NGN-3 nephelometer. In addition to these multi-year data sets, we have 4 weeks of particle size distributions measured with nano- and long-tube SMPS instruments during the summer of 2004.

As a first look, we compute the empirical particle mass scattering efficiency (m2/g) for the aerosol at this site. The scattering coefficient is shown to exhibit discernible seasonal variation, with lower values in the summer. We also examine the long-term and episodic relationships between scattering efficiency and aerosol sulfate, EC, and OC. Sulfate aerosol dominates for a majority of the most intense scattering periods, but OC contributes significantly as well. A combination of the optical BC measurements from the Sunset Labs instrument with the scattering measurements from the nephelometer will allow us to compute an empirical estimate of the PM2.5 single scatter aerosol albedo at the site. Finally, the scattering data will be analyzed in relation to the volume size distributions measured during the 2004 intensive period. We will use the size distributions, in conjunction with composition information, to estimate scattering efficiencies and compare them to measured scattering coefficients from the nephelometer.
1A.01
Urban Air Quality in the Asian Region. PHILIP K. HOPKE (1), David D. Cohen (2), Bilkis A. Begum (3), Swapan K. Biswas (3), Bangfa Ni (4), Gauri Girish Pandit (5), Muhayatun Santos (6), Yong-Sam Chung (7), Perry Davy (8), Andreas Markwitz (8), Shahida Waheed (9), Naila Siddique (9), Flora L. Santos (10), Preciosa Corazon B. Pabroa (10), Manikkuwadura Consy Shirani Seneviratne (11), Wanna Wimolwattanapun (12), Supamaththree Bunprapob (12), Thu Bac Vuong (13), and Andrzej Markowicz (14), 1-Clarkson University, Potsdam, 2-Australian Nuclear Science and Technology Organisation, Menai NSW, Australia, 3-Bangladesh Atomic Energy Commission, Atomic Energy Centre, Dhaka Bangladesh, 4-China Institute of Atomic Energy, Beijing, 5-Bhabha Atomic Research Centre, Mumbai India, 6-National Nuclear Energy Agency, Bandung Indonesia, 7-Korea Atomic Energy Research Institute, Daedeon, Republic of Korea, 8-Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand, 9-Pakistan Atomic Energy Commission, Islamabad, Pakistan, 10-Philippine Nuclear Research Institute, Quezon City Philippines, 11-Atomic Energy Authority, Orugodawatta, Wellampitaya, Sri Lanka, 12-Thailand Institute of Nuclear Technology, Bangkok Thailand, 13-Institute of Nuclear Sciences and Technology, Hanoi, Vietnam, 14-International Atomic Energy Agency, Wien, Austria

Over the past decade, member states of the Regional Co-operation Agreement (RCA), an intergovernmental agreement for the East Asia and Pacific region under the auspices of the IAEA with the assistance of international organizations and financial institutions such as the World Bank and the Asian Development Bank, have started to set in place policies and legislation for air pollution abatement. To support planning and the effectiveness of the control programs, data is needed that focuses on both national and regional scale sources that affect urban air quality and thus, can produce significant adverse health and visibility effects in the high population cities. The focus is on the significant likely impact of particulate air pollution on human health and the potential mitigation of these impacts by identification and quantitative apportionment. The aim of this report is to provide an overview of concentration and composition of particulate air pollution, particularly its trends in the participating countries. For many of the large cities in this region, the measured particulate matter concentrations are greater than air quality standards or guidelines that have been adopted in developed countries.

1A.02
Air Pollution in South Asia: Findings from Multi-city Campaigns. Liaquat Husain(1,2), A.J. Khan (2) B.K. Farhana (2), Badar m. Ghauri (3), (1) Wadsworth Center, NYS Department of Health, Albany, NY 12201-0509. (2) Department of Environmental Health Sciences, School of Public Health, State University of New York, Albany 12201-0509. (3) Division of Space and Environment, SUPARCO, University Road, Karachi, Pakistan

Air pollution in South Asian cities has grown with the progressing industrialization and urbanization. The region is one of the most densely populated in the world, with present population densities of 100-500 persons km$^2$. There are six big cities, namely, Delhi, Dhaka, Karachi, Kolkata, Lahore, and Mumbai, each housing a population around or above 10 million. There is now a real concern about the sustainability of the region's ability to support the population due to air pollution, loss of biodiversity and soil degradation. The anthropogenic aerosols released from this region are projected to become the dominant component of anthropogenic aerosols worldwide in the next 25 years, and to significantly affect the global climate. Therefore, we conducted several extensive campaigns over last 10 years at Lahore, Karachi, and Islamabad in Pakistan to (1) chemically characterize the aerosols (PM$_{2.5}$ mass, concentrations of trace elements, ions, black and organic carbon), and (2) identify the major emission sources in this region.

Exceedingly high concentrations of all species, relative to major urban areas of US and Europe, were observed, and far exceeded WHO and US EPA air quality standard. We use air parcel back trajectories, intercomponent relationships and meteorological observations to explain chemistry and emission sources of aerosol constituents. Source apportionment was conducted using positive matrix factorization. The analysis has classified six emission sources of aerosol components, namely, industrial activities, wood burning, secondary aerosols, metal processing, vehicular emissions, and crustal and road dust. Findings of our study should play an important role in developing a strategy to regulate emissions, and to mitigate the long-term climate change in the region.
1A.03
Source Apportionment of Atmospheric Aerosols in Lahore, Pakistan. Suresh Raja (1), Biswas K. Farhana (2), Liaquat Husain (2,3), Philip K. Hopke (1). (1) Center for Air Resources Engineering and Science and Department of Chemical Engineering, Clarkson University, Potsdam, NY (2) NYS Department of Health, Wadsworth Center, Albany, NY (3) Department of Environmental Health and Toxicology, School of Public Health, State University of New York, Albany, NY

Samples of airborne particulate matter (PM2.5) were collected at a site in Lahore, Pakistan from November 2005 to January 2006. The samples were collected using a RAAS2.5-400 sampler and analyzed for major ion, trace metal, and organic and elemental carbon concentrations. The data set was then analyzed by positive matrix factorization (PMF) to identify the possible sources of the atmospheric aerosols collected from this urban area. Six factors could reproduce the PM2.5 sample composition. The sources include road dust, secondary aerosols, biomass burning, two-stroke vehicles, motor vehicles and industrial sources. The PMF results show that a quarter of the PM2.5 mass at this site comes from soil materials and road dust. Diesel vehicles and two-stroke vehicles contribute nearly a third of the PM2.5 mass. The biomass burning factor contributes about 20% of the PM2.5 mass. Nearly two-thirds of the PM2.5 mass is derived from carbonaceous material.

1A.04
Composition and Sources of Aerosols in a Rapidly Developing Megacity, Lahore, Pakistan. James J. Schauer (1), Tauseef A. Quraishi (2), Abid Mahmood (2), Elizabeth A. Stone (1) and Marya Orf (1). (1) University of Wisconsin-Madison (2) University of Engineering and Technology, Lahore, Pakistan

Lahore, the provincial capital of Punjab, is the second largest city of Pakistan with an area of about 1770 sq. km and a population exceeding 10 million and is growing at a rate of 3.3 percent per year. Lahore has severe air pollution with annual average PM2.5 and PM10 concentrations exceeding 175 ug m-3 and 350 ug m-3, respectively. Like many developing megacities, Lahore has very high emissions of particulate matter from mobile sources, waste combustion, localized power generation and industrial sources. In addition, Lahore is impacted by regional dust and regional air pollution. Clearly, there is a great need to better characterize the particulate matter in cities like Lahore to understand human exposure, develop effective mitigation strategies, and understand the impacts of these megacities on regional and global climate forcing.

Through collaboration between the University of Wisconsin-Madison and the University of Engineering and Technology (UET) in Lahore, Pakistan, PM2.5 and PM10 samples were collected every 6th day for the calendar year of 2007. PM10 samples were collected at two sites in Lahore and PM2.5 samples were collected at a single site. Samples were analyzed for particulate matter mass, organic and elemental carbon, water soluble ions, molecular markers, and trace metals. The results were used to determine the seasonal contributions of sources of fine and coarse particulate matter and to quantify the concentrations of toxic components of particulate matter in Lahore. Extremely high levels of particulate matter and toxic components of particulate matter were observed in Lahore, even in the comparison to other Megacities like developing Beijing and Mexico City.

Results of the study will be presented along with strategies to implement particulate matter studies and source apportionment in highly polluted Megacities that have not been adequately studied in the past.
1A.05
Direct climate forcing by diesel vehicles in Thailand. TAMIC. BOND (1), Ekbordin Winijkul (1), R Subramanian (1,2), Worrarat Thiansathit (3), Nguyen Thi Kim Oanh (3), Ittipol Paw-armart (4), and Peter Hess (5), (1) University of Illinois at Urbana-Champaign (2) Droplet Measurement Technologies (3) Asian Institute of Technology (4) Pollution Control Department, Thailand (5) Cornell University

Measures that improve urban air quality by reducing emissions of particulate matter also have climatic impacts. Here, we quantify the radiative impact of on-road diesel vehicles in Thailand by combining measured emission data, country information on vehicle fleet and driving conditions, and a global climate model.

We obtained data on 101 light- and heavy-duty vehicles by leveraging a vehicle characterization project implemented by the World Bank (DIESEL). We added our own measurements of climate-relevant properties for the particles: chemical composition, light absorption and water activity. We find that diesel emissions are about 40% elemental carbon, and that this fraction is not significantly different for high-emitting vehicles. Average emission factors for normal vehicles are 2.2 g/kg fuel. The absorption of the elemental carbon is about 40% higher than that assumed in radiative-transfer models. Despite the high-sulfur diesel used in Thailand, the particles are not hygroscopic.

Using country information on vehicle fleet and driving conditions, we estimate emissions of particulate matter for vehicles in Thailand. Because short-lived gaseous pollutants also have climatic effects, we also estimate nitrogen oxide, carbon monoxide, and hydrocarbons. We demonstrate how reducing diesel emissions would affect climate, using the Community Atmosphere Model housed at the National Center for Atmospheric Research. We present four model runs: (1) with all emissions [the reference case], (2) with particulate diesel emissions from Thailand halved; (3) with gaseous diesel emissions from Thailand halved; and (4) with both PM and gaseous emissions halved. The resulting change in radiative forcing from these short-lived pollutants is small compared to the global average from all emissions, but it is comparable to the magnitude of other single actions to reduce climate forcing.

2A.01
Long-term Aerosol Characterization in the Mega-city of Sao Paulo, Brazil. MARIA DE FATIMA ANDRADE, Atmospheric Sciences Department, University of Sao Paulo, Sao Paulo, Brazil.

The atmospheric aerosols impacts, especially on radiative process and health impairment, are directly associated to the number size distribution, which is demanding more accurate measurements methods. Historically there are many studies regarding the atmospheric aerosol in the Mega-city of Sao Paulo (MASP). The first studies are from the 70s. These studies were more concerned with the characterization of the inorganic compounds and concentration size distribution to identify the major sources of pollutants emissions. The main source for fine particles was identified to be the vehicular emission. Nowadays, the vehicles remain the principal emission source of fine particles in MASP, accounting for approximately 70% of fine particles, but it is known that the majority of fine particles concentration is related to the diesel emission, that can be as high as 50% of the emission responsibility. Another important point is that although the mass concentration in the lower stages of particles sizes can be small is where dominates the number distribution mode. Studies combining mass, composition and number distribution by scanning mobility particle sizer were conducted to characterize the particles in the mega-city of Sao Paulo and the recovered distributions obtained by these equipments will be presented. To improve the vehicular emissions inventory for the light- and heavy-duty fleet in the MASP, measurements of vehicle emissions in road tunnels located in downtown the city were performed. The estimated light-duty vehicle emission factors were 16.4, 226.3, 133.6 and 93.2 mg/km, respectively, for black carbon, inhalable particulate matter, coarse particles and fine particles. The mean contribution of heavy-duty vehicles to the emissions of black carbon, inhalable particulate matter, coarse particles and fine particles was, respectively, 27, 3, 5 and 4.8 times higher than that of light-duty vehicles. In general, the particle emissions in Sao Paulo measured inside tunnels are higher than those found in other cities around the world.
2A.02

Evolution of Trace Gases and Aerosols in the Mexico City Pollution Outflow during a Long Range Transport Event.


Significant chemical and physical processing of the Mexico City (MC) pollutants is expected to occur as they are advected downwind over a period of several hours to days. Of particular interest are the formation and evolution of ozone and primary/secondary aerosols due to their implications for regional air quality and climate. We report here on the long-range transport episode of March 18-19, 2006, which was successfully characterized by the Controlled Meteorological (CMET) balloon trajectories in the MC outflow over a period of 26 hours. The key tool in our analysis of the various gas-aerosol processes is the new Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), which is applied here in a Lagrangian box-model framework. Comprehensive G1 aircraft measurements of key trace gases and aerosols made just downwind of MC (over the T2 site) are used to initialize the model, while the C130 aircraft measurements made in the same air mass after one day (~450 km downwind) are used to constrain and evaluate the model. Results suggest that significant dilution (~6 % per hour) and photochemical ozone production occurred in the MC outflow. Particulate ammonium nitrate, which constituted a significant fraction of the sub-micron aerosol mass just downwind of MC, almost completely evaporated after one day due to dilution and formation of additional ammonium sulfate. Model calculations also suggest that the evaporated nitric acid re-condenses on the super-micron dust particles to form hygroscopic calcium nitrate. Furthermore, the observed organic aerosol/CO ratio after one day is nearly twice that of the modeled ratio, which suggests continued secondary organic aerosol (SOA) production during the long range transport event. Implications of these results on the downwind air quality and climate-affecting properties of the MC pollutants will be discussed.

2A.03


A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed for the first time on an airborne platform during the MILAGRO campaign in 2006. Measurements of size-resolved non-refractory PM1 aerosol components were made onboard the NCAR C-130. Organic aerosol (OA) accounted for over half of the aerosol mass and showed strong correlation with gas phase measurements of CO and HCN. Due to the correlations with HCN and CO, sources of OA are thought to be a combination of biomass burning (BB), transportation and other urban combustion sources, and (pollution-related) secondary OA. High mass resolution data also allowed for the calculation of the atomic oxygen to carbon (O/C) ratios of OA. This ratio has the lowest values in the city basin and increased values away from the city.

High-resolution OA mass spectra were also analyzed with a Positive Matrix Factorization algorithm, from flights with high and low BB contributions. Four OA components were extracted. Three oxidized components: OOA-I, OOA-II and biomass burning OA (BBOA) were obtained, and a reduced 'hydrocarbon-like' (HOA) component. OOA-I is linked to regional air masses and highly oxidized. OOA-II appears to be a fresh SOA correlated with ammonium nitrate, and the city basin. During low fire periods it is the largest OA component in the city basin. BBOA is identified as biomass burning aerosol from a strong correlation with gas phase HCN, and AMS marker ions. During high burning periods, BBOA makes a large contribution to OA mass in the basin and the outflow. The evolution of the PMF factors as air is transported out of Mexico City shows an increase in OA mass after accounting for dilution, indicative of secondary OA formation in the plume. An increase in the contribution of OOA-I to the total mass is observed during transport from the city.
Organic Aerosols in Mexico City: Urban and Biomass Burning Contributions during MILAGRO / MCMA-2006 at the Urban Supersite (T0). ALLISON C. AIKEN (1), Christine Wiedinmyer (2), Benjamin de Foy (3), Dara Salcedo (1,4), Michael Cubison (1), Ingrid Ulbrich (1), Peter DeCarlo (1,*), J. Alex Huffman (1), Ken Docherty (1), Donna Sueper (1,5), Douglas R. Worsnop (5), Achim Trimborn (5), Megan Northway (5), Andre S.H. Prevot (6), Sonke Szidat (6,7), Miriam N. Wehrl (7), Elizabeth A. Stone (8), James S. Schauer (8), Jian Wang (9), Jun Zheng (10), Edward Fortner (10), Renyi Zhang (10), Alexander Laskin (11), Jeff Gaffney (12), Nancy Marley (12), Luisa Molina (13), Gustavo Sosa (14), and Jose L. Jimenez (1). (1) University of Colorado, Boulder, (2) NCAR, Boulder, (3) St. Louis University, (4) Universidad Autonoma del Estado de Morelos, Mexico, (5) Aerodyne Research Inc., Billerica, MA, (6) Paul Scherrer Institut, Switzerland, (7) University of Bern, Switzerland, (8) University of Wisconsin, Madison, (9) Brookhaven National Laboratory, Upton, NY, (10) Texas A&M, College Station, (11) Pacific Northwest National Laboratory, Richland, WA, (12) University of Arkansas, Little Rock, (13) Molina Center and Massachusetts Institute of Technology, (14) IMP, Mexico City, (*) now at (6)

Non-refractory submicron (−PM$_{1}$) ambient aerosol was analyzed from March 10-30, 2006 in Mexico City at the T0/IMP urban supersite with the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-Tof-AMS, DeCarlo et al., 2006). Mass concentrations and size distributions of inorganic species (ammonium, chloride, nitrate, sulfate) are similar to results from MCMA-2003 (Salcedo et al., 2006). Positive Matrix Factorization (PMF; Ulbrich et al., 2008) analysis of the organic aerosol (OA) fraction identifies large episodic biomass burning plumes in addition to urban primary emissions (hydrocarbon-like OA, HOA) and urban secondary OA (SOA) formation (oxygcnated OA, OOA). SOA is the dominant component of OA, agreeing with previous observations (Volkamer et al., 2006). The presence of a regional highly-oxygenated OA is also observed. Biomass burning OA (BBOA) correlates with satellite fire counts, gas-phase acetonitrile, and other tracers such as potassium and levoglucosan (from both AMS and off-line sampling). Information from satellite fire counts (MODIS) and emissions inventories (Wiedinmyer et al., 2006) are input into a meteorological model (FLEXPART) for the Mexico City basin (de Foy et al., 2006) to derive a T0 fire impact index that is compared with AMS BBOA and other tracers. Perfect agreement is not expected given the difficulties in modeling BB emissions and meteorology in the basin. The modelled fire impact reproduces the general trends of BBOA, indicating wildfires within the Mexico City basin and surrounding mountains as the dominant source of BBOA at T0, meaning urban burning (e.g., trash burning) plays only a minor role. GC-MS Chemical Mass Balance (CMB; Stone et al., 2008) and C-14 filter analysis results are generally consistent with the PMF results. Analysis comparing mass from high versus low fire impact periods (Inorganics -21%; Organics +35%; HOA 0%; OOA +1%; BBOA +260%; soil +93%; black carbon +25%) allows for quantification of the aerosol impact during
3A.02
Fractal Theory Applied to Aerosol Experimental Data Collected in North of Chihuahua City. Eduardo F. Herrera Peraza(1), Balter Trujillo Navarrete(1), Roman Perez Balan(1), Adrian Vazquez Galvez(2), 1 Centro de Investigacion en Materiales Avanzados S.C.: Departamento de Medio Ambiente y Energia. Chihuahua. Mexico. (CIMAV) 2 Comision para la Cooperacion Ambiental (CCA)

Studies of multi-scaled atmospheric particles are based in different mechanisms of nano-particles growing. These mechanisms depend of many variables such as chemical composition, gas phase concentration; meteorological variables etc. and have been the indirect cause of different pulmonary diseases. Epidemiology studies have indicated an association between the mortality and the incidence of decease due to the concentration mass of atmospheric fine particles generated by the combustion. The area of surface of aerosol particles, is the site that involves the interactions gas-particle, that increases to the toxicity of the particles (Ku and Maynard 2005; Wentzel ET to. 2003). Nevertheless, the chemical specific mechanisms and/or physical, relating the effects of the health to the aerosol haven't been understood yet (Linak ET to. 2007). For the understanding of these mechanisms it is necessary detailed studies of the morphology and the chemical composition of particles (Wentzel ET to. 2003; Filippov ET to. 2000). The morphology has been described by different methods based on the contour or density of the particle, example of them is: form factors; chain codification; dimension fractal and functions of contour example the transformation of Fourier and wave (Kindratenko ET to. 1997; Kindratenko ET to. 1995; Kindratenko 2003). There isn't sufficient information of the possible modifications of the size variables and forms of the different particle, with respect to the environmental and temporary conditions. The use of multivariate techniques sets out to know the structures interdependence of the size, forms and atmosphere. Results of the calculations of different form factor parameters, Lacularity, and Hurts coefficients are exposed in this work with using the measurements of particles obtained with MOUDI (Micro orifice Uniform Deposit Impactor) (Marple et al. 1991), with particles cuts until 100 nm , collected in north of the City of Chihuahua during the campaign of March and April of 2007.

3H.01
Specification of Lead and Cadmium in air and soil of the Mitrovica area. Prof.Dr.sc.KADRI BERISHA, Mr.sc.Afrim Syla Ass.Prof., Prof.Dr.sc.Emin Karakashi , University of Pristina, Faculty of Mining and Metalurgy 40000 Mitrovic

The Trepa industrial and mining area includes about 40 mines and various milling, flotation and smelting plant. The principal mining plant is the Zvecan smelter located to the town of Mitrovica. In the period 1930-1950, 825000 t Pb, 566000 t Zn, 1022 t Ag and a similar quantity of Bi were produced. At this time about 20000 miners worked there. In the 1982 a reserves of 50 Mt of ore, with a grade of 5-7% Pb and 4% Zn, was estimated. The ore treatment and smelting created huge quantities of mine wastes accumulated in time in imposing dumps close to the Zvecan plant. The activity of the Zvecan smelter was stopped in August 2000 because of the very dangerous emissions in the atmosphere.

Sampling operations occurred in different campaigns carried out in 2004/2005 and 2006/2007. The first sampling campaign was accomplished in Jun 2004. The systematic sampling was based upon a predetermined geometric pattern consisting of a sampling grid constituted by square meshes. The grid spacing, that is the distance between two adjacent modes along the x and y directions, was fixed at 1 km. The average sampling density was 4 samples / km2.

Table 1. Industrial Hygiene Sample Summary

<table>
<thead>
<tr>
<th>Location, Sample Type, No Samples</th>
<th>Pb (ug/m3)</th>
<th>As (ug/m3)</th>
<th>Cd (ug/m3)</th>
<th>Ni (ug/m3)</th>
<th>Zn (ug/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Area= Area Samples, BZ = Breathing Zone)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mitrovica City Area, Area, n = 13</td>
<td>0.30</td>
<td>0.027</td>
<td>0.063</td>
<td>0.0028</td>
<td>0.6</td>
</tr>
<tr>
<td>NE Mitrovica at Pakistan Base, Area, n = 1</td>
<td>1.13</td>
<td>0.45</td>
<td>0.047</td>
<td>0.0031</td>
<td>0.8</td>
</tr>
<tr>
<td>Zvecan Smelter and MIP, Area, n = 7</td>
<td>0.64</td>
<td>0.37</td>
<td>0.023</td>
<td>0.00024</td>
<td>0.3</td>
</tr>
<tr>
<td>Clean-up workers, Zvecan and MIP, BZ, n = 6</td>
<td>57.5</td>
<td>2.0</td>
<td>0.310</td>
<td>0.01142</td>
<td>0.5</td>
</tr>
<tr>
<td>Special Police Units at Zvecan Smelter, BZ,n = 4</td>
<td>2.7</td>
<td>2.1</td>
<td>0.042</td>
<td>0.0169</td>
<td>0.5</td>
</tr>
<tr>
<td>European Union, Worker Exposure Limit</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WHO Air Quality Guidelines, 2000</td>
<td>0.5</td>
<td>0.0015</td>
<td>0.005</td>
<td>0.00038</td>
<td>N/A</td>
</tr>
</tbody>
</table>
3H.02
Aerosol Growth Events Observed at Urban and Rural Locations in New York. MIN-SUK BAE (1), James J. Schwab (1), Olga Hogrefe (1), G. Garland Lala (1), Brian Frank (2), Qi Zhang (1), Kenneth L. Demerjian (1) , (1) Atmospheric Sciences Research Center, University at Albany, State University of New York, (2) Air Resources Division, Bureau of Mobile Sources, New York State Department of Environmental Conservation, Albany, New York

Measurements of particle number concentrations and size distributions were obtained using two scanning mobility particle sizers (Nano DMA & Long DMA) at the sites of Pinnacle State Park (PSP, summer 2004) and Whiteface Mountain (WFM, summer 2002) in rural areas of New York State and at the urban site of Queens College (QC) in New York City in summer 2001 and winter 2004. Total aerosol number concentrations (for sizes greater than about 8 nm) were also measured with a stand-alone CPC.

Relationships between particle number size distributions and ambient pollutants by a set of co-located measurements yield a rich data set for exploration of particle growth events at urban and rural locations in New York. The co-located measurements include ionic species from PILS-IC, organic aerosol from an Aerodyne Aerosol Mass Spectrometer, organic & elemental carbon from a SUNSET (NIOSH5040) carbon analyzer, gaseous pollutants, PM2.5 using a tapered element oscillating microbalance (TEOM), and metrological data. Analysis of the characteristics of particle growth in comparison to other observations allow classification of the events and illustrate that particle growth exhibits different physical behavior with respect to different compounds for these sites. The observed chemical compounds associated with the growth from nucleation to Aitken mode particles can help explain particle growth mechanisms at these locations.

3H.03
A Multiyear Study of Ultrafine Particle Number Size Distributions and Growth Events in Rochester, NY. JOHN KASUMBA (1), David Chalupa (2), Mark Utell (2), Philip Hopke (1) , (1) Clarkson University, Potsdam NY (2) University of Rochester Medical Center, Rochester NY

Recently, research has linked exposure to elevated concentrations of particulate matter (PM) to increased rates of cardiovascular and respiratory illness, hospitalization and pre-mature mortality. Although it is not clear whether it is mass, number, or even surface area of particles that is the most important determinant of health consequences, some toxicological studies have indicated that the size of airborne PM is an important factor in generating health effects. The mechanisms by which PM induces health effects are still unclear.

There have been many sampling campaigns to study the aerosol size distributions in urban areas, but no body of measurements in the United States provides a clear record of particle number and size over a variety of various locations and over time periods of multiple years. Sustained measurements are needed to elucidate aerosol climatology over long time scales and clarify the underlying drivers of its variability.

Number concentration measurements of particles in the size range 10-500 nano-meters have been conducted from August 2004 to December 2007 at the New York State Department of Environmental Conservation (NYS DEC) monitoring site on the east side of Rochester, NY. Gaseous, PM mass, and meteorological variables were also measured at the same site. The relationships between the number concentrations, gaseous pollutants and meteorological parameters during particle growth events have been studied. These results provide novel information on the variations in particle number size distributions, the occurrence of nucleation and growth events of ultrafine particles, and the relationship of these events with other measured pollutants over an extended time period.

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3H.04
Relating ground-based aerosol size distributions and vertical mixing: Mexico City and other case studies. ALICIA PETTIBONE, William Eichinger, Jameson Schoenfelder, Charles Stanier, University of Iowa

In March 2006, during the MILAGRO field campaign in Mexico City, observations at the T0 location could often be characterized by morning conditions with high particle mass concentrations, low mixing heights, and good correlation between particle number and carbon dioxide, indicative that particle number is controlled by primary emissions. Using this correlation between particle number and carbon dioxide, an average number based-emission factor of $3.4 \times 10^{13}$ #/vehicle-km has been determined.

In the afternoon, the CO2 level drops during ventilation of the daily polluted layer, and the coupling between CO2 and particle number breaks down, with particle number sometimes increasing as CO2 decreases. New particle formation events were observed both simultaneously to and separately from the afternoon ventilation.

While the distinction between morning conditions dominated by primary emissions and afternoon conditions dominated by mixing and photochemical particle production is particularly strong in Mexico City because of local meteorology and intense sources, we show that this pattern is common to several locations. Furthermore, the observed particle size distribution after ventilation of the nighttime inversion is a weighted average of nocturnal capping inversion and the morning boundary layer. Finally, using a vertically resolved new particle formation model, we test the hypothesis that growth rates (high in Mexico City at up to 15 nm per hour) can be influenced by boundary layer growth rates in addition to condensable species concentrations, under certain assumptions about the vertical profile of new particle formation.

3H.05
Long-term characteristics of major chemical constituents in PM2.5 measured in South Korea. Jin-Hee Jung, Young-Ji Han, Kangwon National University, Chuncheon, South Korea.

Fine particles (PM2.5) were collected from November 2005 through April 2008 in Chuncheon, Korea to investigate the characteristics of the major components in PM2.5. The average PM2.5 concentration during this period was 39 ug/m3, which is almost two times higher than the annual US NAAQS PM2.5 standard of 15 ug/m3. The average PM2.5 has the highest concentration in winter, followed by spring, fall, and summer. This higher concentration in winter was most likely due to the combination of increased emissions from combustion sources for heating and the lower mixing heights, while lower PM2.5 in summer was possibly related to the large amounts of wet deposition. The PM2.5 concentrations during yellow sand events were about two to three times higher than during non-yellow sand events. The average sulfate concentration in PM2.5 was the highest in summer while the highest concentration of nitrate appeared in winter. Carbonaceous compounds in PM2.5 including OC and EC were also analyzed. The mean concentration of OC tended to be higher during the winter than the one during the summer, however EC had the lowest concentration in winter. Fraction of secondary organic carbon to total OC was higher in winter as the ammonium availability index, J had the same seasonal variation. This result indicates the possibility that acidic particles in winter might enhance the heterogeneous production of SOC. Size distribution of fine particles were also analyzed using 8-stage MOUDI in this study, and the results will be presented.
Over a year long monitoring of respirable aerosol was performed in a small village situated in a hilly area in the northern part of the Czech Republic. During a 15 month long measuring campaign covering both winter (heating) and summer (non-heating) season continuous (15-minute integration time) data of PM10 were collected by means of a photometer DustTrak (TSI) and 24-hour concentrations of PM10 were obtained using a low flow Harvard Impactor. In addition, Black Smoke variable was also measured to ascertain the contribution of combustion aerosol. Climatic indicators such as wind velocity, temperature and relative humidity were measured as well. A questionnaire was distributed among the local inhabitants to learn about combustion habits, amount of fuel consumed and type of heating technology used in households. The aerosol concentrations from the village were compared with those from nearby larger cities and with a close background measuring point of the national monitoring system. The results showed that the quality of air in the rural location is comparable or even higher than in the two larger urban areas and that the air in the settlement is contaminated mainly by emissions from local sources. Questionnaire data revealed that despite the fact that a large number of houses are connected to natural gas network the people tend to use low quality fossil fuel because of high price of gas. The results, compared with those from other Czech locations obtained in the past, support the presumption that under current trends in fuel prices the improvements of air quality in many Central and East European countries may be delayed.
3H.08
Dicarboxylic Acids In The Particle Phase In Different Locations In East Of France. Temporal And Seasonal Variations. Olivier Delhomme Maurice Milet, Universite de Strasbourg I / CNRS, France

Dicarboxylic acids (DCA) in atmospheric aerosols have received much recent attention because of their potential role in affecting the global climate. Because of the low vapour pressures and high water solubility, diacids have an influence on the chemical and physical properties of aerosols. Consequently, they may have direct and indirect effects on the earth's radiation balance by scattering incoming solar radiation or more have a potential contribution to the formation of cloud condensation nuclei [1]. Although DCA are generally considered to form mainly by photochemical reactions in the atmosphere. Direct emissions from vehicular exhausts, biomass burning, and cooking have also been suggested as their sources [2].

In this paper, results obtained in particle phase collected in urban and suburban sites of East of France will be presented. Field campaigns have been undertaken simultaneously in the sites during summer and winter. Periods of sampling varied between 04:00 to 10:00, 10:00 to 16:00, 16:00 to 22:00 and 22:00 to 04:00 in order to evaluate the spatial and the temporal variations of DCA concentrations.

The oxalic acid concentration was higher than that of any other dicarboxylic acids, with a summer to winter range of 36.2-6.4 ng.m-3 in Strasbourg. Generally, the long chain DCA were less abundant. Seasonal variations have been observed with higher concentrations in summer particularly for the oxalic, malonic or succinic acids, and conversely in higher concentrations in winter period for the adipic or maleic acids. Correlation coefficients were 0.71 for oxalic and malonic acid indicating that these acids all shared similar sources, found to be while weaker correlation was found between succinic acid and oxalic acid. In summer period, diurnal variations indicate that oxalic, malonic and glutaric acids were formed mainly in a secondary way, in contrary to the winter period, where the concentrations of these acids are in adequation with the automobile traffic. On the suburban site, the residential heating becomes a considerable source.

3H.09
Influence Of Season And Location On Pm Size And Composition In Central California. WALTER A HAM, Michael J Kleeman, University of California, Davis

California's San Joaquin Valley (SJV) is one of the most polluted airsheds in the United States where concentrations of airborne particulate matter (PM) routinely reach unhealthy levels. The size and composition distribution of SJV PM varies greatly by location due to a diverse range of urban and rural sources and seasonal influences. Secondary PM builds up across the entire region during stagnation events with localized high concentrations of primary PM close to major emissions sources. Temperatures in the SJV decrease to 0 deg Celsius during winter stagnation episodes and exceed 40 deg Celsius during summer events. Coupled with the fact that epidemiological studies have demonstrated negative health effects associated with PM inhalation, it is important to understand how the size and composition of PM changes throughout the central valley as a function of season and location.

In this study, the size and composition of particulate matter are reported from four field exposure campaigns. Ambient PM measurements were made at Fresno (an urban site) during the summer of 2006 and winter of 2007 and at Coalinga (a rural site) during the summer of 2007 and winter of 2008. Micro-Orifice Uniform Deposit Impactors (MOUDI) were used to collect PM in six size fractions between 0.056 - 1.8 micro-meter diameters on Teflon and Aluminum foil substrates. Bulk PM1.8 filter samples were collected using Reference Ambient Air Samplers (RAAS) and real-time measurements were taken with a Scanning Mobility Particle Sizer (SMPS) and an Aerodynamic Particle Sizer (APS). All samples were analyzed for elemental/organic carbon (Sunset Labs), water-soluble ions (Ion Chromatography), and metals (Inductively Coupled Plasma Mass Spectrometry). Size-resolved chemical composition measurements and real-time size distribution data will be presented for all four campaigns and differences will be discussed.
Regional Policy Implications for Future Air Quality and Human Health in California's San Joaquin Valley. Mark Hixson, Michael J. Kleeman, Department of Civil and Environmental Engineering, University of California, Davis

Air quality within California's San Joaquin Valley is among the worst in the nation. At present this region consistently exceeds both national and state set air quality standards for particulate matter in the 10 micro-meter and 2.5 micro-meter size ranges (PM10 and PM2.5) as well as ozone. Health-based standards for ultrafine particles (PM0.1) have not been set yet, but measurements of PM0.1 concentrations in the San Joaquin Valley rival those in Los Angeles. The challenge for this region lies in determining policies that can improve air quality while factoring in changes due to technology, population growth and climate change.

This study examined the impacts of four different growth scenarios on regional air quality in the San Joaquin Valley for the year 2030. Changing technological factors, population growth, biogenic factors and land use inform the creation of the emissions inventories for each scenario. The different policies will dictate restrictions on certain activities (e.g. wood burning), while also affecting demographics. The four emissions scenarios were input to a regional air quality model and simulated over a three-week, winter period using 2000 meteorology data.

The regional distribution of PM0.1, PM2.5, and PM10 concentrations in the San Joaquin Valley will be compared for the four different scenarios in 2030. The ability of landuse choices alone to mitigate future air pollution problems will be evaluated. Major source contributions to primary and secondary PM in each size fraction will be identified. Population-weighted average exposure estimates will be calculated as a method to contrast the potential health benefits of future policies.

Rapid Shift in Toxicity Due to Gas-Particle Interactions in the Atmosphere. SETH EBERSVILLER (1), Kim de Bruijne (1), Ken G Sexton (1), Cassie Olenick (1), Ilona Jaspers (2), Harvey E Jeffries (1), (1) University of North Carolina, Chapel Hill, (2) Center for Environmental Medicine, Asthma, and Lung Biology, Chapel Hill

A persistent question facing researchers studying the health effects of air pollution is whether particulate matter (PM) is inherently toxic, or if its toxicity can be attributed to pollutants incorporated into the PM from bulk air. Previous experiments using the UNC outdoor chambers have measured significant changes in chemical composition as air pollution mixtures age in sunlight and, in most cases, have measured an accompanying increase in toxicity. In general, these reactions work to create oxidized functional groups (such as aldehydes and ketones), which are more polar than their parent compounds and are, therefore, more likely to partition to particulate matter. The end result is that PM can act as a mechanism to deliver air toxics into the deep lung where the long residence time of PM (relative to gases) can greatly affect the dose of the VOCs absorbed by the body. This study is designed to investigate these phenomena, as well as how the presence of PM can affect the toxicity of air pollution mixtures. Using a continuously stirred tank reactor (CSTR) coupled to in vitro exposure systems, human epithelial lung cells were exposed to mixtures of gases and particles. The in vitro systems used are able to expose cells to air pollution mixtures directly, while maintaining equilibrium between phases until exposure. Once steady state was reached in the CSTR, cells were exposed to each phase independently. Lung cells were exposed separately to clean air, mineral oil aerosol in clean air, a VOC alone (p-tolualdehyde), and mineral oil aerosol mixed with the VOC. Using these mixtures, we were able to see a significant shift in toxicity from the gas phase to the particle phase. As this shift occurs in a matter of seconds, these findings could have important ramifications for understanding the toxicity of PM across the environment.
3H.12
Impact of New Airport on Regional Air Quality : A Case Study from India. A. Mishra (1), M. Tembhare (1), J.S. Pandey (1), Rakesh Kumar (2) and S.R. Wate (1), (1) National Environmental Engineering Research Institute (NEERI), NAGPUR, India (2) Mumbai Zonal Laboratory (NEERI), 89B, Dr. A.B. Road, Worli, Mumbai, India

In the last few decades, air traffic has increased exponentially. Moreover, in view of the recent projections about global climatic changes, air emissions due to airport related activities assume special significance. We are at the moment studying the environmental impact of an upcoming international air port (International Chakan air Port) near Pune city in the state of Maharashtra in India. The proposed project will have two types of impacts, one during construction phase which will be short lived and the other one during the operational phase which will have long term impact. On one hand, the project will have positive impacts in terms of new job openings and extra revenue income for the Government-sector. On the other, the adverse environmental impacts may become serious cause for concern. The proposed site for the Chakan International Airport is 40 km away from the Pune railway station. The Chakan Industrial area lies about 7 km away from the proposed site. Due to the upcoming airport, pollution levels in the proposed site are bound to increase. The number of vehicles in the sector will also increase as there will be transportation from different parts of Pune to carry the passenger to various destination. This will lead to increase in air pollution during the construction as well as operational phases. Therefore, a detailed Environmental Impact Assessment study has been initiated which will take recourse to the assimilative capacity based approach and would be ranking different regions in terms of their over-all air pollution impacts. Subsequently, environmental hot-spots would be identified for evolving appropriate sector-specific environmental management plans.

8A.01
High-resolution Mapping of Ultrafine Particles and Carbon Monoxide in an Urban Near-road Environment. Gayle S.W. Hagler (1), Eben D. Thoma (1), Richard W. Baldauf (1,2), (1) US EPA, Office of Research and Development (2) US EPA, Office of Transportation and Air Quality

Heavily-traveled roadways in urban regions often have complex features that impact the dispersion of emissions, such as roadway design (e.g. cut sections) and bordering barriers. However, the majority of near-road ambient monitoring has focused on establishing concentration gradients along unobstructed transects. In order to better understand the nature of near-road impact in a more complex environment, an all-electric vehicle was outfitted and deployed to perform high spatial- and temporal-resolution mapping of size-resolved ultrafine particle number count (UFP, particles < 100 nm) and carbon monoxide (CO). Onboard the vehicle, location and air monitoring data are collected at 1-second time intervals (translating to 5-20 m spatial resolution at 10-45 mph) using a high-resolution global positioning system (<1 m accuracy), an Engine Exhaust Particle Sizer (TSI, Inc.) to measure UFP, and a Quantum Cascade Laser (Aerodyne, Inc.) to measure CO. A pilot field campaign took place along a highway (I-85) in Durham, NC in March 2008, with approximately 15 hours of mapping conducted during morning and evening commute periods over a one-week period. A specified ~15-minute route was repeatedly driven and included features such as residential areas with obstructed and unobstructed air flow, a highway cut section, and stop-and-go traffic on arterial roadways. In addition to the instrumented electric vehicle, a secondary fixed sampling site was established 20 m from the highway to measure UFP, CO, and meteorology (wind speed and direction, temperature, humidity) at approximately 1-minute intervals. Throughout the sampling study, three different wind patterns were experienced (southerly flow, northerly flow, and stagnation) and were linked to changes in absolute UFP and CO concentration levels as well as alterations in local concentration gradients. In addition, variable topography over the mapped route and activity on arterial roadways substantially affected local concentration patterns surrounding the highway.
8A.02
Microscale Variations of Ultrafine Particle Number and Size Distributions in the Urban Atmosphere. Cheol-Heon Jeong, Greg Evans, Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Toronto, Ontario, Canada

Particle number and size distributions near roads are dominant by ultrafine particles (UFP) smaller than 100 nm in diameter. The high UFP levels are mainly due to vehicle emissions and are suspected to be important for acute and chronic health impacts on the susceptible individual such as elderly and diseased persons. Characterization of microscale variations near roadsides is very useful for assessing potential health risk posed by anthropogenic ultrafine particles. However, the understanding of UFP variations at roadside atmosphere is difficult due to the various traffic conditions and surroundings. In order to evaluate differences in temporal and spatial variations of UFP in the microscale environment, the measurements were taken at urban sites near busy local roads, quiet roads, and a highly trafficked highway in Toronto, Canada. Since the evolution of UFP number and size spectra is significantly faster at the urban site which is located in a street canyon, high time resolution measurements of particle number and size distributions provide the better understanding of rapid changes in UFP concentrations on the order of a few seconds. The high time resolution measurements near the road sides were made using two Fast Mobility Particle Sizers (FMPS, TSI 3091) which allow for the detection of particle size distributions from 6 nm to 523 nm every one second. Particle number and size distributions were continuously measured using a SMPS with an ultrafine water-based CPC (TSI 3786). Total number concentrations of UFP (>6 nm in diameter) were measured using three compact water-based CPCs (TSI 3781). In addition, a continuous recording video device was set up to investigate emissions from individual vehicles. Based on simultaneous measurements of the number and size distributions obtained from two sites, particle formation events were classified into three categories; regional particle nucleation, microscale particle formation, and urban background. We will present an overview of the particle events and elicit the main sources leading to the variations in particle number concentration at the urban site. The influences of meteorological parameters on the classified particle events will be presented in this study. By comparing particle number and size distribution data from upwind/downwind of a highway, the effect of traffic-related particles on the particle concentration throughout the entire size spectrum will be discussed.

8A.03
Mobile Measurements of Composition (AMS, MAAP) and Size Distributions (FMPS) in Different Cities and Regions. Silke Weimer, Claudia Mohr, Claudia Good, M. Rami Alfarra, Andre S.H. Prevot, Urs Baltensperger, Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Switzerland

In several cities and regions (Zurich, Milano, Rhine valley) in Central Europe we have performed mobile measurements, using an Aerodyne Aerosol Mass Spectrometer (AMS), a Multi-Angle Absorption Photometer (MAAP), and a Fast Mobility Particle Sizer (FMPS) for a high time resolved assessment of the spatial distribution aerosol composition and size distribution. Measurements were performed both in winter and summer. Concerning size distribution, we will show that traffic is the dominant source for nanoparticles. Domestic wood burning does not seem to significantly contribute to the nanoparticle concentrations. Domestic wood burning can however be very important concerning the particulate organic mass. Marker methods and positive matrix factorization methods to apportion the contribution of traffic and wood burning and secondary organic aerosols will be compared. It will be shown that both methods compare well and the results concerning contributions of the sources in the different regions will be discussed. In Zurich for example, the contribution of traffic organic mass and black carbon are roughly doubled going from an urban background site to the average found on the street while driving through the city.
8A.04
Wintertime Submicron Aerosol in Rural Atmosphere: Case Study from Two Villages in the Czech Republic. JAN HOVORKA, Jana Vrbova and Zuzana Stankova, Charles University in Prague

Comparative study was conducted to resolve contribution of local heating and transportation to the mass and number of fine aerosol particles in ambient air of two villages, which differ in proximity to the highway. The 5 minute integrates of aerosol size distribution 14-710 nm, PM1 and PM2.5, ozone, NOx, and meteorology were recorded in each village for 15 days in winter 2008. The first village, Koberovice, is situated near the D1 busy highway (average 35000 cars/day) while in the second village, Mokre, there is just local transportation (approx. 50 cars/day). There are about 150 residents in the villages, using wood (50%, 40%), brown coal (50%, 25%), electricity (0%, 20%), and gas (0%, 15%) for home heating in second and first village respectively. Mostly bimodal size distributions were recorded with modes in ultrafine (30 nm) and accumulation (about 100 nm) size ranges. In addition, nucleation bursts followed by condensational particle growth were registered in both the villages. Rainy period a day before and volatile organic carbon emission from local heating an hour before preceded the bursts. Low wind speed and relative humidity, high global radiation and ozone concentrations, and clear sky accompanied the bursts. That points to local feature of new particle formation events. Campaign median of total number concentration was near twice in Koberovice than in Mokre mainly because of episodes of elevated ultrafine particle concentrations. Such episodess were clearly associated with heating periods in Mokre, but in Koberovice, transportation and heating contributed almost equally.

8A.05
Intra-community Spatial Variability of Particulate Matter Size Distributions in Southern California/Los Angeles. MARGARET KRUDYSZ (1), Katharine Moore (2), Michael Geller (2), Constantinos Sioutas (2), John Froines (1), (1) University of California, Los Angeles, (2) University of Southern California

Ultrafine particle (UFP) number concentrations vary significantly on small spatial and temporal scales due to their short atmospheric lifetimes and multiplicity of sources. To determine UFP exposure gradients within a community, simultaneous particle number concentration measurements at a network of sites are necessary. Concurrent particle size distribution measurements aid in identifying UFP sources, while providing data to investigate local scale effects of both photochemical and physical processes on UFP. From April to December 2007, we monitored particle size distributions at 13 sites within 350 m -11 km of each other in the vicinity of the Ports of Los Angeles and Long Beach using Scanning Mobility Particle Sizers (SMPS). Typically, three SMPS units were simultaneously deployed and rotated among sites at 1-2 week intervals. Total particle number concentration measurements were conducted continuously at all sites. Seasonal and diurnal size distribution patterns are complex, highly dependent on local meteorology, nearby PM sources, and times of day, and cannot be generalized over the study area nor inferred from one or two sampling locations. Spatial variation in particle number size distributions was assessed by calculating the coefficient of divergence (COD) and correlation coefficients (r) between site pairs. Results show an overall inverse relationship between particle size and CODs, implying that number concentrations of smaller particles (< 40 nm) differ from site to site, whereas larger particles tend to have similar concentrations at various sampling locations. In addition, variations in r values as a function of particle size are not necessarily consistent with corresponding COD values, indicating that using results from correlation analysis alone may not accurately assess spatial variability.
2B.01
Spatial and Temporal Impacts of Biomass Burning on the Upper Midwest. AMY P. SULLIVAN (1), Donna M. Kenski (2), Jeffrey L. Collett, Jr. (1), (1) Colorado State University, (2) Lake Michigan Air Directors Consortium

During the Urban Organic Study conducted in 2004 in 5 Midwestern cities it was found that biomass burning contributed to about 15 to 25 percent of the total organic carbon (OC). This suggests that biomass burning could be an important source of OC in the Midwest, however there is still much uncertainty in the identification and contribution of biomass burning in this region.

In order to try to better understand the impact of biomass burning in the Midwest an alternative method for measuring levoglucosan (a known smoke marker) was used. This measurement technique couples high-performance anion-exchange chromatography with pulsed amperometric detection. This technique offers numerous advantages over traditional methods in that it can be applied on a more routine basis since an aerosol filter sample can be extracted directly in water and then the a liquid extract can be analyzed directly for levoglucosan.

Two phases of analysis using this method were conducted in order to try to better determine the contribution of biomass burning both spatially and temporally. A years worth of archived daily FRM filters as well as Hi-Volume samples from 6 weeks in the winter and summer collected at several sites in the Midwest were analyzed. Results of the analysis of levoglucosan, water-soluble potassium (another possible tracer), and water-soluble organic carbon will be presented and trends discussed. These results will be used along with source profile information collected from studies conducted at the Fire Science Laboratory in Missoula, MT to determine the impact of biomass burning in this region.

2B.02
Physicochemical and Toxicological Profiles of Particulate Matter (PM) from October 2007 Southern California Wildfires. VISHAL VERMA (1), Andrea Polidori (1), James J. Schauer (2), Martin M. Shafer(2), Flemming R. Cassee (3) and Constantinos Sioutas (1), (1) University of Southern California, Los Angeles (2) University of Wisconsin, Madison (3) National Institute for Public Health and the Environment (RIVM), the Netherlands

The October 2007 Southern California wildfires had a strong influence on the air quality of Los Angeles. To characterize this impact, integrated ambient particulate matter (PM) samples were collected near the University of Southern California between October 24 to November 14. The collected aerosol samples were analyzed for different chemical species (i.e., water soluble organic carbon, water soluble elements, and several organics compounds including levoglucosan), and the redox activity of PM evaluated by two different assays: the Dithiothreitol (DTT) assay and Macrophage Reactive Oxygen Species (ROS) assay. Tracers of biomass burning such as potassium (K) and levoglucosan were elevated by 2-fold during the period impacted by the fires (October 24 -30), compared to the post fire period (November 1-14). Water soluble organic carbon (WSOC) concentrations were also higher during the fire events (7.3 micro-gram/m3 on October 24; 1.7 micro-gram/m3 on November 14). The DTT activity (on a per PM mass basis) increased for samples collected during the fire period (0.024 nmol DTT / min. x micro-gram on October 24) compared to the post fire samples (0.005 nmol DTT / min. x micro-gram on November 14). The ROS activity was not correlated to the occurrence of wildfires, and the highest ROS level was observed on November 1, probably because these two assays are driven by entirely different PM species. While the former assay reflects the redox potential of polar organic compounds, which are in abundance in wood-smoke; the latter is mostly determined by the transition metals (e.g. Fe, Cu, Cr, Zn, Ni, and V), whose concentrations were not affected significantly by the fire events.
Biomass burning presents a significant source of carbonaceous aerosol in many regions of the world. When present these particles have been shown to affect the microphysical properties of clouds through their ability to serve as cloud condensation nuclei. To date little is known about their ice forming potential, which is critical for understanding precipitation processes throughout the atmosphere. To test the ice nucleation ability of biomass burning aerosols we performed laboratory studies at the Fire Lab at Missoula Experiment (FLAME-II). Smoke was generated through burns of approximately 30 biomass fuels under varying controlled combustion conditions. The ice forming potential of the smoke particles was measured at temperatures relevant to cold cumulus clouds (-30 Celsius) and cirrus clouds (-40 to -55 Celsius) using the Colorado State University continuous flow diffusion chambers. Although most of the burns did not generate any ice nuclei, particles from some of the fuels did nucleate ice heterogeneously under cumulus cloud conditions. All smokes produced particles that froze homogeneously near the relative humidity predicted for homogeneous nucleation of haze particles as described by a water activity based parameterization.
3I.01 Altitude Profiles of Biogenic Components of Atmospheric Aerosol in Southwestern Siberia and Element Composition of Aerosol, Galina A. Buryak (1), ALEKSANDR S. SAFATOV (1), Irina S. Andreeva (1), Sergei E. Olikin (1), Irina K. Peznikova (1), Aleksandr N. Sergeev (1), Boris D. Belan (2), Mikhail V. Panchenko (2), Denis V. Simonenkov (2), Gennadii N. Tolmachev (2), 1 Federal State Research Institution State Research Center of Virology and Biotechnology, Novosibirsk Region, Koltsovo, Russia (2) Institute of Atmospheric Optics SB RAS, Tomsk, Russia

Previously data on the total protein and culturable microorganisms concentrations in atmospheric aerosol of Southwestern Siberia at the altitudes 500 - 7000 m were presented. It has been shown that in contrast to the changes of aerosol concentration, which decreases by a factor of more than 10 as altitude increases, the concentrations of biogenic components are practically constant at the same altitudes. The present work is devoted to the analysis of the intra-year variation of altitude profiles of the biogenic components concentrations and the analysis of the relation between their observed concentrations with different elements concentrations in the same aerosol.

Atmospheric air sampling was usually performed using aircraft-based laboratory. The concentrations of total protein and culturable microorganisms in samples, aerosol chemical composition were determined under laboratory conditions after each flight.

Normalization of the altitude profiles of the total protein and culturable microorganisms concentrations averaged for each of the months of 1999-2007 show that it is impossible to reveal intra-year variations of altitude profiles of biogenic components concentrations in Southwestern Siberia. This indicates that the contribution of local sources to the measured concentration values at the altitudes over 500 m is small.

The coefficients of pair and rank correlations of biogenic components and the element composition of atmospheric aerosols were calculated to understand how and from which bioaerosol sources the observed profiles are formed. The sought correlations were practically absent.

The comparison of the observed altitude profiles of measured values has been performed. It revealed the existence of such profiles, which behave similarly to altitude profiles of biogenic components. This suggests a relation between the concentrations of these chemical elements and biogenic components of atmospheric aerosol. But it does not seem possible to refer these elements to any concrete bioaerosol sources.

This work was partially supported by ISTC, project #3275.

3I.02 Estimating Contributions of Primary Biomass Burning to Fine Particulates in Ambient Aerosol in the Western United States, AMANDA S. HOLDEN (1), Amy P. Sullivan (1), Leigh A. Patterson (1), Sonia Kreidenweis (1), Jeffrey L. Collett, Jr. (1), Bret Schichtel (2), William Malm (2), 1 Department of Atmospheric Science, Colorado State University (2) National Park Service/CIRA, Colorado State University

Six day integrated fine particle samples were collected during winter and summer seasons at 12 IMPROVE sites throughout the United States using Hi-Vol samplers. The monitoring sites included urban, near-urban, and rural locations. Measurements of 14C/C were made by accelerator mass spectrometry at Lawrence Livermore National Laboratory and presented by Schichtel et al. [2008]. Results of these analyses indicate a prevalence of contemporary carbon at many of the measurement locations. In order to examine the aerosol fraction associated with biomass combustion, either from residential wood burning or wildland fires, we measured concentrations of levoglucosan in selected samples. Levoglucosan, a breakdown product of cellulose, is a widely used tracer for primary biomass combustion. Measurements were made using a new approach involving aqueous filter extraction followed by direct analysis of levoglucosan and other carbohydrates using High Performance Anion Exchange Chromatography. In this method carbohydrates are separated on a Dionex Carbopac PA-10 column, using a sodium hydroxide gradient elution, and detected using pulsed amperometry.

Fine particle samples were also collected from source burns of approximately 30 various fuels during the FLAME studies at the USFS Fire Science Lab in Missoula, MT. Data from these combustion experiments were used to create source profiles which, along with published source profiles for residential wood burning, were applied to 4 of the IMPROVE sites to determine biomass combustion contributions to fine particulate matter. The IMPROVE samples analyzed represent the winter and summer seasons at 2 rural/urban site pairs in the western United States. The contributions of carbon from primary biomass combustion will be compared by season, population density (rural vs. urban), and geographic region. The contributions of carbon from primary biomass combustion will also be compared to the fractions of contemporary carbon determined using the carbon isotope approach.

3I.03
Nationwide impacts by fire emissions in the United States in summer 2002. Tao Zeng, Yuhang Wang, Georgia Institute of Technology

We analyzed the observed fine aerosol (PM2.5) components of organic carbon (OC) and elemental carbon (EC) from the rural sites of IMPROVE and SEARCH networks in the 5-year period from 2000 to 2004. During this period, nationwide increases of the OC/EC ratios were observed in July and August 2002. We considered 4 possible factors, including the formation of secondary organic carbon (SOA) from biogenic emissions, the SOA formation by glyoxal through cloud processes, intercontinental transport of Asian air pollutants, and fire emissions in summertime. The first 3 factors were ruled out due to the small inter-annual variations of meteorological and photochemical conditions in the 5 years. The global chemical transport model GEOS-Chem was used to study the impacts of fire emissions on the OC/EC ratios. We find that the nationwide OC/EC increases were the results of different fire events in summer 2002. Canadian fire emissions have large impacts on the northern states close to Canada. The wildfires in Oregon and California in 2002 caused the OC/EC spikes in the western United States. In the southern United States, the small inter-annual variations of OC/EC peaks imply a large contribution of biogenic SOA formation in summer.

3I.04
An Alternative Method for Determining the Impact of Biomass Burning. AMY P. SULLIVAN (1), Neil Frank (2), Jeffrey L. Collett, Jr. (1), (1) Colorado State University, (2) US Environmental Protection Agency

Biomass burning is one of the major sources of organic carbon aerosols. The most common method used in order to try to determine the contribution of biomass burning to the total organic carbon aerosol is through the use of smoke marker measurements. However, the traditional methods used to measure smoke markers (e.g., levoglucosan) are quite labor intensive and expensive due to the solvents, reagents, and instrumentation needed. Therefore, these analyses are generally conducted only for selected filter samples from special studies or on composited filter samples. This makes it hard to understand the impact of biomass burning both spatially and temporally. Therefore, an alternative method to measure levoglucosan and various other carbohydrates in aerosol samples has been developed using high-performance anion-exchange chromatography with pulsed amperometric detection. This technique offers numerous advantages including extraction of the filter directly in water and the ability to directly analyze the filter extract for levoglucosan. In addition, this method also appears to have increased sensitivity and require less carbon mass than the traditional methods. Therefore, allowing even daily samples collected on 47 mm filters with typical flowrates of 16.7 LPM to be analyzed for levoglucosan. Details of this method along with analysis of filters impacted by biomass burning will be presented to show the capabilities of this technique.
3I.05

We present highly time-resolved measurements of urban molecular markers in Pittsburgh, taken in the downtown area and at Carnegie Mellon. These are some of the first measurements to provide insight into the temporal variability of organic aerosol composition, and are being used to investigate sources and atmospheric processing of organic aerosols.

Condensed phase organic species (n-alkanes, alkanoic acids, PAHs, hopanes/steranes, etc.) are measured using a Thermal Desorption Aerosol GC-MS (TAG). TAG is a method for automated collection of ambient particles with online GC-MS analysis (Williams et al, AS&T, 2006; JGR, 2007). To investigate instrument sensitivity towards different compounds, sample times vary between 2-12 hours. A custom calibration standard is injected daily to measure decay in MS sensitivity over time for a large suite of organic compounds. Elemental carbon is measured at 5 minute intervals with an Aethalometer.

The data reveal substantial temporal variability in molecular marker concentrations on timescales of hours. In particular, motor vehicle markers (hopanes/steranes) show pronounced diurnal and weekday/weekend patterns. Other markers such as PAHs show patterns more associated with individual plumes than with consistent contributions from a dominant source class. These measurements illustrate the dynamic range of pollutant levels that can be captured with high time resolution, and the accompanying insight gained from such measurements.

3I.06
Chemical Aging of Ambient Organic Aerosol by Hydroxyl Radicals. Ingrid George, Jay Slowik, Jonathan Abbatt, University of Toronto

Chemical aging of atmospheric organic aerosols by heterogeneous reaction with gas-phase oxidants can alter the physical and chemical properties of particulates, thus influencing their climatic and health impacts. In this study, we examine the extent that chemical aging alters the chemical and hygroscopic properties organic aerosols. Specifically, we investigate 1) the heterogeneous chemical transformation of ambient organic aerosol by reaction with OH radicals and 2) the effect of chemical aging on cloud condensation nuclei (CCN) activity of laboratory organic aerosols.

In the first set of experiments, ambient particles sampled in Toronto, Ontario during late summer in 2007 were entrained in a reactor flow tube and exposed to OH radicals at atmospherically-relevant OH exposures. Modification of the chemical composition and degree of oxidation was measured by an Aerodyne Aerosol Mass Spectrometer. Changes in the aerosol mass spectrum indicated a decrease in the hydrocarbon-like organic fraction as the oxygenated component was enriched. Our observations suggest that an atmospheric exposure of no more than 4 days at typical OH concentrations caused significantly enhanced oxidation of the particles.

In the second set of experiments, the effect of chemical aging on the hygroscopicity of organic aerosols was studied by measuring changes in their ability to act as CCN. Monodisperse Bis(2-ethylhexyl)sebacate (BES) and stearic acid particles, used as surrogates for atmospheric organic aerosols, were exposed to OH. We found significantly enhanced CCN activity of oxidized organic particles compared to those not exposed to OH. The atmospheric implications of this work will be discussed.
31.07
Characteristics of Carbonaceous Aerosols during Winter in Kathmandu, Nepal. Kabindra M. Shakya, Robert J. Griffin, University of New Hampshire

Carbonaceous aerosols, comprised of elemental carbon (EC) and organic carbon (OC), play an important role in direct and indirect climate forcing and have adverse health effects. EC can be used as an indicator of combustion sources, and water-soluble organic carbon (WSOC) contributes to cloud formation processes. To examine the characteristics of carbonaceous aerosols, EC, OC, and WSOC concentrations and carbon isotopic ratios were measured from samples collected using quartz filters. Bulk aerosols were collected in Kathmandu, Nepal, during December 2007 and January 2008. EC and OC were measured in filter punches by a thermal-optical transmission technique, and WSOC was measured in filter extracts using a total organic carbon analyzer. Carbon and nitrogen stable isotopes were measured using a Costech Elemental Analyzer coupled to a Delta Plus XP Mass Spectrometer. Mean concentrations of OC, EC, and WSOC in Kathmandu were 20.02 +/- 0.24 (two standard deviations), 4.48 +/- 0.01, and 10.09 +/- 0.65 micro-grams per cubic meter. Carbonaceous aerosols in Kathmandu were characterized mainly by primarily emitted aerosols. A good correlation ($R^2 = 0.60$) was observed between OC and EC, indicating the likely dominant sources to be motor vehicles and other combustion processes. A good correlation ($R^2 = 0.68$) was also observed between WSOC and secondary OC (calculated considering EC as a tracer for primary OC emissions) indicating a water solubility associated with both primary and secondary OC aerosols in Kathmandu in winter. Future analysis will be focused on WSOC characterization using proton nuclear magnetic resonance spectroscopy and ion chromatography.

31.08
Seasonal Variations of Levoglucosan in the NYC Area. HARMONIE HAWLEY (1), Min Li (1), Monica Mazurek (1), Steve McDow (2), Dirk Felton (3), Oliver Rattigan (3), James Schwab (4), Ken Demerjian (4), (1) Civil & Environmental Engineering Department, Rutgers The State University of NJ, Piscataway, NJ, (2) National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, (3) Division of Air Resources, NY State Department of Environmental Conservation (4) Atmospheric Sciences Research Center, University at Albany - State University of NY

Levoglucosan was quantified at six sites (Chester, NJ; Elizabeth, NJ; Westport, CT; Queens, NY; Bronx, NY; Pinnacle State Park, NY) over a five-year (2002-2007) time span in fine PM samples. Levoglucosan showed seasonal trends in both the urban and rural sites with concentrations ranging from 2 ng/m3 (Pinnacle, NY, rural) in the summer to 189 ng/m3 (Westport, CT, suburban) in the late fall, making it one of largest single organic compounds quantified in the samples (6% TC). Levoglucosan ambient mass concentrations were normalized with EC, OC and PM2.5 mass concentrations to study the seasonal and temporal trends of this marker with major carbon fractions and fine particle mass. The ratios of levoglucosan to EC, OC and PM2.5 varied with season in similar patterns to the ambient concentrations. Urban sites exhibited lowest ratios to EC (3.60 ng/ug, Elizabeth, NJ); rural sites consistently exhibited highest mass concentration ratios (656 ng/ug, Pinnacle State Park, NY).

Levoglucosan ambient mass concentrations were compared with EC, OC and PM2.5 concentrations. Pearson correlation values of 0.54 or less were found in all cases, indicating poor or no correlations of levoglucosan with these PM species. ANOVA (2-sided) statistical results indicated no difference between urban and rural levoglucosan average year-round ambient concentrations (5% significance level). This also was true for the individual seasons (winter, spring, summer and fall) urban versus rural concentrations. These statistical results indicate little variation of the levoglucosan average annual and seasonal ambient concentrations between urban and rural NY, NJ, and CT sites. ANOVA results comparing the SOAP 2002-2003 and SOAP 2005-2007 ambient average year-round ambient concentrations demonstrated no difference between sample means. These results indicate no secular trends at the 5% significance level in the level of emissions from wood smoke and cellulose combustion observed over a 5-year period.
Aerosol carbon constitutes a significant fraction of PM$_{2.5}$ mass in many regions and considerable efforts are made to understand ambient concentrations. Several different sampling techniques including continuous and 24-hr integrated methods are frequently used to determine ambient carbon concentrations. Twenty four hour integrated filter measurements provide important information on long term seasonal trends useful for compliance strategies related to the annual standard. The higher temporally resolved information provided by the continuous measurements is more useful for strategies related to attainment of the daily standard. Continuous measurements are also useful for understanding plume events. At a site in the South Bronx, NY aerosol carbon has been measured using continuous and 24-hr integrated filter methods for several years. Continuous measurements of elemental and organic carbon (EC, OC) are made using a Sunset labs ECOC analyzer. Black carbon (BC) is measured using a Magee Scientific Aethalometer and a Thermo Electron MAAP. Integrated 24-hr 1 in 3 day carbon measurements using the Speciation Trends Network (STN) and IMPROVE protocols are collected at the site. In June 2007 the STN sampler was changed from a MetOne to a URG 3000N sampler which is similar in operation to the IMPROVE. The long term data sets allow us to compare aerosol carbon measurements between the STN and IMPROVE prior to and after the STN sampler change. The Sunset data is very useful for this comparison since it provides additional collocated carbon measurements prior to and following the change. Significant biases between different carbon sampling methods can be expected for EC and OC fractions whereas total carbon (TC) is usually expected to be equivalent. Our long term carbon data sets are used to compare TC and EC and OC fractions and determine systematic biases between the different sampling methods.

Two national fine particulate chemical speciation-monitoring networks are currently in operation across the U.S.: the U.S. EPA's PM$_{2.5}$ Chemical Speciation Network (CSN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. These networks were designed to obtain information about the chemical composition of PM$_{2.5}$, (particles less than 2.5 um in aerodynamic diameter). Both networks rely on laboratory analysis of 24-hour filter samples collected every third or every sixth day and analyzed by gravimetry, ion chromatography, x-ray fluorescence, and thermal-optical carbon analysis.

The CSN began monitoring operations in February, 2000, and was established to monitor concentration trends and to assist state and local air monitoring agencies with meeting the PM National Ambient Air Quality Standards (NAAQS) for PM$_{2.5}$. The IMPROVE network was initiated in 1988 to assess and help address visibility impairment in Class I areas.

The sampling and chemical analysis methods utilized by the two networks are similar; however, different filter sizes and sampler flow rates were chosen to optimize sample capture for the different target environments. In addition, the thermal-optical carbon analyses performed by the two networks, though similar in principle, differ in a number of respects that can affect the major fractions (OC and EC) and subfractions.

EPA is in the process of replacing the CSN's original OC/EC sampling and analysis methods with methods like those used by the IMPROVE network in order to establish better comparability with historical data. This paper will explore comparability of data obtained at several sites where CSN and IMPROVE samplers have been collocated. We will also examine OC/EC data obtained in the CSN program using the new URG 3000N sampler, which is based on the IMPROVE sampler and began sampling at 57 CSN sites in May, 2007.
Tanveer Ahmed (1), Abdul J Khan (2), Liaquat Husain (1,2), (1) Department of Environmental Health Sciences, State University of New York, Albany, NY. (2) New York State Department of Health, Wadsworth Center, Empire State Plaza, Albany, NY.

Elemental carbon (EC) or Black carbon (BC), produced from incomplete combustion of fossil or bio-fuels, is strongly light absorbing and considered to be the second biggest contributor to global warming. Unlike greenhouse gases, the concentrations of carbonaceous aerosols are not uniformly distributed throughout the atmosphere, with concentration varying from very high values in polluted areas to very low levels in the background or rural areas. For global warming calculation, it is important to have the data representative of a region. In this paper, we report direct measurement of annual mean concentration of atmospheric EC, \([\text{EC}]_{\text{atm}}\), collected daily on filters papers from 1978 to 2007 at Whiteface Mountain (1.5 km above sea level), NY. Aerosols samples were collected daily using high-volume sampler on Whatman 41 filter paper (20 cm x 25 cm). Whatman 41 filters because of their high organic carbon content were not suitable for EC measurement by thermal-optical methods. Therefore a new technique was developed in which the EC on Whatman 41 filters was transferred onto quartz filters which can then be used with thermal-optical, elemental/organic carbon (EC/OC) analyzer. Monthly composites were prepared from a known portion of the daily samples and after removing the cellulose were transferred on 47 mm quartz filters which were then subsequently analyzed with Sunset lab EC/OC analyzer. The annual mean \([\text{EC}]_{\text{atm}}\) concentration during the period 1978-1986, 1987-1996, and 1997-2007 were found as 539, 225 and 67 ng m\(^{-3}\). A 59% decrease in the \([\text{EC}]_{\text{atm}}\) concentration was observed between 1978-1986 and 1987-1996 period and 70% decreased was observed between 1987-1996 and 1997-2007 period. \([\text{EC}]_{\text{atm}}\) concentration showed a decreasing trend during the period of sampling owing to better technology and improved regulation with time. The direct measured long-term concentration of \([\text{EC}]_{\text{atm}}\) will be used in model for predicting the impact on global warming.

3I.12 Intra-community spatial variation of size-fractionated organic compounds in Long Beach, CA. Margaret A. Krudysz (1), Philip M. Fine (2), Michael P. Hannigan (3), (1) Department of Environmental Health Sciences, University of California - Los Angeles, 650 Young Drive South, Los Angeles, CA (2) Department of Civil and Environmental Engineering, University of Southern California, 3620 South Vermont Avenue, Los Angeles, CA. (3) Department of Mechanical Engineering, College of Engineering and Applied Science, University of Colorado, Boulder, CO 80309, USA.

Local traffic patterns and proximity to complex pollution sources are important in assessing particulate matter exposure in urban communities. This study investigates the intra-community spatial variation of individual organic compounds from one of the most heavily traffic-impacted communities in southern California. UF (Ultrafine), Acc (accumulation), and C (coarse) PM were collected at 4 sites no more than 5 miles apart from each other. Sites were sampled simultaneously for 10 weeks during winter 2005, allowing for comparisons across spatial and temporal scales. This analysis will aid in the identification of the individual organic compounds, or groups of compounds impacting each site and the differences between them given proximity to important PM sources such as freeways, airports, or the ports. Results show that hopes quantified in the UF size fraction are not correlated well with n-alkanes, implying that different sources emit hopanes and n-alkanes in the smallest particles. Conversely, the Acc fraction is composed of slightly aged aerosols with similar sources emitting hopanes and n-alkanes. Differences in organic tracer concentrations were observed between the sampling sites, although the degree of spatial divergence depended on the sites being compared as well as the proximity to significant sources. Previously studied source profiles for major sources categories in the Long Beach area are used in conjunction with results from Positive Matrix Factorization analysis to estimate contributions of different source types to the measured pollutant concentrations. Spatial and temporal variability in the source contributions is assessed on a micro-scale. Partitioning of the various compounds between the different PM sizes collected at numerous sites can provide information on the spatial distribution of individual compounds and the types of sources contributing to PM exposure in urban communities.

QI CHEN (1), Delphine Farmer (2), James Allan (3), Stephan Borrmann (4), Hugh Coe (4), Niall Robinson (4), Joel Kimmel (2), Johannes Schneider (4), Soeren Zorn (4), Paulo Artaxo (5), Jose Jimenez (2), Scot Martin (*) (1), (1) Harvard University, USA, (2) University of Colorado, Boulder, USA, (3) University of Manchester, (4) Max Planck Institute for Chemistry, Mainz, Germany, (5) University of Sao Paulo, Brazil, (*) scot_martin@harvard.edu

The Amazonian Aerosol Characterization Experiment (AMAZE-08), carried out in the northern Amazon during the wet season (February and March, 2008), provided an opportunity to investigate the chemical and microphysical properties of nearly pure biogenic organic aerosol. The non-refractory components (i.e., ammonium, chloride, nitrate, sulfate, and organic) of submicron particles were analyzed with the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). Results show that the most of the non-refractory mass was composed of organic material. Furthermore, analysis of the high-resolution spectra reveal that this organic material is dominated by highly oxygenated species. Diurnal profiles of the atomic oxygen-to-carbon ratio of the organic mass will be presented and discussed. In addition, the O/C profiles yield valuable insights into the effect of atmospheric processes such as precipitation, aging, and SOA formation, on the oxidation state of atmospheric organic aerosol.

Organic Aerosol in the Greater-Edmonton Air Shed during the PrAIRie 2005 Field Intensive: Primary and Secondary Components and their NOx Dependence.

CRAIG STROUD (1), Paul Makar (1), Mike Moran (1), Wanmin Gong (1), Brian Wiens (2), John Liggio (1), Shao-Meng Li (1), (1) Science and Technology Branch, Environment Canada, (2) Prairie and Northern Region, Environment Canada

Airborne measurements of organic aerosol (OA) in the size range (0.1-0.7 micro-meters) were performed in the Greater-Edmonton air shed during the PrAIRie 2005 field intensive. Measurements are used to evaluate Environment Canada's unified regional air quality modelling system (AURAMS). Time series measurement-model comparisons of OA were performed for transects downwind of urban and petrochemical sources. Model-measurement OA comparisons during vertical profiles were also performed to evaluate regional-scale emissions, chemistry, advection and vertical mixing processes in the model. Aerosol mass spectrometer measurements of OA were deconvolved into hydrocarbon-like OA factors (HOA) and oxygenated OA factors (OOA). Model predictions of OA were separated into secondary OA components (SOA) and primary OA components (POA). The measurement-derived HOA and model-derived POA components were observed to have very similar NOx dependence only differing by a scaling factor. However, the measurement-derived OOA and model-derived SOA components had quite a different NOx dependence. The model-derived SOA component peaked at intermediate NOx mixing ratios, similar to model OH. This likely reflects the fact that the rate limiting step in SOA formation in the model is the initial OH-VOC oxidation step. The measurement-derived OOA component did not show a strong dependence on NOx mixing ratios. This likely reflects the complex nature of SOA formation in the atmosphere. Initial VOC oxidation rates play a role but also the secondary pathways and the volatility of the product functional groups varies depending on the NOx mixing ratio (e.g. saturation vapour pressures and Henry's law constants for organic peroxide, organic acid, and organic nitrate functional groups differ). We conclude that the model organic aerosol yield parameterization must include a more complex dependence on NOx mixing ratios.
4A.02
Modelling Semivolatile PAHs in Canada and the USA.
ELISABETH GALARNEAU (1) PAUL A. MAKAR (1)
MIRIAM L. DIAMOND (2), (1) Air Quality Research Division, Environment Canada, Toronto, Canada (2) Department of Geography, University of Toronto, Toronto, Canada

Polycyclic aromatic hydrocarbons (PAHs) are toxic contaminants subject to long-range atmospheric transport. PAHs are currently emitted from a variety of combustion sources and biotic exposure occurs through inhalation and ingestion of food, water and soil contaminated by atmospheric deposition. The chemical transport modelling needed for the development of possible emission reductions has not yet been conducted in North America. Environment Canada's regional air quality model, AURAMS, was originally developed to study issues relating to ground-level ozone and particulate matter, but has recently been modified to account for the processes specific to semivolatile toxic contaminants such as PAHs. Two alternative expressions that account for particle/gas partitioning were added to the model, in addition to an expansion of the emissions interface and modification of the algorithms for gas-phase chemistry, precipitation scavenging and cloud processing. Results are presented for an annual run of the model for 2002 using an updated version of a recent North American emissions inventory. Results are compared to observations from various areas in the study region. A comparison of results between the two partitioning expressions is presented as well as an assessment of the relative importance of the different atmospheric fate processes relevant to PAHs.

References


4A.03
Organic Aerosols in Mexico City: Sources, Formation Processes and Responses to Emission Controls.
ALEXANDRA TSIMPIDI (1), Vlassis Karydis(1), Miguel Zavala (2), Wenfang Lei (2), Ingrid Ulbrich (3), Jose Jimenez (3), Luisa Molina (2), Spyros Pandis (1) , (1) Department of Chemical Engineering, University of Patras, Greece, (2) Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology (MIT), and Molina Center for Energy and the Environment (MCE2), USA, (3) Department of Chemistry and CIRES, University of Colorado, Boulder, CO, USA

Organic material (OM) contributes ~20-50% to the total fine aerosol mass at continental mid-latitudes. Nevertheless, the contributions of primary (POA) and secondary organic aerosol (SOA) have been difficult to quantify. In this study, new primary and secondary organic aerosol modules were added to PMCAMx, a three dimensional chemical transport model (Gaydos et al., 2007). The new modeling framework is based on the volatility basis-set approach (Lane et al., 2007): both primary and secondary organic components are assumed to be semivolatile and photochemically reactive and are distributed in logarithmically spaced volatility bins. The emission inventory, which uses as starting point the MCMA 2004 official inventory (CAM, 2006), is modified and the POA emissions are distributed by volatility based on dilution experiments (Robinson et al., 2007). PMCAMx is applied in the Mexico City Metropolitan Area during April 2003. The model predictions are compared with Aerodyne's Aerosol Mass Spectrometer (AMS) observations from the MCMA Campaign. We investigate the sensitivity of model predictions to the volatility distribution of emissions, emission levels of intermediate volatility organic compounds (IVOCs), aging rates and the dependence of SOA formation on NOx levels. The effectiveness of the different emission reductions (NOx, VOCs, and primary organic PM) is also discussed.

References


4A.04

An integrated laboratory/field study/modeling program was implemented to improve simulations of secondary organic aerosol (SOA) by the Community Multi-Scale Air Quality (CMAQ) modeling system. Modifications to the SOA module include the addition of NOx-dependence for aromatic SOA and updated, empirical enthalpies of vaporization. Recently identified SOA precursors, benzene, isoprene and sesquiterpenes were added in addition to new formation pathways: 1) H+-dependent enhancement of isoprene SOA, 2) polymerization of semi-volatile species and 3) cloud production from glyoxal and methylglyoxal.

CMAQ SOA predictions for individual precursors were specifically evaluated through comparison with ambient secondary organic carbon (SOC) concentrations, estimated using a laboratory-based source tracer technique. Measurements collected in Research Triangle Park, NC, averaged over a three-week summer period indicate biogenic SOC concentrations of 2.7 ugC/m3, with roughly equal contributions from isoprene, sesquiterpenes and monoterpenes. Preliminary model results also show equal contribution from these three biogenic precursors, but their total concentration is less, 0.6 ugC/m3. Aromatic SOC increased substantially as a result of aerosol module improvements, from 0.04 ugC/m3 to 0.11 ugC/m3, but estimates of aromatic SOC in RTP are substantially more, 0.63 ugC/m3, averaged over the time period. This suggests that CMAQ underestimates biogenic and aromatic SOC. Improvements in CMAQ SOA predictions are noted through the model's enhanced ability to reproduce variability in total carbon.

5D.01
Detection of nitrooxypolyols in secondary organic aerosol formed from the photooxidation of isoprene under high NOx conditions. KEI SATO, Takashi Imamura, Natl. Inst. for Environmental Studies, Tsukuba, Japan

2-Methyltetrols produced by the oxidation of isoprene have been recently found to contribute toward the formation of atmospheric secondary organic aerosol (SOA). However, the oxidation mechanism relevant to the formation of these polyols has not been completely understood. In this study, the photooxidation of isoprene in the presence of 0.2-1 ppmv NO was examined by a series of laboratory experiments, and the polyols, organic acids and nitric acid in an aqueous solution of the resulting SOA were analysed by using ion-exclusion liquid chromatography/mass spectrometry (LC-MS). 2-methyltetrols (comprising 0.5-2% of aerosol mass), methyl-nitroxybutanetriols (comprising 1-7% of aerosol mass), methyl-nitroxybutanediols (comprising 0.3-8% of aerosol mass) and nitric acid (comprising 4-9% of aerosol mass) were found in the aqueous solution of the SOA samples. Three days after the extraction, the concentrations of nitrooxypolyols (i.e. methyl-nitroxybutanetriols and methyl-nitroxybutanediols) decreased, whereas the concentrations of polyols and nitric acid increased. Nitrooxypolyols, which are produced by the gas-phase oxidation of isoprene in the presence of NOx, contribute toward the SOA formation, and these compounds can decompose to polyols and nitric acid in an aqueous solution. Polyols and nitric acid present in the aqueous solution are not real components of the SOA. The direct gas-phase formation of polyols from the isoprene oxidation is suppressed in the presence of NOx.
5D.02
Secondary organic aerosols formation from anthropogenic and biogenic sources: bridging field and smog chamber experiments.

Emanuela Finessi (1), M. CRISTINA FACCHINI (1), Stefano Decesari (1) and Urs Baltensperger (2), 1) Institute of Atmospheric Science and Climate (ISAC), CNR, Bologna, Italy (2) Laboratory of Atmospheric Chemistry (LAC), Paul Scherrer Institut (PSI), Villigen, Switzerland

A suite of spectroscopic and chromatographic methods were employed to investigate the chemical composition of SOA produced in smog chambers by oxidation of 1,3,5-trimethylbenzene (TMB) and alpha-pinene. Selected ambient samples containing SOA and collected in both polluted and pristine environments were also analysed with aim of comparison with the smog chamber data.

The analytical methods included determination of Total Carbon (TC) and Water-Soluble Organic Carbon (WSOC), the speciation of WSOC into main chemical classes, including polyacids (assimilated to humic-like substances, HULIS), and characterization of WSOC by Proton Nuclear Magnetic Resonance (1H-NMR) spectroscopy for functional group analysis.

Significant differences between the composition of TMB SOA and that of ambient polluted samples have been observed. Clearly, the SOA produced from TMB are unable to explain the content of oxygenated functional groups, such as carboxylic acids, as well of aromatics observed in the ambient samples. By contrast, the chemical characteristics of alpha-pinene SOA fit fairly well those of oxidized organic aerosols found in conifer forests, reproducing both the occurrence of semivolatile compounds, such as pinonic acid, whose contribution to aerosol mass can be described by partitioning models, as well as the more oxidized products which become more important at low aerosol concentrations and give rise to similar HNMR features in smog chamber samples and in ambient samples. So far, the occurrence of aromatic compounds and HULIS in ambient oxidized organic aerosols could not be efficiently reproduced in laboratory conditions, calling for investigating alternative anthropogenic SOA precursors, or suggesting a larger contribution from other sources of oxidized organic compounds, such as biomass burning, than previously expected.

5D.03
Formation and Properties of Secondary Organic Aerosol from Toluene.

LEA HILDEBRANDT, Neil M. Donahue, Spyros N. Pandis, Center for Atmospheric Particle Studies, Carnegie Mellon University

Air quality models currently under-predict the amount of organic aerosol in the atmosphere especially in the summer and in urban areas, suggesting that we do not understand anthropogenic secondary organic aerosol (SOA) formation well. Toluene and other light aromatics are thought to be the dominant anthropogenic SOA precursors. The aerosol yields (defined as the ratio of the mass of organic aerosol formed to the mass of toluene reacted) reported in previous studies vary widely. We studied the formation and properties of SOA from photo-oxidation of toluene under different conditions in a 12 m³ temperature-controlled smog chamber. We corrected the data for wall loss of aerosol particles and for condensation of semi-volatile vapors onto the chamber walls. To our knowledge, we are the first to correct SOA yield data for this loss of semi-volatile vapors.

We calculated aerosol yields using aerosol volume measurements from a Scanning Mobility Particte Sizer (SMPS) and using aerosol mass measurements of a Quadrupole Aerosol Mass Spectrometer (Q-AMS). We use the volatility basis set to parameterize the aerosol yields for use in air quality models. Major conclusions from our study are that the aerosol yields from toluene are much higher than the yields that are currently used in air quality models. Further, aerosol yields depend strongly on experimental conditions, especially temperature, but also UV light intensity. This can be explained with volatility and partitioning behavior of the aerosol particles.
5D.04
Investigation of Products formed during Hydroxyl Radical Initiated Photo-oxidation of beta-Pinene. JANEEN AULD, Julie Bennett, Don Hastie, York University Department of Chemistry and The Centre for Atmospheric Chemistry

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 and formation pathways of these secondary organic products are not well known. We are using an indoor smog chamber to perform hydroxyl radical initiated oxidation of beta-Pinene under controlled conditions with the objective of improving our knowledge of the chemical composition and formation of the reaction products. A suite of instruments is employed to monitor the reaction system both quantitatively and qualitatively. Quantitatively we are able to determine the reacted beta-Pinene and the produced organic particulate mass resulting in an understanding of the particulate yield for each experiment. The main focus of this project is largely qualitative product identification, utilizing a TAGA 6000E atmospheric pressure chemical ionization triple quadrupole mass spectrometer. The gas phase products are isolated using an in line quartz fibre filter prior to real time analysis by the TAGA. Particulate phase products are isolated using a Counter Flow Diffusion Denuder (see Bennett et al.). So far the focus has been on gas phase products since understanding particle composition requires extensive knowledge of the gas phase products as they lead to the formation and growth of particles. Collision induced dissociation has been used to identify product composition in conjunction with multiple reaction monitoring to obtain product reaction profiles. The reaction profiles are providing valuable information regarding product formation mechanisms, which at present are largely dependent on extrapolation from smaller chemical systems. Varying the initial NOx concentration in the chamber has extended information regarding these mechanisms. Results to date will be presented regarding proposed products identified as well as information regarding their formation in relation to beta-Pinene and other products.

5D.05
Collection efficiencies with various temperature conditions in photoelectric ESP. Woojin Kim (1), Jehee Jung (1), Hakjoon Kim (2), Young Jin Kang (1), Yong Jin Kim (2) and Sang Soo Kim (1), (1) Korea Advanced Institute of Science and Technology, South Korea (2) Korea Institute of Machinery & Materials, South Korea

Recently, DPFs have been globalized to remove PM and preserve human health. However, conventional DPFs have various problems such as pressure drop, redispersion of nano-sized particles generated in filter at high temperature and limits of application for light-duty vehicles. Accordingly, we have expected to solve the disadvantages using ESP. ESP has been used to remove the particles exhausted from coal-fired power plants or industrial facilities. But, because the majority of PM are several tens nano-sized particles based on number concentration, a photoelectric chamber was mounted with ESP in order to improve the charge effect in this work. We considered collection effect of several tens nano sized carbon particles using direct photoelectric charging concurrent with electrostatic precipitator (ESP). Because the photoelectric charging effect is maximized in the range of several tens nano sized particles, the ESP has been connected to the photoelectric charging chamber directly, and we have studied in various temperature conditions because photoelectric yield change in high temperature.

Particles were generated by carbon spark discharge generator, and the carbon particles were injected to photoelectric chamber and ESP by nitrogen gas and clean air. We measured number concentrations of sampled particles at 3 temperature conditions using SMPS, and then studied changes of collection efficiency by photoelectric effect.
**5D.06**

**Anthropogenic Influences on Biogenic Secondary Organic Aerosol.** Annmarie G. Carlton, Robert W. Pinder, Prakash V. Bhave, NOAA* In partnership with the U.S. EPA, Research Triangle Park

Anthropogenic pollution facilitates conversion of naturally emitted volatile organic compounds (VOCs) to the particle phase, enhancing biogenic secondary organic aerosol (SOA) in the atmosphere. Biogenic SOA consists of natural precursor VOCs as well as anthropogenic constituents that contribute to and enhance biogenic SOA. Anthropogenic pollution increases concentrations of oxidants (O3, OH, NO3) that facilitate the conversion of biogenic VOCs to semi-volatile (i.e., condensable, SOA-contributing) species, and increases concentrations of pre-existing particles that facilitate condensation of semi-volatile biogenic species to the particle phase. Therefore, a portion of biogenic SOA can be attributed to anthropogenic emissions. This component is difficult to measure but can be estimated through modeling.

To test the contribution of anthropogenic pollution to biogenic SOA, CMAQ model simulations were conducted for the continental U.S. (August 18 - September 4) using a recently developed SOA module that includes several biogenic SOA precursors: isoprene, sesquiterpenes and monoterpenes. Biogenic SOA formation pathways include oxidation of volatile species to semi-volatile products followed by gas-to-particle partitioning, oligomerization and in-cloud processes. CMAQ simulations were conducted with and without anthropogenic emissions. The relative contributions of individual pollution classes including NOx, VOCs, NH3, SO2 and primary organic particulate matter emissions were also evaluated by removing pollutant classes from the emissions one at a time. To comprehensively test the individual contribution and the interacting relationships between these anthropogenic pollutants, an orthogonally-designed matrix of reduction factors for each pollutant class was developed. Model results demonstrate a strong influence of anthropogenic pollution on predicted biogenic SOA concentrations. Combined, anthropogenic pollution enhances biogenic SOA in the eastern U.S. by an average of ~150% for the tested time period. In these simulations, biogenic SOA was most sensitive to primary particulate matter emissions, which enhanced biogenic SOA by ~20%.

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**5D.07**


Experiments were undertaken at the Paul Scherrer Institut environmental chamber to investigate the oxidative aging of primary emissions. In one set of experiments diesel exhaust diluted by 500-1000x from a Euro 3 standard engine, was introduced into the chamber and underwent photooxidative aging. A second set of experiments focused on the photooxidative aging of wood smoke from a conventional wood stove. Aerosol and gas phase components were measured with a large suite of instruments including: size resolved chemical composition with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), water uptake with a Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA), size distribution with a Scanning Mobility Particle Sizer (SMPS), black carbon concentration with an Aethalometer, number concentration with a Condensation Particle Counter (CPC), concentration of organic acids with Ion Chromatography coupled to Mass Spectrometry (IC-MS), gas phase composition with Proton Transfer Reaction Mass Spectrometry (PTRMS), and CO2, CO, NOx, and ozone monitors. In order for photochemistry to proceed on the timescale of an experiment, the Diesel experiments required the addition of ozone, to titrate the high concentration of NO in the exhaust, and the addition of propene to bring the VOC/NOx ratio to atmospherically relevant values. Wood burning experiments did not require the addition of any other compounds.

Early results for both the diesel and wood burning experiments show increases in organic aerosol mass (OM). OM concentrations were ratioed to the absorption measurements of the aethalometer to give an indication of the secondary organic aerosol production and a first order normalization for wall losses. This ratio indicates that the majority of the OM is secondary. Gas phase organic acids show an increase for small acids such as formic and acetic acid, consistent with field observations of biomass burning plumes. These and other results will be presented.
5D.08
Composition of Secondary Organic Particulate Matter from the Photo-Oxidation of Hydrocarbons Using APCI/MS-MS.
JULIE BENNETT, Janeen Auld, Donald Hastie, York University, Canada

The particle phase products from the oxidation of atmospherically important hydrocarbons are not well known. We are studying the oxidation of specific hydrocarbons produced in a photochemical flow reactor. The particles produced are isolated from the gases and introduced to an APCI MS-MS (TAGA 6000E) for composition analysis.

The newest online gas/particle separation for this system that is being utilized is the Counter Flow Diffusion Denuder (Ruiz et al., Environ. Sci. Technol. 2006, 40, 5058-5056). It consists of three stacked channels separated by a polytetrafluoroethylene porous membrane. The sample flow consisting of gases and particles is introduced into the center channel, while pure air is sent to the outer channels in a counter flow. The gases in the center channel will diffuse through the membrane into the outer channels and be swept away to waste. Only particles will remain in the center channel, since their diffusion coefficients are greater than the gases, and can be sent directly to the TAGA 6000E for analysis. Characterization studies show that with a range of flow rates through the center channel, and outer channels, gases are efficiently removed and particles are transmitted. Currently online studies using the Flow Reactor / CFDD / MS-MS system are being conducted using m-xylene as the precursor hydrocarbon. Several products have already been identified including furans, quinones and other ring retaining addition products.

5D.09
Optical closure experiments for biomass smoke aerosols.
LAURA MACK (1), Daniel Obrist (2), Hans Moosmüller (2), Kristin Lewis (2), Patrick Arnott (2), Gavin McMeeking (1), Ezra Levin (1), Sonia Kreidenweis (1), Cyle Wold (3), Wei Min Hao (3), Jeffrey Collett, Jr. (1), and William Malm (4), (1) Colorado State University, (2) Desert Research Institute, (3) Fire Sciences Lab, Missoula MT (4) CIRA, Fort Collins CO

The FLAME I (2006) and II (2007) experiments were a series of laboratory studies of the chemical, physical, and optical properties of fresh smokes from the combustion of a variety of wildland fuels typical for the western and southeastern U.S. Laboratory burns were conducted in the combustion chamber of the USFS Fire Sciences Laboratory in Missoula, Montana. This presentation focuses on the retrieval of smoke optical properties from the combustion of a variety of fuels using nephelometer-measured scattering coefficients, photoacoustically-measured aerosol absorption, extinction coefficients measured using a cavity ring-down extinction cell, and size distribution measurements. Uncertainties of the retrieved optical properties are estimated from instrument characteristics and from instrument calibration studies. We evaluate the degree of optical closure between measurements of extinction, scattering, and absorption and present estimates of single scattering albedo (SSA) for smokes having widely varying composition. In selected case studies from FLAME II, we are able to retrieve the complex refractive index from the measurements and compare it with literature values.
5D.10  
Modeling SOA Formation from OH reactions with C8 - C17 n-Alkanes. CAROLYN JORDAN (1), Paul Ziemann (2), Robert Griffin (1), Yong Lim (2), Roger Atkinson (2), Janet Arey (2), Donald Dabdub (3), (1) University of New Hampshire, (2) University of California - Riverside, (3) University of California - Irvine

Laboratory studies show that delta-hydroxycarbonyls formed via OH-initiated reactions with alkanes cyclize then dehydrate to form substituted dihydrofurans. These dihydrofurans are highly reactive, with estimated lifetimes in the atmosphere of 1.3 h (OH), 24 s (NO3), and 7 min (O3). These studies also show that secondary organic aerosol (SOA) yields from alkanes increase with carbon number from 4%-90% for C8-C17. The reaction mechanism proposed for these observations has been incorporated explicitly into the Caltech Atmospheric Chemistry Mechanism (CACM). Prior versions of CACM did not include SOA formation from medium chain alkanes (C8-C12), now observed to have SOA yields from 4-35%. The majority of SOA for these alkanes derives from second and third generation compounds (99%-88%). Long-chain alkanes in CACM previously were allowed to form aerosol, but only first generation products were represented. When the updated CACM was coupled to an equilibrium thermodynamic partitioning module, second and third generation products were found to constitute 78%-69% of the SOA mass for C13-C17, indicating the importance of including this additional chemistry in simulations of SOA formation from n-alkanes.

The explicit mechanism developed using CACM in a zero-dimensional model has been modified for use with the California Institute of Technology (CIT) regional air quality model using n-decane and n-hexadecane to represent medium-chain (C7-C12) and long-chain (&#8805;C13) alkanes, respectively. CIT is an Eulerian model that includes detailed mechanisms for advective transport, dry deposition, and vertical mixing. With a computational domain of 80 horizontal and 30 vertical cells, each 5 km in size, CIT extends to 1100 m vertically, resolved into 5 layers. Using an air quality episode observed in the South Coast Air Basin (SoCAB) of California on September 8-9, 1993, CIT coupled with the updated CACM is used to test the importance of SOA formation from medium and long-chain n-alkanes in a realistic atmosphere where n-alkane emissions are expected to be important. Preliminary results indicate that inclusion of SOA from medium chain alkanes increases simulated SOA throughout the SoCAB, though to the greatest extent in downwind, inland locations.

5D.11  
Hygroscopic Properties of Biogenically Derived Secondary Organic Aerosol. KEITH BROEKHUIZEN, Douglas Collins, Kashif Ahmed, Michael Prinsell, Colgate University, Hamilton, NY

Organic coatings can significantly impact the chemistry and fate of aerosols in the atmosphere. Organic coatings can be naturally derived, as with sea salt aerosols. They may also be deposited as a result of gas-phase reactions of volatile precursors. Reactions of biogenic volatile organic precursors such as isoprene and alpha-pinene are one such source of condensable organic matter. These organic coatings may have dramatic impacts on the aerosol particles ability to uptake water vapor and act as cloud condensation nuclei. An important class of aerosol particles in the atmosphere is mineral dust. Freshly emitted mineral dust does not significantly uptake water vapor, however, as it ages, it may become significantly more hygroscopic. This change will impact the role and fate of mineral dust in the atmosphere. In this study, we investigate the impact of organic coatings derived from the gas-phase reactions of biogenic VOCs such as alpha-pinene, limonene, and isoprene on the hygroscopic properties of mineral dust aerosols. These organic coatings are deposited on both neutral and acidified mineral dust aerosols. MALDI-TOF analysis of the oxygenated organic products will also be presented.
5D.12
MARKUS PETTERS (1), Heike Wex (2), Eva Hallberger (2), Laurent Poulain (2), Christian Carrico (1), Gavin McMeeking (1), Sonia Kreidenweis (1), Frank Stratmann (2), Andreas Massling (2), (1) Colorado State University, Department of Atmospheric Science, Fort Collins, Colorado, USA (2) Institute for Tropospheric Research, Leipzig, Germany

Organic compounds of low and intermediate volatility contribute to atmospheric aerosols that impact air quality and climate. Previous studies suggest that although secondary organic aerosols take up water hygroscopically below 100% relative humidity, the observed water contents are too small to account for their measured ability to serve as cloud condensation nuclei. This requires unrealistically low surface tensions of the aqueous solutions to reconcile these observations. Here we examine secondary organic aerosol properties generated through the reaction of alpha-pinene and ozone using a continuous flow reaction chamber. These measurements are focused on the ability of the aerosol to grow hygroscopically, both below and above water saturation. Using our measurements of hygroscopic growth factors at relative humidities up to 99.4% to constrain the water activity versus composition relationship, we show that one possible explanation is that the secondary organic aerosol acts as a pseudo binary mixture of infinitely water soluble compounds and sparingly soluble compounds. Alternatively, thermodynamic modeling predicts that gradual dissolution is not required to explain the data, pointing to strongly non-ideal solution behavior that is expected for dissolved organic compounds that contain a certain fraction of nonpolar functional groups. We suggest that this is the reason why observed hygroscopic growth factors and cloud condensation nuclei activities are so similar for a broad range of hydrocarbon precursors and oxidants forming those aerosols.

5D.13
Hidden Organics on Diesel PM: Resolving Differences between Thermal Desorption and Solvent Extraction for Determining the PM Organic Fraction. JOHN STOREY, Samuel Lewis, Oak Ridge National Laboratory

In studies of diesel particulate matter (PM) properties for diesel aftertreatment technologies, there is often poor agreement between the thermally labile fraction of the PM and the mass of organic compounds in the soluble organic fraction (SOF) of the PM. Conventional methodology for the determination of the PM SOF is solvent extraction followed by gas chromatography/ flame ionization or gas chromatography/ mass spectrometry (GC/MS) analysis. Recently, our laboratory identified a family of aromatic carboxylic acids, including pyromellitic acid, and their corresponding anhydrides on diesel PM. Conventional GC/MS analysis revealed very poor sensitivity for these compounds, thus indicating a potentially large abundance of the compounds on diesel PM. In addition, these compounds are only weakly soluble in typical solvent systems used for SOF analysis. In this paper, we report on unique solvent extraction methods for the extraction of these oxygenated aromatics as well as the use of liquid chromatography/ mass spectrometry for the determination and the quantification of pyromellitic acid and similar aromatic compounds on diesel PM. The identification and quantification of this family of compounds may be valuable in the understanding of combustion mechanisms, PM formation and possible heath impacts.
5D.14  
**Secondary organic aerosol formation from photooxidation of naphthalene and alkyl-naphthalenes.** Arthur W.H. Chan, Kathryn E. Kautzman, Puneet S. Chhabra, Jason D. Surratt, Man N. Chan, John D. Crounse, Scott P. Hersey, Paul O. Wennberg, Richard C. Flagan, John H. Seinfeld, *California Institute of Technology, Departments of Chemical Engineering and Environmental Science and Engineering, Pasadena, CA*

6A.01  
**Molecular Structure and Yield of Oligomers in Biogenic SOA.** Wiley Hall, Katherine Heaton, MURRAY JOHNSTON, *University of Delaware*

Although it has been known for several years that secondary organic aerosol (SOA) contains oligomeric compounds, several important questions remain: What is the structure of these compounds? How are they formed? What fraction of the SOA mass do they represent? This presentation will bring together the results of various ongoing experiments in our laboratory to answer these questions. Measurements with an evaporative light scattering detector (ELSD) allow oligomer yields to be determined. For aerosol produced by the reaction of monoterpenes with ozone, our initial results suggest that oligomers may constitute half of the total organic mass. Accurate mass measurements of oligomer molecules allow their elemental formulas to be determined along with O:C and H:C ratios. Parallel measurements with the nanoaerosol mass spectrometer (NAMS) allow the elemental composition of the entire aerosol sample to be determined. The O:C ratio measured in this manner is consistent with the ratio predicted from the individual oligomer molecules. Accurate mass measurements of an oligomer molecular ion and its fragmentation products allow the elemental composition of structural units within the oligomer molecule to be determined and the corresponding structures to be inferred. SOA produced in a flow tube reactor (3-22 s reaction time) appears to have the same composition as SOA produced in a Teflon bag over the period of 30 minutes. The results will be discussed in the context of ambient organic aerosol measurements by our group and others.
Organic aerosol behavior is driven in large measure by oxidized organic vapors about which we know painfully little. However, they evidently engage in semi-volatile partitioning with organic particles (this is the fundamental basis for Pankow partitioning theory) and without question they will react with OH radicals and possibly other oxidants. These reactions are equally certain to generate products with different vapor pressures than the parent vapors. Thus, reactions will drive "evolution of the volatility distribution". The fundamental question is: which way??. If reactions functionalize the carbon backbone, by adding HO-, O=, =NO2, and other functional groups, the products will have a lower vapor pressure than the parent and the organic particle loading will increase. If the reactions instead fragment the parent by breaking the carbon backbone, the products will almost always have a higher vapor pressure than the parent and the organic particle loading will decrease. The fundamental question thus reduces to the branching ratio of functionalization vs fragmentation. We hypothesize that this essential behavior (with respect to organic particles) of the thousands of organic compounds found in the atmosphere can be captured in a two-dimensional space. The principal dimension is volatility (C*, the saturation concentration), while the secondary dimension is the oxidation state, approximated by the oxygen to carbon ratio (O:C), which we suggest ranges from 0 to 1 in almost all cases. Finally, the critical branching ratio can be approximated as a simple function of O:C. We shall present various examples of organic aerosol evolution, drawn mostly from smog-chamber experiments at Carnegie Mellon.
6A.04
Characterization of SOA Formed from the Photooxidation of Benzene and Its Implication for Ambient PM2.5.
M. Jaoui (1), T. Gerald (1), E. Corse (1), T.E. Kleindienst (2), J.H. Offenberg (2), M. Lewandowski (2),
(1) Alion Science and Technology, Inc., Research Triangle Park, NC, (2) National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC

Recently, several major advances have been made in secondary organic aerosol (SOA) research, and new precursors (e.g., isoprene, benzene) have been identified that were previously believed not to lead to SOA formation. Although the oxidation of monoterpenes has been widely studied, less attention has been given to benzene, one of the most abundant in the atmosphere, despite its potential for aerosol formation. To date, there have been very limited studies on the chemical characteristics of gas or particulate reaction products formed from benzene oxidation, and only a few reaction products have been reported. The formation of SOA from benzene has been incorporated into air quality models even though no direct evidence has been reported based on individual organic tracers and many uncertainties still exist regarding its reaction mechanism. In this study, SOA formation from benzene/NOx systems was investigated in a series of experiments conducted in a 14.5-m³ indoor smog chamber operated in dynamic or static mode. To determine and understand the relative contributions of SOA products originating from benzene to ambient PM2.5, a detailed analysis was also carried out for ambient samples (PM2.5) collected in the southeastern United States in 2003, 2006 and 2007.

Chamber SOA and PM2.5 samples were derivatized using bis(trimethylsilyl)trifluoroacetamide and/or o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) and then analyzed by GC-MS. Emphasis was placed on polar oxygenated organic compounds. GC-MS analysis showed the occurrence of newly detected organic compounds in benzene SOA (e.g., 2,3-dihydroxy succinic acid). In addition, an effective enthalpy of vaporization for benzene SOA was measured using volatility differential mobility analysis and found to be in the range of 6 - 9 KJ/mol, a value considerably lower than for SOA from any organic system previously examined. We are currently investigating whether compounds are present in both chamber SOA and ambient aerosol that could serve as indicators for benzene in atmospheric particulate matter. SOA yield as well as tentative reaction schemes leading to most of these compounds are to be presented.

Disclaimer: This work has been funded wholly or in part by the United States Environmental Protection Agency under Contract EP-D-05-065 to Alion Science and Technology. It has been subjected to Agency review and approved for publication.
13A.01

Important contribution of secondary organic nitrogen to marine aerosol. MARIA CRISTINA FACCHINI (1), Matteo Rinaldi (1), Stefano De Cesari (1), Claudio Carbone (1), Fabio Moretti (2), Colin. D. O’Dowd (3), (1) Institute of Atmospheric Sciences and Climate, CNR, Bologna Italy (2) Department of Chemistry, University of Bologna, Italy (3) School of Physics and Centre for Climate and Air Pollution Studies, Environmental Change Institute, National University of Ireland, Galway.

Ammonium salts of dimethyl and diethyl amine (DMA+ and DEA+) have been detected in size segregated marine samples collected in the North Atlantic over open ocean and at a coastal site. DMA+ and DEA+ concentration peak in the accumulation mode range while very low concentration, close to detection limit, are observed in the coarse size fractions, as well as in sea spray aerosol artificially generated in the laboratory using sea water. These results indicate a secondary formation pathway. DMA+ and DEA+ represent up to 20% of secondary organic aerosol (SOA) in our samples, and to our knowledge they are the most abundant organic species besides MSA ever detected in clean marine aerosol. Maximum concentrations have been observed during spring and summer when the biological activity is high and in clean marine air masses, thus indicating biogenic sources. Total organic nitrogen (ON) concentration also peaks in the accumulation mode range and represents in our samples a fraction from 32 to 54% of the total SOA. These results suggest that organic nitrogen species might have an important role in marine SOA formation thus modifying the current wisdom which considers only sulphur (MSA) and isoprene chemistry.

13A.02

Effects of Pre-Heating on the Numbers of Atmospheric Aerosol in Classes Defined by their Single-Particle Laser-Induced Fluorescence Spectra. STEVEN C. HILL (1), Hermes Huang (2), Ron G. Pinnick (1), Yong-Le Pan (2), James M. Rosen (3), Elena Fernandez (3), Richard K. Chang (2), (1) US Army Research Laboratory, Adelphi (2) Yale University (3) New Mexico State University

Single-particle laser-induced fluorescence (LIF) spectral measurements of atmospheric aerosol have been reported previously [Pan et al., J. Geophys. Res., 112, D24S19, 2007]. There we used a hierarchical cluster analysis to assign about 90% of the LIF spectra to one of 8-10 clusters. Some compounds that occur in the atmosphere and have fluorescence spectra similar to the different cluster spectra were mentioned. Here we report new measurements where we heated atmospheric and test aerosols to different temperatures prior to their entering the particle fluorescence spectrometer (PFS) in order to obtain additional information about the possible materials in the clusters. The measurements were made in New Haven, CT, USA, using pre-heating temperatures of 100, 200, and 300 °C. We found that the numbers of particles in the cluster with a spectrum similar to that of washed bacteria, proteins, and tryptophan, are particularly sensitive to heat: at 200 °C only a small fraction of the particles in this category retain their fluorescence. Test particles made from bacteria were also found to be especially heat sensitive. Another of the eight clusters tended to be relatively insensitive to heat, even at 300 °C. In the measurements in New Haven, the fraction of atmospheric aerosol remaining at 300 °C varied 25% and 100%. This cluster has a spectrum similar to some recorded spectra for humic or fulvic acids, or humic-like substances (HULIS), and to some combustion aromatics, PAH. We suggest that of all the particles in this cluster, those that are unaffected by pre-heating are probably combustion aerosols, because these tend to be relatively resistant to heat, many of the known combustion compounds such as benzopyrene and benzantracene are relatively stable at 300 °C, and we have no reason to expect the fluorescence of humic and fulvic substances to be particularly heat stable.
Among low molecular weight (LMW) dicarboxylic acids (DCAs) studied through the past decade, oxalic acid (C2-DCA) often exhibits a dominant concentration followed by malonic acid (C3-DCA) although some studies reported negligible amounts of oxalic acid in atmospheric organic aerosols. Since data obtained from similar urban locations show discrepancies, factors other than atmospheric processes may cause inconsistent observations of oxalic acid in atmospheric aerosol. To reconcile different observations among various studies, standards were tested and atmospheric particulate samples were investigated. Our standard tests demonstrate that methods employing water extraction followed by IC analysis measured total of oxalic acid, oxalate, malonic acid, and malonate without differentiating acids from salt forms. However, methods using organic solvents to extract DCAs selectively quantified oxalic acid and malonic acid, while excluded oxalates and malonates. This indicates that depending on analytical methods employed, resultant concentrations of oxalic acid and malonic acid can be overestimated when water extraction is adopted. On the other hand, using solvent extraction can maintain integrity of DCAs and separate dicarboxylic acids from dicarboxylates in aerosol samples. Applying the findings to particulate samples collected in Singapore (an urban atmosphere), we quantified oxalates vs. oxalic acid, and malonates vs. malonic acid; oxalate containing a substantial amounts (361.4-481.4 ng/m^3) dominated over oxalic acid, with an oxalate-to-oxalic-acid concentration ratio ranging from 10.6-14.7. Unlike oxalate vs. oxalic acid, malonic acid (43.8-53.9 ng/m^3) showed a higher concentration than malonates (10.5-23.4 ng/m^3). Since oxalates and malonates can exhibit properties (e.g., degradation rate and hygroscopicity) differing from oxalic and malonic acids, quantification of individual DCAs and dicarboxylates is important to accurately estimate their atmospheric life and potential effects on the atmospheric environment. More information will be discussed during presentation.
13A.05 Analysis of polar compounds by methylation- and silylation-thermal desorption GCMS with time-of-day resolution for Riverside and Fresno. REBECCA J SHEESLEY (1), James J Schauer (1), Jeff DeMinter (2), Mark Mieritz (2), David C Snyder (1), Michael J Kleeman (3), (1) Environmental Chemistry and Technology Program, University of Wisconsin-Madison (2) Wisconsin State Laboratory of Hygiene, University of Wisconsin (3) University of California, Davis

In order to achieve better resolution of the daily progression of polar organic constituents in atmospheric particulate matter (PM), two thermal desorption-GCMS (TD-GCMS) methods were developed; a diazomethane derivatization method for organic acids and a silylation method for simple carbohydrates. The methylation method was used for the analysis of ambient samples collected in Southern California. The Study of Organic Aerosols at Riverside (SOAR) 2005 was an EPA and CARB-funded field study of organic aerosol composition that took place in July and Aug. 2005, on the campus of the University of California-Riverside. The SOAR samples included higher time-resolved four-per-day samples (5-10:00, 10-15:00, 15-20:00 and 20:00 to 5:00). One week of 6 hour SOAR samples have been analyzed using the methylation TD-GCMS method to focus on time-of-day fluctuations in the full list of polar acids and nonpolar compounds. Measurement of acidic compounds such as aliphatic and aromatic diacids combined with nonpolar tracers such as hopanes are essential to understanding sources and secondary processing occurring in ambient particulate matter. The aromatic diacids showed distinct time-of-day trends with mid-day peaks. Samples collected in Fresno, CA during the winter 2007 season were analyzed by the silylation method. Four, 6 hour samples were collected each day using a 92 lpm medium volume sampler equipped with a 90mm quartz fiber filter. The simple carbohydrate concentrations were quite low for this sampling set, but illustrated the low detection limits that can be achieved with the method. Levoglucosan concentrations were at the other extreme; these numbers indicate the unique condition of very high wood smoke contribution in the San Joaquin valley in the winter time.

14B.01 Diurnal and daily variations of organic aerosol composition at a polluted rural site in Po Valley, Italy. Sanna Saarikoski (1), Kimmo Teinila (1), Minna Aurela (1), RISTO HILLAMO (1), Stafano Decesari (2), Emanuela Finessi (2), Maria Cristina Facchini (2), Fabio Moretti (3), Emilio Tagliavini (3), Doug Worsnop (4), Markku Kulmala (5), (1) Finnish Meteorological Institute, Helsinki, Finland, (2) National Research Council, Bologna, Italy, (3) University of Bologna, Bologna and Ravenna, Italy, (4) Aerodyne Research, Inc., Billerica, USA, (5) University of Helsinki, Helsinki, Finland

The Po Valley area between Alps and Apennines forms a special area concerning the transport and mixing of pollutants from intensive industrial and traffic-related sources. An extensive aerosol measurement campaign was carried out during April, 2008 in San Pietro Capofiume, which is a rural site located in the Po Valley. One goal of the campaign was to give a further insight into the sources and evolution of organic aerosol. The data analyzed in this paper is based on the almost four weeks measurement using a high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS), and on the simultaneous off-line filter samplings for subsequent chemical analysis using proton nuclear magnetic resonance spectroscopy (HNMRI), ion chromatograph - mass spectrometry (IC-MS) and analysis of carbonaceous material for total (elemental and organic) and water-soluble fraction (WSOC).

The analysis of the HR-ToF-AMS data shows that aerosols have most of the time clear diurnal cycle where aerosol concentrations start to rise during late afternoon and are constantly high during night. A rapid drop of concentrations takes place usually around noon due to expanding mixing layer. For organic material the diurnal cycle can be identified for both hydrocarbon-like (HOA) and oxygenated organic (OOA) aerosols. Further trends in the composition of WSOC (which accounts for most OOA) with respect to functional group distribution were highlighted by HNMR analysis. Filter samples of submicrometer size fraction of Po Valley aerosol will be analyzed with the IC-MS for major inorganic ions and for 12 organic acids. First results show that 5-6 of the analyzed acids are permanently above the detection limit.

In this paper the organic fraction of Po Valley aerosol will be characterized for the potential sources and atmospheric chemical transformation processes using the online data from the aerosol mass spectrometry and the speciation data from offline samples and two different analytical techniques.
14B.02

Residential wood combustion is increasingly being identified as a major contributor to air pollution at a number of sites in Switzerland and in other countries. A recently developed source apportionment method using the aethalometer light absorption parameters is applied to five winter campaigns at three sites in Switzerland: a village with high wood combustion activity in winter, an urban background site and a highway site. The particulate mass from traffic (PMtraffic) and woodburning (PMwb) obtained with this model compared fairly well with results from the 14C source apportionment method. PMwb from the model is also compared to well known wood smoke markers such as anhydrosugars (levoglucosan and mannosan) and fine mode potassium, as well as to a marker recently suggested from the Aerodyne aerosol mass spectrometer (mass fragment m/z 60). Additionally the anhydrosugars were compared to the 14C results and they are shown to be comparable to literature values from wood burning emission studies using different types of wood (hardwood, softwood). The levoglucosan to PMwb ratios varied much more strongly between the different campaigns compared to mannosan to PMwb with a range of 1-1.5%. Possible uncertainty aspects for the various methods and markers are discussed.

14B.03
Origins of Fine Atmospheric Carbonaceous Aerosol in the Sierra Nevada Mountains, California. DAVID R. WORTON (1), Allen Goldstein (1), Brent J. Williams (1), Yunliang Zhao (1), Nicole C. Bouvier-Brown (1), Daniel M. Matross (1), Nathan M. Kreisberg (2), Susanne V. Hering (2), Graham Bench (3), Kenneth Docherty (4), Delphine K. Farmer (4), Jose-Luis Jimenez (4, (1) University of California, Berkeley (2) Aerosol Dynamics Inc. (3) Lawrence Livermore National Laboratory (4) University of Colorado, Boulder

We present hourly in-situ measurements of organic speciation of atmospheric aerosol (diameters less than 2.5 micrometers) collected above a ponderosa pine plantation owned by Sierra Pacific Industries adjacent to the Blodgett Forest research station in the Sierra Nevada Mountains, California. The measurements were obtained using thermal desorption aerosol GC-MS (TAG) as part of the Bioparticle Effects on Aerosols and Photochemistry EXperiment (BEARPEX) from September 9th - October 10th 2007 during the transition from the summer to fall seasons. The early part of the campaign was characterized by hot and dry conditions (daily average temperature ~20 degrees C and relative humidity ~30%) and frequent influence from forest fire events as indicated by specific burning aerosol marker compounds, e.g., retene and levoglucosenone. The later part was generally cooler and more humid (daily average temperature ~10 degrees C and relative humidity ~60%) with sporadic precipitation, which lead to significant increases in biogenic emissions and subsequently biogenic oxidation products observed in the particle phase.

The hourly time resolution of TAG provides far greater information on diurnal variations than more traditional filter samples. We observe higher concentrations of anthropogenic marker compounds (e.g., phthalic and benzoic acids) in the early afternoon with the arrival of the pollution plume from Sacramento. While higher concentrations of biogenic marker compounds (e.g., pinonaldehyde and nopinone) are observed at night suggesting local oxidation of primary biogenic emissions in the shallow nocturnal boundary layer. Radiocarbon (carbon -14) analysis at the site shows that 70 - 100% of the carbon present in the PM2.5 aerosol is modern indicating the importance of biogenic sources on aerosol composition at this site. We use the TAG data in conjunction with aerosol mass spectrometer (AMS) measurements to investigate the relative contributions of different source categories (e.g., biomass burning, primary biogenic emissions, secondary biogenic oxidation etc) to aerosol composition during the BEARPEX campaign.
14B.04

PM2.5 samples were collected using high volume samplers from one of the Southeastern Aerosol Research and Characterization (SEARCH) sites in North Birmingham, Alabama during winter (December, 2004-February, 2005) and summer (June-August, 2005). Based on the ratios of organic carbon (OC) to elemental carbon (EC), samples were selected and classified into four groups: summer high OC/EC ratio (SH), summer low OC/EC ratio (SL), winter high OC/EC ratio (WH), and winter low OC/EC ratio (WL). In addition, the emission from coke plant in Birmingham (CP) was also analyzed in order to compare to the ambient samples. For each group, polycyclic aromatic hydrocarbons (PAHs), alkanes and fatty acids were quantified by gas chromatography/mass spectrometry (GC/MS); and radiocarbon signatures and abundances of PAHs, alkanes and fatty acids were determined by accelerator mass spectrometry to apportion their origin between fossil and modern sources. For PAHs, the delta C-14 and delta C-13 values ranged from -915 % to -993 % and -33.6 % to -23.7 %, respectively. For alkanes, it varied from -712 % to -844 % and -30.4 % to -23.9 %, respectively. The delta C-14 and delta C-13 values of fatty acids were in the range of -235 % to 104 % and -31.7 % to -23.3 %, respectively. 14C data indicated that PAHs and alkanes were dominated by fossil source; while fatty acids were mainly from modern origin. The concentrations and radiocarbon abundances of these compounds varied with seasons and OC/EC ratios, demonstrating that radiocarbon analysis of individual organic compounds can be a helpful tool to better understand the sources of carbonaceous aerosols.

14B.05

Recent studies show a quantitative correlation between water soluble organic carbon (WSOC) measured by Particle-into-Liquid-Samplers (PILS) and the oxygenated organic aerosol (OOA) component derived from aerosol mass spectra. Both WSOC and OOA have been proposed as surrogates for secondary organic aerosol (SOA), but the chemical composition of neither is well-constrained. Oxalate and other dicarboxylic acids have been observed to constitute a significant fraction of water soluble organic mass in several field studies. In addition to being products of gas-phase photooxidation reactions, a large fraction of particle-phase dicarboxylic acids are thought to be formed through cloud processing. Thus, it is reasonable to expect oxalate and other dicarboxylic acids to be major contributors to WSOC, especially in areas with active cloud processing.

We present results from three airborne field campaigns conducted off the Central Coast of California and near Houston, Texas in which we flew an Aerodyne compact Time of Flight Aerosol Mass Spectrometer (cToF-AMS) side by side with a PILS instrument configured to do offline ion-chromatographic analysis. The off-line analysis enables us to measure oxalate and several other dicarboxylic acids not typically measured by online methods. We explore the relationship between dicarboxylic acids, AMS organic mass, and the AMS OOA component in both cloudy and clear air. We also explore how these relationships change in air masses dominated by urban pollution, urban outflow, agricultural emissions and both pristine and shipping-influenced marine air.
Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. MARIA CRISTINA FACCHINI (1) Matteo Rinaldi (1), Stefano Decesari (1), Claudio Carbone (1), Emanuela Finessi (1), Darius Ceburnis (2), and Colin D. O'Dowd (2), E. Douglas Nilsson (3), 1) Institute of Atmospheric Sciences and Climate (ISAC), CNR, Bologna Italy 2) School of Physics and Centre for Climate and Air Pollution Studies, Environmental Change Institute, National University of Ireland, Galway, Ireland. 3) Department of Applied Environmental Science, Stockholm University, Sweden

The chemical properties of sea-spray aerosol particles produced by artificially generated bubbles from oceanic waters were investigated during a phytoplankton bloom in the North Atlantic (11 June - 5 July, 2006). Spray particles were generated on board the oceanographic vessel Celtic Explorer in airtight stainless steel tanks continuously fed with seawater collected at about 2 m below the sea surface. The experiment was held under the frame of the EU Project MAP (Marine Aerosol Production). Nascent aerosol was analyzed for total carbon, water soluble organic carbon and main inorganic ions; organics (both water soluble and insoluble) characterization was performed by high-resolution proton Nuclear Magnetic Resonance (1H NMR). Nascent spray particles exhibited a progressive increase in the organic matter (OM) content from 3 +/- 0.4 % up to 77 +/- 5 % with decreasing particle size, the rest being sea salt. Submicron OM was almost entirely water insoluble (WIOM): up to 96 +/- 2 % in the 0.125-0.25 micro-meter size range.

1H NMR analysis shows that WIOM in nascent marine aerosol forms from aggregation of lipo-polysaccharides exuded by phytoplankton. Colloids and aggregates are responsible for the decrease of surface tension observed in the aerosol water extracts. Our observations indicate that size dependent transfer of sea water organic material to primary marine particles is mainly controlled by the solubility and surface tension properties of marine OM.

The pattern of WIOM and sea-salt content in the different size intervals observed in bubble bursting experiments is similar to that measured in atmospheric marine aerosol samples collected during periods of high biological activity at the same location and on the coast at Mace Head Research Station. The results point to a WIOM/sea-salt fingerprint associated with submicron primary marine aerosol production in biologically rich waters.

Impact of primary particulate matter from ocean going engines in southern California air basin is quantified by collocating in-stack measurements, from in-use Ocean going vessels (OGVs), with the ambient measurements made at several monitoring stations in southern California. Vanadium and nickel will be demonstrated as robust markers for the combustion of heavy fuel oil in the ocean going engines in southern California with the concentration profiles in the southern California air basin dropping inversely with increased distance from the port. The in-stack measurements were conducted on the propulsion engines of two different in-use ocean going vessels. The vanadium and nickel emission rate (g/hr) normalized by vanadium and nickel content in the fuel correlates with PM emission rate (g/hr) with slope of 8205 (g of PM/g of V) and 8045 (g of PM/g of Ni) for vanadium and nickel, respectively. The primary PM2.5 emissions from ships are then predicted from the ambient measurements of vanadium and nickel. The primary PM2.5 from the ships is around 8.8 percent of the total PM2.5 at the location close to the port and at 50 miles inland from the port, the primary PM2.5 is 1.4 percent of total PM2.5. The methodology demonstrated in this research should be useful in studies determining human health impact of the emission of OGVs on people living in the vicinity of ports.

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The St. Louis Advanced Monitoring Initiative (AMI) project was initiated to assist the State of Illinois and the State of Missouri in developing State Implementation Plans (SIP) for fine particulate matter (PM2.5) in the St. Louis non-attainment area. A source sampling study and ambient monitoring study were conducted to assist in the identification of sources contributing to non-attainment status in St. Louis. As part of the source sampling study, grab samples were collected in and around the Granite City Steel Works (GCSW) in Granite City, IL - considered to be a significant source in the St. Louis area in general and the largest point source contributor at the current design value site for the PM2.5 annual-average NAAQS. Source samples included the basic oxygen furnace, steel and iron slag crushing, coal pulverizing, baghouse dust, paved road dust, and unpaved road dust. The bulk source samples were resuspended using a PM2.5 cutpoint and collected on Teflon, quartz, and polycarbonate filters. Samples will be analyzed for inorganic elements by XRF and ICP-MS; elemental and organic carbon; inorganic anions and cations by IC; and organic species by GC/MS. The resulting process-specific steel operations source profiles and road dust source profiles will be combined with ambient monitoring data to determine the impact of the steel facility in the Granite City area. For the ambient monitoring study, both active dichotomous samplers and passive aerosol samplers were deployed upwind and downwind of the GCSW facility. This presentation will highlight the study design and present some of the preliminary results of PM2.5 inorganic species observed in the source samples and in the upwind and downwind dichotomous samples.

A field study was conducted in Granite City, IL as part of the St. Louis Advanced Monitoring Initiative to assess the impact of local emission sources on PM10-2.5 concentrations at monitoring sites located near the Granite City Steel Works (GCSW) facility in Granite City, IL. Ambient sampling was conducted at four sites during five 3-day periods between 10/13/07 and 12/14/07. Sites were located to target different sources or operations within the GCSW facility. The 3-day sampling events were chosen based on local weather forecasts to maximize the likelihood that two sites would be primarily upwind and two sites would be primarily downwind of the GCSW facility during the sampling period. During each sampling period, filter-based PM2.5 and PM10-2.5 ambient samples were collected at one upwind site and one downwind site using sequential dichotomous samplers, while UNC passive PM samplers were simultaneously deployed at all four sampling sites. Dichot samples were analyzed by XRF to determine PM2.5 and PM10-2.5 mass and inorganic elemental concentrations, while passive samples were analyzed by Computer-Controlled Scanning Electron Microscopy (CCSEM) to determine particle size distributions, and individual particle morphology and composition. Interpretation of the ambient data and assessment of specific source impacts was aided by elemental (XRF) and particle-based (SEM) source profiles generated from grab samples collected from suspected emission and fugitive dust sources in and around the GCSW facility. Preliminary results showing the impact of local sources based on comparison of upwind and downwind samples will be discussed.
3B.06
Particle Size Distribution and Chemical Composition in and around a Swine Operation. PHILIP J. SILVA (1), Randal S. Martin (2), Kori Moore (3), and Mark Erupe (1), (1) Department of Chemistry and Biochemistry, Utah State University, Logan, Utah (2) Department of Civil and Environmental Engineering, Utah State University, Logan, Utah (3) Space Dynamics Laboratory, North Logan, Utah

Agricultural facilities are the source of many types of particles and gases that can exhibit an influence on air quality. Particle mass concentration influences from agricultural sources can include both primary emissions and secondary particle formation through emission of gaseous precursors.

In support of other investigations at a swine production facility using a Lidar instrument, continuous and near-real-time measurements of particulate size distribution and composition were obtained. The facility consisted of three separate, parallel, deep-pit style barns. Each barn housed around 1250 pigs with an average weight of approximately 90 lbs per animal. A single trailer for was equipped with a aerosol mass spectrometer (AMS-Aerodyne, Inc.), a PM2.5 elemental/organic carbon (EC/OC) analyzer (R&P, Inc., Series 5400) and an eight-stage cascade impactor (Tisch Environmental, Inc., Model TE-20 -800). In addition, several optical particle counters (MetOne, Inc. Model 9012) and portable PM10/PM2.5 samplers (AirMetrics MiniVol) were arrayed within and around the facility in order to determine particle plume transport throughout the facility.

Background PM10 and PM2.5 concentrations were found to average around 35 and 10 micrograms m$^{-3}$, respectively. In-plume values were 40-60 and 10-15 micrograms m$^{-3}$, respectively. The optical particle counters showed size distribution variations as a function of time and sampler location. Throughout the study, the AMS detected mass concentrations of 3-5 micrograms m$^{-3}$. The AMS consistently observed organic carbon as the dominant constituent with OC making up ~60% of the total mass. Smaller amounts of sulfate and nitrate were detected. The real-time carbon analyzer found typical out-of-plume elemental and organic PM2.5 carbon concentrations on the order of 0.4 and 1.2 micrograms m$^{-3}$, respectively. In-plume concentrations were observed with nominal values of 2.2 and 4.0 micrograms m$^{-3}$, respectively.

7B.01
Highly Time-Resolved Organic Compounds Concentrations of Primary and Secondary Nature during the Baltimore PM2.5-Supersite Study. Wolfgang F. Rogge (1), Anna Bernardo-Bricker (2), John M. Ondov (3), (1) University of California, Merced, (2) Florida International University, Miami, (3) University of Maryland, College Park

Most of the knowledge about the nature of ambient organic compounds associated with airborne fine particulate matter is obtained from integrated sampling of 24 hours or longer. While major insight has been gained, little is known about diurnal changes in concentrations due to the interplay of local sources and pollutant transport from distant sources. Likewise, the impact of atmospheric chemistry on the composition of organic aerosol is mainly unknown or limited to smog chamber experiments.

Here, a specially designed sampling system was deployed during the 2002-2003 Baltimore PM-Supersite Study to collect PM2.5 on filters and PUFs with a 3-hourly resolution for three weeks during summer and another three weeks during winter. From the sample sets, a total of four weeks for summer and winter were subjected to chemical analysis. Over 100 individual compounds including homologues series of n-alkanes, n-alkanoic acids, n-alkenoic acids, n-alkylcyclohexanes, hopanes, PAHs, oxy-PAHs, levoglucosan, resin acids, syringyl-moieties, aromatic and aliphatic dicarboxylic acids, secondary biogenic compounds, sterols, tris(2,4-di-tert-butylyphenyl)phosphate and others were quantified.

For primary organics, no repeatable diurnal concentration patterns on a day to day basis are observed as one would expect if major local sources such as vehicular traffic would be isolated from nearby or more distant source regions. In contrast, averaging the daily diurnal ambient concentrations reveal ambient diurnal patterns that relate to diurnal emission patterns of major source classes. Also, the short-term release of pollutants from a temporary source has been detected. For example, for a two day period, higher molecular weight n-alkanes, indicators for plastic waste burning, have been measured at substantially elevated concentrations together with the locally prevailing meteorology, allowing pinpointing possible source regions. Another surprise is the substantial depletion of unsaturated fatty acids during the summer and a pronounced diurnal variation for these compounds during day and night in winter. Biogenic secondary organic compounds have been detected as well, and their ambient concentration levels increase during the night when the relative humidity levels increase and chemical formation is favored.
Concentrations Of Polycyclic Aromatic Hydrocarbons And Metoxphenols In Urban And Suburban Air Particulates In East Of France. Olivier Delhomme Maurice Millet, University of Strasbourg I / CNRS, France

Polycyclic aromatic hydrocarbons are ubiquitous pollutants resulting from incomplete combustion and hence normally unavoidable. The metoxyphenols are as for them emitted in the atmosphere only at the time of the biomass combustion.

To improve air quality it is necessary to understand the reasons that caused high levels of these different pollutants. In this paper we present the results obtained in the evolution of the air quality levels. The work is focused on the seasonal and temporal variations for the identification of pollution sources.

Field measurements and particulate collection were performed during summer and winter campaigns in Strasbourg (urban site) and Spicheren (suburban site) in 2006 and 2007. Periods of sampling varied between 04:00 to 10:00, 10:00 to 16:00, 16:00 to 22:00 and 22:00 to 04:00 in order to evaluate the spatial and the temporal variations.

The results obtained suggest that the principal source of the HAP in the atmosphere seems particularly related to the automobile traffic. The residential heating, in winter period becomes the majority source. In addition, on the urban site, one can have contributions in HAP due to transport coming from the industrial parks.

The emission of the metoxyphenols by combustion of biomass (primarily wood combustion), causes a great seasonal influence, with very weak concentration during summer period. In winter period, the contribution by the residential heating, makes increase the abundance of these compounds. In urban zone, less influenced by the heating with wood, the compounds can come from industries.

Carbohydrates as Molecular Markers for Source Apportionment of Ambient Fine and Course Particulate Matter to Agricultural and Native Soils in Central Arizona. ANDREA L. CLEMENTS (1), Yuling Jia (1), Matthew P. Fraser (2), (1) Civil and Environmental Engineering, Rice University, Houston (2) Global Institute of Sustainability, Arizona State University, Tempe

In the desert southwest, fugitive dust emissions contribute significantly to ambient aerosol concentrations. Wind erosion from the arid land is a primary contributor to ambient particulate matter (PM) concentrations but, in regions including Central Arizona, desert lands have been converted for agriculture use and thus agriculture processes constitute another contributor. As the metropolitan Phoenix region expands into these agricultural lands, urban sources and construction also contribute to the ambient PM load. In an effort to identify and assess the relative contribution of these and other major PM sources in the region, a series of ambient PM samples and soil samples were collected near Higley, AZ, a suburb of Phoenix which has seen rapid urbanization onto agricultural lands. Size segregated soil and ambient PM samples were analyzed for bulk mass, elemental and organic carbon content, and a number of specific compounds including ions, metals, alkanes, organic acids, polycyclic aromatic hydrocarbons, and saccharides. Key contributors to PM10 and PM2.5 levels have been determined by positive matrix factorization (PMF) of the ambient marker concentrations determined from PM samples. Subsequently, samples of local soil from native and agricultural fields and local roadways were size-segregated and analyzed in an effort to create a source profile for the dust in the area. A chemical mass balance model has been compared with the PMF results.
7B.04
KENNETH S. DOCHERTY (1,2), Ingrid M. Ulbrich (1,2), Peter F. DeCarlo (1,3,9), Allison C. Aiken (1,2), John A. Huffman (1,2), Michael J. Cubison (1,2), Edward J. Dunlea (1,2,10), Donna Sueper (1,4), Joel R. Kimmel (1,4), Richard E. Peltier (5,11), Rodney J. Weber (5), Elizabeth A. Stone (6), David C. Snyder (6), James J. Schauer (6), Brett D. Grover (7,12), Delbert J. Eatough (7), Brent J. Williams (8), Megan McKay (8), Allen Goldstein (8), and Jose L. Jimenez (1,2), (1) Cooperative Institute for Research in Environmental Sciences, (2) Department of Chemistry and Biochemistry and (3) Department of Atmospheric and Oceanic Sciences, University of Colorado, Boulder, Colorado (4) Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc., Billerica, MA (5) School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia (6) Environmental Chemistry and Technology Program, University of Wisconsin, Madison, Wisconsin (7) Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah (8) Department of Environmental Science and Policy Management, University of California, Berkeley, California (9) Currently at Paul Scherrer Institut, Switzerland (10) Currently at United States National Oceanic and Atmospheric Administration, Boulder, Colorado (11) Currently at NYU School of Medicine, Department of Environmental Medicine, Tuxedo, New York (12) Currently at the United States Environmental Protection Agency, National Exposure Research Laboratory, Research Triangle Park, North Carolina

Ambient sampling was conducted during the summer 2005 Study of Organic Aerosols in Riverside (SOAR-1) using state-of-the-art instruments, including the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). Riverside and surrounding areas are characterized by poor air quality, consistently rating as the worst in the US for fine particle concentrations.

The organic aerosol (OA) during SOAR-1 was overwhelmingly secondary in nature according to six different estimation techniques, including positive matrix factorization of HR-ToF-AMS mass spectra (PMF-AMS). These results are contrary to those of previous studies in the LA basin that found a dominance of secondary organics only during short-term photochemical events. Similar results appear to hold for Pasadena based on the comparison of the AMS spectra.

We will also present the results of PMF-AMS OA analysis. Several components are identified that were evaluated by comparing PMF-AMS factor mass spectra and time series with standard spectra and time series of tracer species (Ulbrich, et al., ACPD, 2008), respectively, including those from a collocated Thermal Desorption Aerosol GC/MS-FID (TAG) instrument. One primary surrogate factor (hydrocarbon-like OA, HOA) was identified. The mass spectrum of this factor is highly correlated with primary spectra (e.g., vehicle exhaust) and has a diurnal profile similar to primary tracer species including CO, NOx, and EC. On average, the sum of identified oxygenated organic aerosol (OOA) factors contributes ~80% of OA, which are interpreted as surrogates for SOA. Mass spectra and time series of OOA factors are well correlated with time-resolved data from a Thermal Desorption Aerosol GC/MS-FID (TAG) instrument. The high correlation between PMF factors and TAG spectra further supports the use of positive matrix factorization for source apportionment studies. These analyses indicate that urban organic aerosol is dominated by hydrocarbon-like Organic Aerosol (HOA) and oxygenated organic aerosol (OOA). HOA has been linked to primary organic PM from mobile emissions and other sources while OOA has a major contribution from secondary organic aerosol. In this study, PMF is used to systematically analyze various urban datasets and to extract the key organic components in each of the environments. The main goal of this work is to find a common component description of urban organic aerosols. Such a description would be useful for developing better parameterizations in aerosol models.

7B.05

Organic aerosol species account for a large fraction of the aerosol mass measured in urban environments. The Aerosol Mass Spectrometer (AMS) provides real-time quantitative mass concentrations of the non-refractory organic species in/on ambient aerosol. Principal component analysis-based techniques and multivariate analysis techniques such as positive matrix factorization and the multilinear engine (PMF and ME ) have been used for the analysis of AMS organic mass spectra. These analyses indicate that urban organic aerosol is dominated by hydrocarbon-like Organic Aerosol (HOA) and oxygenated organic aerosol (OOA). HOA has been linked to primary organic PM from mobile emissions and other sources while OOA has a major contribution from secondary organic aerosol. In this study, PMF is used to systematically analyze various urban datasets and to extract the key organic components in each of the environments. The main goal of this work is to find a common component description of urban organic aerosols. Such a description would be useful for developing better parameterizations in aerosol models.
Source Characterization and Apportionment

7B.06
Redox Activity and Chemical Speciation of Size Fractioned PM in the Communities of the Los Angeles - Long Beach Harbor. Shaohua Hu (1), Andrea Polidori (2), Mohammed Arhami (2), Martin M. Shafer (3), James J. Schauer (3), Arthur Cho (4) and Constantinos Sioutas (2), (1) California Air Resource Board (CARB) (2) University of Southern California (3) University of Wisconsin-Madison (4) University of California, Los Angeles

In this study, two different types of assays were used to quantitatively measure the redox activity of PM and to examine its intrinsic toxicity: 1) in vitro exposure to rat alveolar macrophage (AM) cells using dichlorofluorescin diacetate (DCFH-DA) as the fluorescent probe (macrophage ROS assay), and: 2) consumption of dithiothreitol (DTT) in a cell-free system (DTT assay). Coarse (PM$_{10-2.5}$), accumulation (PM$_{2.5-0.25}$), and quasi-ultrafine (quasi-UF, PM$_{0.25}$) mode particles were collected weekly at five sampling sites in the Los Angeles-Long Beach Harbor and at one site near the University of Southern California campus (urban site). All PM samples were analyzed for organic (total and water-soluble) and elemental carbon, organic species, inorganic ions, and total and water-soluble elements. Quasi-UF mode particles showed the highest redox activity at all Long Beach sites (on both a per-mass and per-air volume basis). A significant association ($\text{R}^2 = 0.61$) was observed between the two assays, indicating that macrophage ROS and DTT levels are affected at least partially by similar PM species. Relatively small variation was observed for the DTT measurements across all size fractions and sites, whereas macrophage ROS levels showed more significant ranges across the three different particle size modes and throughout the sites (coefficients of variation, or CVs, were 0.35, 0.24 and 0.53 for quasi-UF, accumulation, and coarse mode particles, respectively). Association between the PM constituents and the redox activity was further investigated using multiple linear regression models. The results showed that OC was the most important component influencing the DTT activity of PM samples. The variability of macrophage ROS was explained by changes in OC concentrations and water-soluble vanadium (probably originating from ship emissions - bunker oil combustion). The multiple regression models were used to predict the average diurnal macrophage ROS and DTT levels as a function of the OC concentration at one of the sampling sites.

8B.01
The Use of Potential Source Contribution Functions to Examine Potential Source Areas and Transport Pathways of Nitrate and Sulfate in UK. Yetan Li(1), Philip Hopke(2), Roy Harrison(2), (1) Clarkson University (2) The University of Birmingham

PM10 is among the most harmful of all air pollutants. PM10 can increase the number and severity of asthma attacks, cause or aggravate bronchitis and other lung diseases, and reduce the body's ability to fight infections. Nitrate and sulfate are major contributors to atmospheric concentrations of PM10 in the UK. In this study, the utility of potential source contribution function (PSCF) to identify the potential source areas and transport pathways that give rise to the observed high concentrations of nitrate and sulfate measured at three monitoring sites in the UK (Belfast, Harwell, and North Kensington) from October 2001 to December 2006 is explored. 5-day backward trajectories arriving at the midpoint of 24-h integration period at 500 m above ground level were calculated using NOAA HYSPLIT. The PSCF analyses were based on the average values as criterion values for the measured particulate parameters. The resulting maps identifies specific geographic areas associated with nitrate and sulfate sources regions or preferred transport pathways to sampling locations.
Source Characterization and Apportionment

8B.02
Size-Segregated Inorganic and Organic Components of PM in the Communities of the Long Angeles Harbor.

MOHAMMAD ARHAMI (1), Markus Sillanp??(1), Shaohua Hu(1), Michael R. Olson(2), James J. Schauer(2) and Constantinos Sioutas(1), (1) university of Southern California, (2) University of Wisconsin-Madison

The Los Angeles Ports complex consists of the Port of Long Beach and the Port of Los Angeles. Due to the high levels of particulate matter (PM) emitted from many sources in the vicinity of these ports and to their projected massive expansion, the Harbor area will be the focus of future governmental regulations. This study aims to characterize the physicochemical properties of PM at locations influenced by port-affiliated sources. PM samples were collected concurrently at six sites in the southern Los Angeles basin for a 7-weeks period between March and May 2007. Four sites were set-up within the communities of Wilmington and Long Beach; one site was located at a background location near the harbors of the Los Angeles port; the sixth site, near downtown Los Angeles, was chosen to represent a typical urban area. Coarse (PM2.5-10), accumulation (PM0.25-2.5), and quasi-ultrafine (PM0.25) mode particles were collected at each site. Samples were analyzed for organic and elemental carbon content (OC and EC, respectively), organic species, inorganic ions and water soluble and total elements. The carbon preference index (CPI) varied from 0.65 to 1.84 among sites, suggesting high influence of anthropogenic sources in both the accumulation and the quasi-Uf modes. Vehicular emissions from the nearby traffic were the most prominent anthropogenic sources of both quasi-ultrafine and accumulation mode PM (except at the background site). Secondary reactions were also a significant source of accumulation mode particles. Marine vessels were found to be major emitters of vanadium, nickel and sulfur in the quasi-ultrafine mode. Overall, traffic sources were major contributors to the PM and organic matter mass, and prevailed over ship emissions and oil combustion even in the studied harbor community.

8B.03
Spatial and Temporal Trends in Carbonaceous Aerosols within two midwestern cities.

David C. Snyder(1), Rebecca C. Bader(1), Christopher Worley(1), Michael Olson(1), Martin Shafer(1,2), Timothy Dallmann(1), Andrew P. Rutter(1), and James J. Schauer(1,2) , (1) University of Wisconsin-Madison, Environmental Chemistry & Technology Program, (2) Wisconsin State Laboratory for Hygiene

Daily, twenty-four-hour filter-based collections of PM2.5 were obtained over one month, intensive, concurrent, sampling periods in Detroit, MI and Cleveland, OH during the summer of 2007 and the winter of 2008. Samples were collected at three (3) sites within each city and analyzed for organic and elemental carbon (OC/EC), water soluble organic carbon (WSOC), and water soluble metals. The temporal and spatial variability of these species were examined in order to understand the source contributions to the organic fraction of aerosols at these locations. Trends in OC concentrations were strongly correlated across all six sites during the summer intensive study period, suggesting that OC was primarily regional in nature. However in winter, the trends in carbonaceous aerosols appear to be more episodic and less impacted by regional aerosols. During the summer campaign, trends in WSOC were also well correlated temporally across all six sites and consistently comprised 50 to 60% of organic carbon suggesting that SOA formation is a dominant source of OC at these locations. Correlations between WSOC and OC were stronger for sites located in more suburban locations then those located adjacent to probable industrial sources. For sites in industrial zones, trends in water soluble Iron, OC, and EC concentrations were used to identify days during both summer and winter intensives in which local sources contributions were more likely to be greater. Potential point sources for these days were identified using data obtained from real-time measurements of carbonaceous aerosols, Mercury, and criteria gases, which were then compared with wind direction and back trajectories to identify specific sources contained within the national emissions inventory. Results from both summer and winter intensive campaigns suggested that elemental carbon was more strongly influenced by local sources than was OC.
8B.04
Urban Aerosol Chemistry in the City of Edmonton. Paul Makar (1), CRAIG STROUD (1), Sunhee Cho (2), Brian Wiens (3), Win Lee (4), John Liggio (1), Shao-Meng Li (1), Lisa Graham (5), Jeff Brook (1), Mourad Sassi (6), Mike Moran (1), Wanmin Gong (1), Sunling Gong (1), Kevin Strawbridge (1), Kurt Anlauf (1), Cristian Mihele (1), Desiree Toom-Sauntry (1), (1) Air Quality Research Division, Environment Canada, Toronto, Canada (2) Alberta Environment, Edmonton, Alberta, Canada (3) Prairie and Northern Region, Environment Canada, Edmonton, Alberta, Canada (4) CANMET Energy Technology Centre, Natural Resources Canada, Ottawa. (5) STB - ESTCD - Emissions Research and Measurement, Environment Canada, Ottawa (6) Air Quality Model Applications Unit, Environment Canada, Dorval, Quebec.

Edmonton, Alberta, Canada (pop. 1M) is home to a large and growing number of petrochemical processing plants (8000 industrial point sources within 150 km of the city center), several coal-fired power-plants 60 km upwind of the city, and, depending on the wind direction, is sometimes downwind of Canada's oil sands, a major petrochemical extraction facility. These combined sources along with unique meteorological circulation patterns along the eastern edge of the Rockies combine to create significant particulate matter events in and around the city.

Several of these events were captured in a measurement study in the summer of 2005 (PrAIRie2005), in which airborne AMS, particle size probes, and gas analysis on two aircraft were combined with ground-based mobile AMS, PTR-MS, OC/EC, gas and lidar measurements in order to characterize particulate matter in the city.

The measurements as well as subsequent high resolution (3 km horizontal, 2 minute time step) nested regional model simulations using Environment Canada's A Unified Regional Air-Quality Modelling System (AURAMS) have allowed the identification and chemical characterization of individual sources in and around the city. Observed (AMS) and model-generated PM1 species were compared along individual flight tracks at two minute intervals using standard statistical measures (e.g. correlation coefficient, normalized mean bias, etc.).

The picture that has emerged is one of a complex interaction between regional and local urban circulation and chemistry. On the larger scale, pollutants leaving Edmonton have been found to return to the city several days later, after sufficient processing to create significant particulate sulphate. Individual local sources have also been shown to create significant and chemically distinct high PM concentration events (e.g. primary and or secondary organics versus sulphate dominating in the fine mode in accord with source). Both the long-range and local chemistry associated with these events will be described.

8B.05
Single Particle Observations of Variability within the Urban Aerosol. ANDREW AULT, Cassandra Gaston, Ying Wang, Melanie Zauscher, Robert Moission, Kimberly Prather, University of California, San Diego.

Spatial variability in the size and chemistry of the urban aerosol in the Los Angeles Basin was monitored in November 2007 with a transportable laboratory containing gas and particle phase instrumentation. Real-time size-resolved chemical measurements of individual particles were made using an aerosol time-of-flight mass spectrometer (ATOFMS) and an ultrafine aerosol time-of-flight mass spectrometer (UF-ATOFMS) together measuring the size-resolved chemical composition of particles from 50 nm - 3 um. The focus of the study was characterizing both local sources (cars, trucks, and ships) and regionally transported particles (dust and sea salt) and their variation on a neighborhood scale (5-10 miles), which impact human health. Gas phase instrumentation (NOx, O3, SO2, and CO), size distribution measurements (SMPS and APS), and black carbon mass concentrations (aethalometer) were used to identify overall pollution characteristics and times with unique influences. The high time resolution of the peripheral and ATOFMS instrumentation (~5 min) identified rapid changes in the aerosol from vehicular, ship, and stationary plumes improving source apportionment of primary particles. Variations in wind patterns encountered during sampling provided unique opportunities to observe fluctuations in the primary and secondary chemical composition of the aerosol. Significant differences were observed between fresh and aged time periods; the unique fingerprints of the individual particles provided insight into the aging processes of different particle types, such as dust, sea salt, organic carbon, and elemental carbon, which were transformed through the addition of major secondary species including nitrate, sulfate, and ammonium. Proximity to local sources and concentrations of gas and particle phase pollution played a key role in the spatial variability of the urban aerosol.
Chemical Speciation of PM Emissions from Heavy Duty Diesel Vehicles Equipped with Diesel Particulate Filter (DPF) and SCR Retrofits. S. Hu(1,3), S. Biswas(1), V. Verma(1), J. Schauer(2), J. Herner(3), A. Ayala(3) and C. Sioutas(1), (1)University of Southern California, Los Angeles, (2)University of Wisconsin-Madison, Madison, (3)California Air Resources Board, Sacramento

Chemical profiles have been well established to characterize the source contribution of diesel powered engines to ambient air quality for decades. However, there is limited knowledge about the emissions from some of the emerging diesel systems designated to reduce PM with a diesel particulate filter (DPF) and NOx control by selective catalytic reduction (SCR). It is expected that with the introduction of advanced aftertreatment in diesel applications, the chemical composition of emitted particles will be substantially altered.

A collaborative project is ongoing between the California Air Resources Board (CARB) and the University of Southern California, to investigate the physicochemical and toxicological properties of the semi-volatile and non-volatile fractions of PM emissions from heavy duty diesel vehicles (HDDV) retrofitted with state-of-the-art PM and NOx control systems. Four HDDVs in six retrofit configurations and a Baseline vehicle (without aftertreatment) were tested under cruise, transient (UDDS) and idle operation at CARB heavy duty diesel test laboratory in Los Angeles. PM physical properties including size distribution, volatility and surface characteristics from these diesel vehicles have been described in detail by Biswas et al (2008). In addition, size resolved aerosols were collected using a MOUDI and nano MOUDI loaded with pre-baked Al foil substrate and analyzed for EC/OC, ion (composite samples) concentrations. High volume sampler loaded with Teflon coated glass fiber filter was analyzed for ion, metal and elements, water soluble OC and organic species.

PM emissions from vehicles with significant formation of nucleation mode particles were dominated by sulfate particles. Compared to the baseline vehicle, along with the significant reduction of TC, OC dominated EC as the major species for the retrofitted vehicles. Water-soluble OC predominated in OC emissions from retrofitted vehicles. Ammonium was mainly presented in the emissions from vehicles equipped with diesel oxidative catalyst (DOC). Ammonium was neutralized by sulfate particle to some extent in the ultrafine mode, inferring ternary nucleation mechanism. Elevated levels of certain metals and elements were observed for the retrofitted vehicles. Effect of driving cycles for the chemical emissions will be discussed in this paper.

Reference:

Parameters Affecting In-cabin to On-roadway (I/O) Ultrafine Particle Concentration Ratios. B. Xu and Yifang Zhu, Texas A&M University, Kingsville

A mass-balance indoor particle dynamic model was adopted and modified to investigate how on-roadway ultrafine particle (UFP, diameter < 100 nm) concentrations and vehicle ventilation settings affect UFP levels inside vehicles. Analysis focused on how the model input parameters, such as ventilation settings, vehicle speed, filtration, penetration, deposition, and human respiration, affect in-cabin to on-roadway (I/O) UFP concentration ratios. Under three different ventilation conditions, (i) Fan off-recirculation (RC) off, (ii) Fan on-RC off, and (iii) Fan on-RC on, the average UFP I/O ratios were found to be 0.45, 0.30 and 0.18, respectively. Under condition (i), the modeled I/O ratios increased linearly, up to ~25%, within the literature reported penetration factor range. The I/O ratios were directly proportional to vehicle speeds, increased by ~15% from 20 mph to 70 mph, and were inversely affected by deposition coefficient for approximately 10-30%. Under condition (ii), the airflow rate of mechanical ventilation was the predominant factor and inversely proportional to the I/O ratios in the range of 0-110 m$^3$ h$^{-1}$ but directly proportional to the I/O ratios in the range of 110-360 m$^3$ h$^{-1}$. The I/O ratios may increase to 50% when the mechanical supply air rises from 110 m$^3$ h$^{-1}$ to 360 m$^3$ h$^{-1}$. Penetration factor, deposition coefficient and vehicle speed showed much less effects. Under condition (iii), the effects of penetration factor (<10%), deposition coefficient (<10%) and vehicle speed (<8%) were comparable. Mechanical ventilation was inversely proportional to the I/O ratios in the whole range (0-360 m$^3$ h$^{-1}$) with 10%-20% influence depending on the particle size. It usually takes 5 to 210 seconds for the in-cabin UFP concentrations to achieve a new mass balance with respect to on-roadway UFP variations under studied ventilation settings.
Although commuting time typically accounts for only 6% of the day for Americans, it has become a significant source of exposure to ultrafine particles (< 0.1 micro-meter) from vehicular emissions, which has been associated with various respiratory and cardiovascular adverse health effects. Particle deposition onto indoor surfaces, as an important particle loss mechanism, has been studied extensively. However since both air velocities and surface to volume ratios differ greatly between indoor and in-cabin, conclusions from indoor studies may not be directly applied to the in-cabin microenvironments. In this study, we measured UFP deposition rates under a range of air velocities and surface areas conditions inside different type of passenger cars. A diesel generator was used as a particle source and a Scanning Mobility Particle Sizer (SMPS) was used to measure UFP size distribution inside the test vehicles. As in-vehicle air velocities increased from natural convection to 0.65 m/s, UFP deposition rates increased with the greatest increases occurred for smaller particles. Other influencing factors, such as number of people inside the vehicles were also considered and investigated in this study. It was found UFP deposition rates are proportional to the surface areas inside vehicles with larger particles exhibiting greater effects than smaller ones. Compared with available data in the literature, the in-cabin UFP deposition rates are higher than those measured and modeled in many other indoor locations such as an experimental chamber or a residential house. This is probably due to the larger surface area to volume ratio and the more dramatic air movement inside vehicles.

Increasing evidences have demonstrated toxic effects of vehicular emitted ultrafine particles (UFPs, diameter < 100 nano-meter), with the highest exposure occurs on roadways. Children are particularly at risk due to immature respiratory systems and faster breathing rates. While previous studies have quantified school bus in-cabin air pollutant concentrations, research that specifically focuses on the impacts of retrofit devices on in-cabin diesel-related pollutant concentrations is limited. In this study, number concentration and size distribution of UFPs, total particle number concentration, PM2.5, PM10, CO, CO2, Black Carbon, and NOx concentrations were monitored inside diesel-powered school buses before and after retrofitting while driving on various roadways under different ventilation settings in south Texas. Retrofit devices used in this study included Spiracle, Diesel Oxidation Catalyst (DOC) and their combination. Each bus was tested both in the morning pick-up and the afternoon drop-off hours on a 90-120 minutes route which includes three sections: rural local streets, highways, and inner-city busy streets. Higher air pollutant concentrations were observed inside tested school buses than in the surrounding background air. The relative importance of various operating parameters was studied, among which retrofit devices, bus age, roadway type, and operation time had the greatest impact on the UFP concentrations inside school buses. In-cabin air quality improvements with respect to different retrofitting technologies were quantified.
9A.05
Carbonyls in Biodiesel and Diesel Exhaust in Gas and Particulate Phases and Effects of Photochemical Oxidation.
Kenneth G. Sexton  Kim de Bruijne  Seth Ebersviller  Cassie O'Lenick Ruby Woodside  Ilona Jaspers  Harvey E. Jeffries ,
University of North Carolina, Chapel Hill

The \'One Atmosphere\' research group at the University of North Carolina\'s School of Public Health has been conducting smog chamber experiments with diesel and biodiesel exhaust to study the photochemical reactivity of these two sources and to compare compositional and toxicological differences of the fresh and photochemically aged exhaust. Carbonyl analyses using PFBHA derivatization were performed on the gas and particle phases. While biodiesel (100% soybean based: B100) exhaust contains many of the same carbonyls found in diesel exhaust, there are many more and different carbonyls found in biodiesel, perhaps because of the difference in the fuel composition. Many elude identification using gas chromatography and mass spectrometry even when using extensive NIST and prepared chemical libraries based on scientific reports. Photochemical aging of the exhaust further modifies and complicates the carbonyl composition and enhances toxicological responses as measured by inflammation (IL-8) and cytotoxicity.

9A.06
Light- And Heavy-Duty Vehicle Emission Factors Of Pm Species Based On Freeway Measurements And Comparison With Tunnel And Dynamometer Studies. ZHI NING(1), Andrea Polidori(1), James J. Schauer(2), Constantinos Sioutas (1), (1) Department of Civil and Environmental Engineering, University of Southern California (2) Environmental Chemistry and Technology Program, University of Wisconsin-Madison

Emission factors of various particle species from light and heavy duty vehicles (LDVs and HDVs, respectively), including organic and elemental carbon (OC and EC,), sulfate, polycyclic aromatic hydrocarbons (PAHs), hopanes, steranes, trace metals, elements, and particle number (PN), were estimated based on roadway measurements. Sampling campaigns were conducted at two different roadways: the CA-110 highway (where only gasoline-powered vehicles are allowed), and the I-710 freeway (where about 20% of the total number of vehicles are diesel-powered trucks). The derived PM emission factors were compared to those reconstructed from recent source emission data from the Caldecott tunnel, and those from previous tunnel and chassis dynamometer studies. Very good agreement between estimated and reconstructed emission factors was found for PN, EC, sulfate, high molecular weight (MW) PAHs, hopanes and steranes. The agreement between our results and other studies in the emission factors of trace elements and metals varied from very good (for species such as Cu, Mo, Ba, Pb) to poor (for species such as Mg, Fe, Ca) probably because the atmospheric concentrations of the latter elements are associated with both traffic and non-traffic sources, and the relative abundances of Mg, Ca, and Fe in road dust varies considerably across locations. The emission factors of OC and EC were clearly highest for HDVs, and those of PAHs, hopanes, and steranes from our roadway measurements were well within the range of values reported in the literature from tunnel and dynamometer studies. The approach allows for a straightforward estimation of PM emission factors from ambient, near-freeway measurements.
9A.07
Real-Time Characterization Of Particle-Bound Polycyclic Aromatic Hydrocarbons In Ambient Aerosols And From Motor-Vehicle Exhaust. Andrea Polidori (1), Shaohua Hu (2), Subhasis Biswas (1), Ralph J. Delfino (3), and Constantinos Sioutas (1), (1) University of Southern California (2) California Air Resource Board (CARB) (3) University of California Irvine

A photo-electric aerosol sensor, a diffusion charger, an Aethalometer, and a continuous particle counter were used along with other real-time instruments to characterize the particle-bound polycyclic aromatic hydrocarbon (p-PAH) content, and the physical/chemical characteristics of aerosols collected a) in Wilmington (CA) near the Los Angeles port and close to 2 major freeways, and b) at a dynamometer testing facility in downtown Los Angeles (CA), where 3 diesel trucks were tested. In Wilmington, the p-PAH, surface area, particle number, and black carbon concentrations were 4-8 times higher at 09:00-11:00am than between 17:00 and 18:00pm, suggesting that during rush hour traffic people living in that area are exposed to a higher number of diesel combustion particles enriched in p-PAH coatings. Dynamometer tests revealed that the p-PAH emissions from the baseline truck (no catalytic converter) were up to 200 times higher than those from the 2 vehicles equipped with advanced emission control technologies, and increased when the truck was accelerating. In Wilmington, integrated filter samples were collected and analyzed to determine the concentrations of the most abundant p-PAHs. A correlation between the total p-PAH concentration (ug/m$^3$) and the measured photo-electric aerosol sensor signal (fA) was also established. Estimated ambient p-PAH concentrations (Average = 0.64 ng/m$^3$; Standard deviation = 0.46 ng/m$^3$) were in good agreement with those reported in previous studies conducted in Los Angeles during a similar time period. Finally, we calculated the approximate theoretical lifetime (70 years per 24-hr/day) lung-cancer risk in the Wilmington area due to inhalation of multi-component p-PAHs and black carbon. Our results indicate that the lung-cancer risk is highest during rush hour traffic and lowest in the afternoon, and that the genotoxic risk of the considered p-PAHs does not seem to contribute to a significant part of the total lung-cancer risk attributable to black carbon.

9A.08
Construction and Utility of a Mobile Monitoring Platform to Measure Community Level PM and Characterize Point and Line Sources. Steve Mara (1), Seong Suk Park (1), Kathleen Kozawa (1), Alberto Ayala (1), JORN HERNER (1) and Aruthru Winer (2), (1) California Air Resources Board, (2) Environmental Science and Engineering, School of Public Health, UCLA

The California Air Resources Board (CARB) has constructed a mobile monitoring platform (MMP) to conduct community level measurements of ambient air quality and investigate air pollutant concentration gradients near line and point sources such as freeways, rail yards and ports. These measurements are important additions to the existing CARB network of ambient monitoring stations. The purpose of this study is to demonstrate the practicality of a MMP to characterize the spatial variability of a wide range of air pollutant concentrations by describing the construction of the platform and the results from measurements taken near the Roseville rail yard in California.

The MMP is an electric Toyota RAV 4 with zero self-pollution during operation. An in-vehicle battery pack provides power to the on-board air monitoring instruments. These instruments measure real time ultrafine particle number and size distribution, carbon monoxide (CO), carbon dioxide (CO$_2$), nitrogen oxides (NO$_X$), PM10, black carbon (BC), particle-bound polycyclic aromatic hydrocarbons (PB-PAHs) and volatile organic compounds (VOCs), in addition to meteorological data, GPS and video.

Measurements showed consistent responses between instruments to diesel locomotive plumes from the rail yard. For example, the ratio of NO to NO$_X$ and concentration of BC dropped sharply as the MMP moved away from the rail yard and approached background levels within 300 to 500 meters from the fence line. In this work, the results of particle number, size distributions, PM10 and other air pollutants will also be presented. The data supports the conclusion that the impact of the rail yard emissions is significant close to the boundary fence line. Thus the MMP is capable of measuring community level concentration gradients which may have health and environmental justice policy implications.
9A.09
Number Size Distributions of Ambient Ultrafine Particles During Traffic Rush-hour Periods, YI-TING WANG, Ya-Wun Jhang, Cheng-Hang Sie, Li-Hao Young, China Medical University, Taiwan

The objective of this study is to characterize the number size distributions of 0.01 - 1 um particles during traffic rush-hour periods along a major traffic roadway in an urban city, of which its daily PM2.5 frequently exceeds the US NAAQS. This roadway is of particular interest because there are a number of schools and hospitals located adjacent to the road. We used a sequential mobility particle spectrometer and condensation particle counter (SMPS/CPC) to measure the particle size distributions every 3-min on overpasses and at roadsides of 4 heavily-congested intersections, where the traffic volumes range from 9000 - 13000 vehicles hr\(^{-1}\). The measured average (+- standard deviation) number concentrations on the overpasses (5.1-m above ground level) and at the roadsides (1.1-m AGL) were \(8.2 \pm 4.0 \times 10^4\) and \(20.7 \pm 14.5 \times 10^4\) cm\(^{-3}\), respectively. With respect to particle size, the concentration variability increased considerably with decreasing particle sizes. In addition, the minimum concentration often occurs at around 0.5 um. On average, ultrafine particles (0.01 - 0.1 um) contributed 88\% of the measured particle number concentration. Regardless of the sampling locations, the number size distributions showed none or multiple (up to 4) modes with the average geometric mean diameter of 0.03 um, and geometric standard deviation of ~ 2.2. However, the variabilities in concentration and size distribution at roadsides were consistently larger than that on the overpasses. This large variability shows the transient nature of ultrafine particles, especially the smallest ones, and the complex nature of traffic emissions. The results also underscore that commuters are exposed to high concentrations of ultrafine particles during rush-hour periods near the major traffic roadway, particularly those riding scooters, driving with the vehicle windows open, waiting at the bus stops and walking near those intersections.

9A.10

Aerosol particles have the largest uncertainty of all anthropogenic climate-forcing-factors and they are also the most important air pollutant from the effects on people's health point of view. Because the main aerosol source in Stockholm is road traffic, there is a big exigency on the quantification and parameterization of the aerosol emitted by road traffic. The eddy covariance method has been used in Stockholm to quantify the emissions of particles from traffic. This method allows us to obtain integral measurements of the amount of particles emitted from a large number of vehicles under real world driving conditions over a large part of the urban area.

The measurement setup consist of an ultrasonic anemometer, two CPCs that measure the aerosol number concentration >10nm , two identical Optical Particle Counters (OPC), which count the particles in 15 size classes, from 0.25 to 2.5 um diameter, or from 2.5 to 30 um and an open path fast infrared gas analyzer for CO2 and H2O, to measure the CO2 emissions from the traffic. Using two parallel CPC's and OPC's allows us to discriminate between volatile and non-volatile particle fluxes. There is also a traffic database available,( traffic activity/h).

In the current study we focus on a quantification of the emitted aerosols, by linking the emission factors to traffic activity and fuel consumption (in terms of the amount of CO2 emitted from fossil fuel). During the end of the first half year of measurements in Stockholm we clearly see a diurnal variation of turbulent heat flux (peaks at noon), coarse and fine particle fluxes as well as CO2 fluxes. We also see in the measurements a correlation between the CO2 flux and the total OPC flux. Assuming all fuel combusted to CO2 emission factors per volume of fuel could be estimated and compared to other measurements.
9A.11
Characterization of Air Contamination at a Busy Roadside of Seoul, Korea in Spring. Gwi-Nam Bae (1), Seung-Bok Lee (1), Su-Mi Park (1), Jungho Hwang (2), (1) Korea Institute of Science and Technology, Seoul, Korea, (2) Yonsei University, Seoul, Korea

Urban air is contaminated with vehicle exhaust. In particular, roadside air is directly affected with highly concentrated vehicle exhaust. Apartment is a very popular and preferred housing in Seoul, Korea. Most apartments are located next to busy roads and most school buildings are not situated far way from roads. Office buildings are also positioned near roads. Living environments might be highly affected by local emission sources such as vehicles. Information of air contamination at a busy roadside could give an insight to approach air contamination problem in living environments. In this study, air toxic contaminants related with vehicles were intensively monitored or sampled at a busy roadside of Seoul, Korea in spring of 2005. Particle size distribution was monitored using a scanning mobility particle sizer. Black carbon concentration was continuously monitored. Polycyclic aromatic hydrocarbons (PAHs) both particulate and gas phases were sampled using a high volume sampler. NOx and CO concentrations were also continuously observed to identify vehicle emission. The contamination levels were compared with those obtained at remote urban sites in Seoul. Diurnal variations for real-time data show two peaks at both morning and evening rush hours. The trends from late night to morning traffic time follow trend of traffic volume. The daily average concentration of ultrafine particles is about four times higher than that at a remote urban site. The daily average concentration of black carbon is about one-third at tunnels. Although 24-h average NO2 concentration meets the limit (60 ppb) of Korean standard, 24-h average NOx concentration increases up to 200 ppb. The particulate-phase PAHs distribution shows high concentrations in fluoranthene, pyrene, indeno[1,2,3-cd]pyrene, and benzo[g,h,i]perylene, which represents indicators of diesel and gasoline vehicles.

9A.12
Maximum Exposure Levels of Particulate Matters Caused by Vehicles. Seung-Bok Lee, Su-Mi Park, Hyun-Cheol Jin, Gwi-Nam Bae, Korea Institute of Science and Technology

Vehicle is a one of important air pollutant sources in urban area. Living environments such as roadside, office buildings, school buildings, inside of vehicles are easily exposed to urban air highly contaminated with vehicle emissions. Contamination levels due to vehicle emission could be classified into tailpipe, tunnel, on road, roadside, near road, building indoor next to a road, etc. In general, vehicle emissions are regulated based on chassis or engine dynamometer tests. Here, tailpipe exhaust is diluted with clean air to simulate real environment. Therefore, the tunnel is supposed to be the highest polluted zone among them. Black carbon is used as an indicator of particulate matters emitted from vehicles, especially diesel-powered vehicles. To estimate maximum exposure levels of particulate matters caused by vehicles, measurements of black carbon, PM2.5, and PM10 were made in a roadway tunnel of Seoul, Korea. The black carbon concentration was continuously monitored using an aethalometer (Model AE42-7-ER-MC, Magee Scientific) in April of 2005 and February of 2007. PM2.5 and PM10 were sampled by two mini-volume samplers in February of 2007. The sampling time ranged from three to twelve hours. The one-way traffic volume of the tunnel ranges from 10,000 to 18,000 vehicles/day. The hourly total traffic volume was obtained from a governmental on-line service. The traffic volumes of vehicles by fuels and by types were also counted from CCTV images in February of 2007. The hourly average concentration of black carbon ranged from 2.2 to 43.8 ug/m3 in April of 2005 and from 1.2 to 45.1 ug/m3 in February of 2007. The CCTV image analysis provided information that the maximum concentration of black carbon occurred when heavy-duty trucks passed. The mass concentrations of PM2.5 and PM10 ranged from 45 to 123 ug/m3, and 63 to 136 ug/m3, respectively. The fractions of PM2.5 to PM10 were higher than 0.7 except for one sample. Relationship between black carbon concentration and traffic volume of vehicle types was analysed.
9A.13
Emission Measurements at Sea. Harshit Agrawal (1,2), William A. Welch (2), J. Wayne Miller (1,2), David R. Cocker (1,2), (1) University of California, Riverside, (2) College of Engineering-Center for Environmental Research and Technology (CE-CERT), Riverside

Ocean-going vessels (OGVs) are significant sources of anthropogenic emissions yet emission data from these sources remains scarce. The contribution of OGVs to the total NOx and PM10 emissions from goods movement sources is growing significantly, as projected by the analyses of goods movement in many coastal states in United States. The goal of this research was to measure the full slate of criteria and greenhouse gas emissions from two different ocean going vessels for ISO cycle additionally real-time measurement of gases and PM emissions were conducted for the actual operating activities of the vessel; for example, maneuvering in and out the port and voluntary speed reduction (VSR).

Methods for sampling and analyses of the gases conformed to the requirements of ISO 8178-1. PM measurement was performed using a modified ISO 8178-1 cycle. The emissions of particulate matter (PM), criteria gases (NOx, SO2 and CO) and carbon dioxide will be presented. Additional speciation of gas-phase hydrocarbons and particulate matter (including elemental and organic carbon, sulfate, and metals) will be presented for the main and auxiliary diesel engines and for the boiler, on the ocean going vessel.

The main engine and boiler operated on heavy fuel oil (HFO) while the auxiliary engine operated on marine gas oil (MGO). PM from main engine was comprised of 70 to 80% sulfate, 15% organic carbon (OC) and <5% elemental carbon (EC). PM emissions per kilowatt-hour from the auxiliary engine were about 5% of the PM emissions from the main engines. Complete chemical characterization of emissions for different engines was performed. The criteria pollutant emissions from these Ocean going engines are then compared with the emission factors estimated by regulatory agencies. A comparison of the emissions from the Ocean going engine and on-road diesel engines will be presented.

9A.14
Heterogeneous Reaction Products of Bio- versus Petro-diesel Particles with Ozone. N. Tucker Stevens Dan Nielsen Britt A. Holmen, University of Vermont

Biodiesel use is on the rise in the U.S. because of its potential to reduce dependence on imported oil and to reduce regulated emissions. Recent literature shows total hydrocarbons, carbon monoxide, and particulate matter emissions are lower for biodiesel compared to petrodiesel, but unregulated air toxic emissions from biodiesel-fueled engines have not been well characterized. The emitted particles with surface adsorbed organic compounds undergo aging reactions in the atmosphere with oxidants to form more carcinogenic or more mutagenic species. Previous studies have shown that, compared to petrodiesel, biodiesel fuel has lower aromatics, negligible sulfur, and higher oxygenates; therefore combustion product speciation and heterogeneous product reaction products should differ from those of petrodiesel. This study quantifies the fresh and aged organic chemical speciation of biodiesel exhaust for different feed stock fuels to that of petroleum diesel exhaust in order to identify the types of unregulated compounds emitted, the kinetics of compound reaction with ozone, and new species formation via heterogeneous reactions occurring on particle surfaces.

Here, heterogeneous aging of bio- and petro-diesel particle organic compounds are characterized over a 72-hour exposure period at three concentrations of ozone. Particle and gas-phase reaction products are identified using a thermal-desorption gas chromatography/mass spectrometry analysis procedure coupled with derivatization to quantify the more polar reaction products. Preliminary data on reaction rates of polycyclic aromatic hydrocarbons reacting with ozone to produce oxidized products is consistent with the gas-phase literature in identifying the formation of quinone-type compounds.
Comparison of Diesel Crankcase and Tailpipe PM Emissions with Species Collected in School Bus Cabins. BARBARA ZIELINSKA(1), Robert Ireson(2), Christopher Weaver(3), Timothy Larson(4), Douglas Lawson(5), Thomas Hesterberg(6), and L.-J. Sally Liu(4), 1 Desert Research Institute, Reno, NV; 2 Air Quality Management Consulting, Greenbrae, CA; 3 Engine, Fuel, and Emissions Engineering, Inc., Rancho Cordova, CA; 4 Dept. of Environmental and Occupational Health Sciences, Univ. of Washington, Seattle WA; 5 National Renewable Energy Laboratory, Golden, CO; 6 International Truck and Engine Corp., Warrenville, IL

In August-September 2005 a monitoring campaign was performed in Seattle, WA, to compare different experimental approaches to quantify self-pollution from two school buses. As part of this monitoring campaign, a detailed characterization of PM2.5 from diesel engine emissions via tailpipe and crankcase emissions via the road draft tubes was performed. In addition, PM samples collected in the bus cabins were also analyzed for the same chemical species. To distinguish between tailpipe and crankcase vent emissions, a deuterated alkane, n-hexatriacontane-d74 (n-C36D74) was added to the engine oil, and an organometallic iridium (Ir) complex was added to the diesel fuel to serve as intentional quantitative tracers for lubricating oil and fuel combustion PM emissions, respectively. This presentation will focus on the comparison of species quantified from crankcase and tailpipe PM emissions with those found in samples collected in the cabins of these school buses. We found that organic carbon emission rates were generally higher from the crankcase than from the tailpipe for these buses, while elemental carbon contributed significantly only in the tailpipe emissions. The n-C36D74 that was added to the engine oil was emitted at higher rates from the crankcase than the tailpipe. Tracers of engine oil (hopanes and steranes) were present in much higher proportion in crankcase emissions. Particle-associated PAH emission rates were generally very low, but more PAH species were present in crankcase than in tailpipe emissions. The speciation of samples collected in the bus cabins was consistent with most of the bus self-pollution originating from crankcase emissions.

Light scattering measurements of soot agglomerate size, mass, and primary particle number for diesel engines. Donald Holve, Process Metrix, Pleasanton, CA

We have developed a light scattering method for measurement of soot agglomerate, size, mass, and primary particle number, with sensitivity down to 1 micro-gram/m^3. This method is based on two-angle ratio scattering, and provides a fast quantitative measure (10hz) of soot emissions from gas turbines and diesel engines, using an in situ or sampling configuration. A simple theory has been developed based on Rayleigh-Debye-Gans, which relates the total mass concentration, and mean agglomerate size to the measured scattering signals at two angles, and the fundamental soot properties of primary particles, without the need for arbitrary calibration. From these results, one can then compute the surface area and number of primary particles.

We have obtained quantitative measurements for mobile heavy equipment diesel engines (including locomotives) under actual operating conditions, and in engine test cells which simulate conventional off road transient operational cycles. Results have been obtained with and without diesel particulate filters, and following constant volume sampling and dilution.
Source Characterization and Apportionment

9A.17
Using Natural Isotope Variations of Iron and Copper to Determine the Source of Automobile Emissions. BRIAN J MAJESTIC, Ariel D. Anbar, Pierre Herckes, Arizona State University, Tempe

During chemical or biological reactions, inherent differences in an isotope's bonding environment can lead to a shift in local isotopic abundances. This often results in a pool of 'heavy' isotopes and a pool of 'light' isotopes. Ultimately, the magnitude and direction of this fractionation depends upon the history of the particle, or the chemical reactions in which it has undergone.

Although these effects are quite small (in most natural samples, delta56Fe (56Fe/54Fe) varies between +/- 3 % compared to a natural isotopic standard), these differences can give insight into the history (source and prior chemistry) of an aerosol. In this study, we measured the natural iron and copper isotope variations of PM2.5 samples collected in a parking garage at Arizona State University. deltaFe and delta63Cu (63Cu/65Cu) were measured using a Thermo Electron Neptune multi-collector (MC) ICP-MS. In these samples, an iron isotope composition (delta56Fe) ranging from -0.5 to -1.5 % was observed for iron, relative to the IRM-014 standard. This is compared with a composition of about -0.2 % with PM2.5 aerosols collected in Nogales, AZ and +0.10 % for San Joaquin Soil (NIST standard reference material #2709). In order to explain these large differences in Fe isotope compositions between an ambient site, soil samples, and a site dominated by automobile emissions, source materials (brake pads, tire tread, gasoline, and waste motor oil) which contribute to iron and copper emissions from automobiles were digested and analyzed by MC-ICP-MS. When compared to the PM collected at the parking garage, the relative iron and copper fractionation of these source materials provide a more thorough understanding of the emission of trace metals from automobiles.

9A.18
Size-resolved reactivity of engine combustion particulate matter with ozone. DAN NIELSEN, Tucker Stevens, Britt Holmen, University of Vermont

Diesel exhaust is an increasingly important source of fine and ultrafine particulate matter (PM) in the polluted urban environment. New emissions regulations announced by the Federal Government for calendar years 2007 and 2010 are forcing auto, diesel and catalyst manufacturers to better understand their combustion and emission reduction processes. The composition of these particles (e.g., adsorbed organic species) has very important implications for particle reactivity and the resulting endpoint effects on environmental and human health. The organic fraction of diesel exhaust has been found to consist of many known carcinogenic and mutagenic compounds, and some organic groups react readily with ozone. Ozone is one of three (OH, NO3, and O3) important atmospheric reaction initiators that can further modify species (e.g., PAHs) sorbed to diesel particulate matter (DPM). Currently there is an effort to better understand the products of heterogeneous reaction between organic compounds on the surfaces of DPM and ozone. This work examines the feasibility of quantifying new polar organic species formation via heterogeneous reactions with ozone that occur on particle surfaces for size-resolved particles in diesel and biodiesel exhaust. Supercritical fluid extraction (SFE) and thermal desorption (td) extraction techniques were investigated for corroborative analysis of sample derivatization and extraction procedures. An electrical low-pressure impactor (ELPI) is used for real-time particle size distribution and subsequent PM analysis by td-GC/MS as a function of particle size. Oxidation products in the particle phase were treated with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) and N,O-Bis(trimethylsilyl)-acetamide (BSTFA) to derivatize carbonyl and hydroxyl groups, respectively, prior to GC/MS analysis. Gas-phase species have been separated from particulate matter utilizing an annular denuder coated with XAD-4 resin for separation of gas-phase species.
As regulatory limits in California and the US for 2007 heavy-duty diesel engines introduce significant reductions in PM emissions, there is considerable interest in new PM emission measurement methodology that can accurately measure low PM levels. One such methodology, particle number measurement, has been extensively investigated in Europe as part of Europe's Particle Measurement Program (PMP) for light-duty diesel vehicles. This program has put forth a new methodology, including instrument specifications and sampling protocols, for 'solid'-particle number measurements. While counting only solid particles results in better precision, it may not be fully indicative of the diesel PM emissions from health effects viewpoints. The PMP protocol still represents a significant advancement as it is currently the only methodology with low PM detection limits to produce precise measurements from DPF equipped engines. CARB sought explore in detail the utility of the new protocol for potential use in California.

The proposed PMP method was critically evaluated for determining 'solid'-particle number emissions from heavy-duty diesel vehicles (HDDV) in the laboratory and under on-road driving conditions. In-lab experiments were conducted on the chassis dynamometer at the CARB HDDV emissions laboratory in Los Angeles and on-road experiments were performed with the CE-CERT mobile emissions laboratory (MEL). Two PMP compliant dilution systems for measuring solid particle numbers were investigated and compared with filter-based PM measurements on two HDDVs equipped with a DPF. A full suite of real-time particle instruments were also used in these experiments including an EEPS, a Cambustion DMS, CPCs with cut-off size ranges from 3 to 20 nm, a Dekati DMM, and a TSI DustTrak. The test cycles included a 50 mph cruise, UDDS, idle, and some European driving schedules. The results of this study will be reviewed and placed in the context of other on-going and past studies of PM emissions.

To better understand diesel exhaust particulates (DEPs) as one of major primary emission sources affecting air quality, size distribution and composition of metals and organic compounds in DEPs emitting from four driving conditions were characterized. Eighteen metals in DEPs (34 -1000 nm) were quantified with a total concentration ranging from 6.1 -7.7 micro-gram per cubic meter. Depending on driving conditions, ultrafine (<100 nm) and accumulation-mode DEPs carried up to 43% and 75% of the quantified metals, respectively. Under an engine load of 60%, metals favorably partitioned in accumulation-mode DEPs. Enhancing the engine load up to 100% substantially increased metals in ultrafine DEPs (from 1.5-3.1 micro-gram per cubic meter) and peaked at DEP of <66 nm. Under the maximum engine load, metals and elemental carbon showed an opposite trend in size distribution, providing tailpipe evidence that metals may reduce DEPs during combustion. Among the identified metals, Fe (2.3-3.9 micro-gram per cubic meter) is most abundant contributing to more than 38% of quantified metals, followed by Li, Cr, V, and Pb. A Cr-to-Fe ratio (0.08-0.29) can be employed as a fingerprint differentiating diesel- vs. gasoline-origin particulates at locations under heavy traffic influences.

For all four driving conditions, concentration of identifiable organic compounds in DEPs ultrafine (34-94 nm) and accumulation (94-1000 nm) modes ranged from 2.9-5.7 micro-gram per cubic meter and 9.5 -16.4 micro-gram per cubic meter, respectively. As a function of driving conditions, the non-oxygen-containing organics exhibited a reversed concentration trend to the oxygen-containing organics. The identified organic compounds were classified into eleven classes: alkanes, alkenes, aromatic hydrocarbons, carboxylic acids, esters, ketones, alcohols, ethers, nitrogen-containing compounds, and sulfur-containing compounds. For all driving conditions, alkane class consistently showed the highest concentration (8.3 micro-gram per cubic meter to 18.0 micro-gram per cubic meter) followed by carboxylic acid, esters, ketones and alcohols. Twelve polycyclic aromatic hydrocarbons (PAHs) were identified with a total concentration ranging from 37.9-174.8 nano-gram per cubic meter. In addition, nine nitrogen-containing polycyclic aromatic compounds (NPCs) were identified with a total concentration ranging from 7.0-10.3 nano-gram per cubic meter. The most abundant PAH (phenanthrene) and NPC’s (7,8-benzoquinoline and 3-nitrophenanthrene) comprise a similar molecular (3 aromatic-ring) structure under the highest engine speed and engine load.
9A.21
Spatial Distribution of the Ambient Fine Aerosol in Syracuse, NY. Edmund, McAddy (1), Jennifer Ehrhardt (1), Philip K. Hopke (1), Thomas Holsen (1), Xing Wang (2), K. Max Zhang (2), Myron Mitchell (3), (1) Clarkson University (2) Cornell University (3) SUNY College of Environmental Science and Forestry

As part of the characterization of the air quality in the vicinity of a new ultra-green building being built to the southeast of the intersection of I-80 and I-690 in Syracuse, NY, a study of the distribution of pollutants up and down wind of these highways has been conducted. Using the Clarkson Mobile Air Pollution Laboratory, particle size distributions, black carbon, NOx, and ozone concentrations were measured at twelve locations 3 times per day during campaigns in March and June 2008. These measurements will continue to be made for a week in each calendar quarter. The temporal - spatial patterns of these measured pollutants will be presented.

9A.22
The impact of the change in the public transport system in air pollution emissions: a study at a street level in Santiago, Chile. Pablo Ruiz (1) Pedro Oyola (1) Ernesto Gramsch (2) Gianni Lopez (1) Jorge Caceres (1), (1) Centro Mario Molina Chile (2) Universidad de Santiago

Air pollution levels are very high in Santiago, with levels that usually exceed air quality standards. One of the main sources of pollutants is traffic either from private vehicles or from public transportation. Because of concerns about air pollution and traffic congestion, the public transport system has been recently modified in Santiago, in a comprehensive transport plan named TRANSANTIAGO, which included a change in the bus fleet, and also bus routes and frequencies. To assess the effect of the implementation of this plan on traffic emissions we measured air pollutants at the street level in campaigns spanning a period of 3 years (2005-2007), when the change in transport system took place. In this study, pollutants were sampled in streets representing mainly public transport and mainly private transport, and also streets representing routes with an older fleet. Measurements included continuous recording of PM1, PM2.5 and PM10, NO2, CO, elemental carbon and meteorological variables. Additionally, we measured size distribution of ultrafine and fine particles using a DMPS. We show results comparing the change in concentrations during the years and also comparing the daily profiles for pollutants of pollutants for different streets.
9A.23
Horizontal Profiling to Assess the Spatial Influence of Main Roads on PM$_{10}$ and Ultrafine Particle Number Concentrations in South Manchester, UK.

ANNA LEAVEY (1), Ian Longley (2), Frank de Vocht (1), Carl Percival (1), Martin Gallagher (1), (1) University of Manchester, (2) National Institute of Water and Atmospheric Research Ltd

Road transport is an important source of PM$_{10}$ and UFP. It is within the vicinity of main roads that one may expect their highest exposure to airborne particles. Thus residents who live on or near to main roads, as well as commuters using the roads, may be exposed to elevated particle concentrations. This study investigates the extent of elevated particle concentrations close to main roads, compared to distances further away.

Measurements were collected at main roads between October and December 2007, in residential locations within the south Manchester area. One portable CPC (TSI-TRAK 8525) and one Sidepak (TSI AM510) sampled on a kerb by the road while a second set of identical instruments sampled simultaneously at different distances away from the road. Ambient background levels were recorded upwind from the measurement site, while local meteorological data was collected using a hand-held weather station, and a rooftop station in Manchester's city centre. Finally, the frequency and type of traffic that passed during each sampling interval were also recorded.

In total 6 roads were sampled an average of 6 times over 15 non-consecutive days. Average measured kerb side PM$_{10}$ concentrations at the different sites ranged from 11 to 114 (micro-grams/cubic-metre) with ambient varying from 13 to 29 (micro-grams/cubic-metre), while average UFP concentrations ranged from 15,000 to 98,000 (particles/cubic-centimetre) with ambient fluctuating between 5,000 and 20,000 (particles/cubic-centimetre). Preliminary analysis suggests decreasing UFP concentrations with increasing distance from the road, characterised by a rapid exponential decline within the first 20 metres and stabilising at approximately 40 metres from the road. Analysis of PM$_{10}$ proved more complex, but in both cases the variability of concentrations was found to decline with increasing distance from the road. Additional analysis will assess this association as a function of street geometry, meteorology and traffic characteristics.

9A.24
Modeling the Impact of Diesel Emissions on Air Quality in South Bronx: Methodology and Preliminary Results.

PRUEK PONGPRUEKSA (1), Ke Zhang (1), Huaizhu Gao (1), Steven Denero (1), James Reagan (1), Vladilen Isakov (2), Patrick Kinney (3), Molini Patel (3), Steven Chillrud (3), (1) Cornell University, Ithaca (2) NOAA/EPA, Research Triangle Park (3) Columbia University, New York City

Among the five boroughs of New York City, the Bronx has ranked highest in both asthma hospitalizations and deaths in recent years. Recent studies have linked asthma to exposure to diesel particulate matters from transportation emissions. South Bronx has large volumes of diesel traffic passing through it along several major highways as well as local roadways. This study employs two dispersion models (AERMOD and QUIC) to study the impact of diesel emissions on local air quality in South Bronx. The AMS/EPA Regulatory Model (AERMOD) is an advanced plume model that incorporates updated treatments of the boundary layer theory, understanding of turbulence and dispersion, including treatment of both surface and elevated sources, and both simple and complex terrain. The Quick Urban and Industrial Complex (QUIC), which is a fast response urban dispersion model that accounts for the effects of buildings, is used to compare with modeling results from AERMOD. Model inputs are essential for comprehensive modeling. For meteorological input, the data is obtained from onsite monitoring stations as well as National Weather Service (NWS) stations. As for emission inventory, we use TransCAD outputs from New York Metropolitan Transportation Council (NYMTC) to provide traffic volume data and further being processed with MOBILE6.2 model output from New York State Department of Transportation (NYSDOT) and EPA's SPECIATE4.0 database to generate on-road emission sources. The other emission sources (point, non-road, and area) are based on EPA's National Emission Inventory (NEIv2002). Our preliminary results show a good relationship between modeled and observed black carbon concentrations for AERMOD. However, a discrepancy can be seen during particular meteorological conditions such as calm wind period, which is a limitation for AERMOD model.
9A.25
Air Pollution in Beijing: A \Particulate\ Experience. Dane Westerdahl (1), Xing Wang (1), K. Max Zhang (1), Xiaochuan Pan (2), Yuping Jia (2), (1) Cornell University, (2) Peking University School of Public Health

We report the results and analysis of a recent field campaign in August 2007 investigating the impacts of emissions from transportation on air quality and community concentrations in Beijing, China. We conducted measurements in three different environments, on-road, roadside and ambient. The carbon monoxide, black carbon and ultrafine particle number emission factors for on-road light-duty vehicles are derived to be 95 g/kg-fuel, 0.3 g/kg-fuel and 1.8e15 particles/kg-fuel, respectively. The emission factors for on-road heavy-duty vehicles are 50 g/kg-fuel, 1.3 g/kg-fuel and 1.1e16 particles/kg-fuel, respectively. The carbon monoxide emission factors from this study agree with those derived from remote-sensing and on-board vehicle emission testing systems in China. The on-road black carbon and particle number emissions factors for Chinese vehicles are reported for the first time in the literature. Strong traffic impacts can be observed from the concentrations measured in these different environments. Most clear is a reflection of diesel truck traffic activity in black carbon concentrations. The comparison of the particle size distributions measured at the three environments suggests that the ultrafine particles in Beijing are less volatile than those in Los Angeles. A four-day traffic control experiment conducted by the Beijing Government as a pilot to test the effectiveness of proposed controls was found to be effective in reducing extreme concentrations that occurred at both on-road and ambient environments.

9A.26
Elements Emitted from Advanced Technology Heavy Duty Diesel Vehicles. JORN D. HERNER (1), Martin Shafer (2), William Robertson (1), Shaohua Hu (1), John Collins (1), Tao Huai (1), James J. Schauer (2), Constantinos Sioutas (3), Alberto Ayala (1), (1) California Air Resources Board, Sacramento/El Monte, CA, (2) University of Wisconsin-Madison, Madison, MA, (3) University of Southern California, Los Angeles, CA

Both epidemiological and toxicological studies have demonstrated that some trace metals in PM such as V, Ni, Cu, and Pt contribute to adverse health effects. Recent efforts have focused on emissions from vehicles with advanced aftertreatment devices such as diesel particulate filters (DPF) and selective catalytic reduction (SCR) technology, but knowledge about emissions of elemental compounds from these control systems is still scarce. The catalysts used in the control systems, such as V for the SCR system, are of particular interest due to their potential environmental and health impacts.

The California Air Resources Board (CARB) and the University of Southern California, in collaboration with South Coast Air Quality Management District (SCAQMD) and California Energy Commission (CEC) conducted a comprehensive project to investigate the physicochemical and toxicological properties of the semi-volatile and non-volatile fractions of PM emissions from heavy duty diesel vehicles (HDDV) retrofitted with state-of-the-art PM and NOx control systems. The technologies in this study include four types of diesel particulate filters (DPF) either catalyzed or un-catalyzed, vanadium or zeolite based SCRs, and a hybrid diesel electric drive fitted with an OEM DPF. Among the tested vehicles two were equipped with both DPFs and either vanadium or zeolite based SCR, and are of particular interest because they are designed to reduce both PM and NOx emissions to comply with US07 and 2010 heavy duty diesel regulations. A HDDV with no aftertreatment served as the baseline vehicle. The test driving cycles consisted of steady state cruise, transient (UDDS), and idle operation to simulate a number of the real world emission modes. The vehicles were driven on a heavy duty chassis dynamometer at the CARB heavy duty diesel test laboratory in Los Angeles.

PM 2.5 emissions were collected onto acid washed Teflon filters for elemental analysis by magnetic-sector ICP-MS. Size-resolved aerosols were collected using parallel, five stage, Sioutas (R) Cascade Impactors loaded with either Teflon or high-purity aluminum foil substrates for detailed vanadium speciation (including the pentoxide (V+5) form) analysis for the two DPF + SCR equipped vehicles.

Elemental compositions of PM emissions from the test fleet are reported, and the emissions from aftertreatment technologies are compared against baseline. The vanadium-based SCR vehicle exhibited higher emission rates of elemental V compared to the zeolite-based SCR vehicle. Preliminary results of size-resolved V species are also presented. Elevated levels of elemental S is observed for those retrofitted vehicles which showed substantial formation of nucleation mode particles. The effect of driving cycles on the chemical emissions is also discussed. Finally, the change in atmospheric trace metal burden from diesel vehicles due to the introduction of advanced aftertreatment will be discussed, as will any change in the composition of elemental emissions and their possible health implications.
9A.27

We report results of collaborative experiments conducted to evaluate the effects of alternative aviation fuels on the performance and emissions of modern gas turbine engines. This work was motivated by the pressing need to increase available fuel stocks, reduce U.S. dependence on foreign oil sources, increase energy security, and understand how fuel parameters regulate soot and volatile aerosol emissions from aircraft engines. The tests evaluated a commercially-available, synthetic fuel produced from natural gas using the Fischer-Tropsch (FT) process. This fuel was essentially free of aromatic compounds and long-chain (i.e., > C$_{(12)}$) hydrocarbons and contained only small concentrations of sulfur contaminants. In the primary test venue, 100% FT fuel, a 50:50 blend of FT and JP-8 and 100% JP-8 were alternately burned in a test-stand-mounted commercial gas-turbine engine typical of those used on small regional jet aircraft. Gas and aerosol samples were drawn from inlet probes mounted 1- and 50-m downstream of the engine exit plane while engine power was varied from idle to about 85% of maximum thrust. Samples were analyzed for concentrations of CO$_2$, CO, SO$_2$, NO, NO$_2$, and total hydrocarbons along with aerosol particle size, number, black carbon mass, composition and smoke number. Data collected from the downstream sampling location facilitated an assessment of differences in plume chemistry and the tendency of each fuel to promote or suppress formation of volatile aerosols. In a secondary test venue, measurements of gas-phase species and particulate composition were performed while the three fuel types discussed above were burned in a high-pressure flame tube mounted in a combustion test cell at the NASA Glenn Research Center. Inlet pressure, temperature and fuel flow were varied during testing.

The presentation will provide additional experimental details and examine the ratio of volatile and non-volatile emissions from the synthetic and blended fuels relative to standard JP-8.

9A.28
A Hybrid Urban Air Pollution Model. Meilu He, Pier Marzocca, Suresh Dhaniyala, Clarkson University

Air pollution modeling in urban environments is necessary to assess urban air quality and its impact on human health. There are several existing models available for such modeling, including: box models (AURORA), Gaussian models (CALINE4, CAR-FMI), Lagrangian/Eulerian models (GRAL), and CFD models (ARIA). A particularly simple model is the parameterized Gaussian plume model. However, Gaussian models inherently cannot include fluctuations from wind velocity, temperature, and traffic in the environment, which are particularly significant in urban areas. Also, Gaussian models are often not applicable in low wind situations. Some Lagrangian models, such as GRAL, consider velocity fluctuations, but at significant computational cost. This talk will describe a hybrid urban air pollution model, based on the Gaussian plume model considering particle dispersion due to atmospheric turbulence, traffic-produced turbulence (TPT), and building downwash wake effect. Also, the role of stochastic processes from fluctuations in the environment on the particle concentration field is determined. Then based on tri-lognormal size distribution, particle size distributions in a fluctuating environment can be predicted. This model will be tested against field measurement data obtained from Syracuse and Potsdam, NY. For these measurements, we use a photo-electric tandem differential mobility analyzer (PTDMA) to select the diesel fraction from the ambient particle size distribution. Under appropriate sampling conditions, diesel particulates at the monitoring location originate only from the nearby highway, and thus our measurements signify particle dispersion from a line-source and can be compared with modeling results. Model development and comparison with experimental results will be discussed.
There are many records in scientific literature on ubiquity of transient particulate matter (PM) events mainly in urban atmosphere in which PM mass concentrations rapidly rise and fall over a period of few hours. Such PM events, though they may have specific health effect, are undetected with traditional time-integrated measurements. To reveal possible resources/processes lying behind the transient PM events, we applied the Positive Matrix Factorization technique (PMF2) to hourly averages of aerosol size distributions (14 nm-10 micrometers), gaseous components (CO, SO$_2$, NOx and O$_3$), and complete meteorology (WS/D, UV-A,B, RH, T).

The datasets were recorded at roof-top station situated in the University Botanic garden at the Prague centre (Loc. 50 deg. 4' 17.46" N, 14 deg. 25' 14.92" E) during winter from 7 to 23 Jan 2008. This study is in continuation of aerosol apportionment for spring 2007 that had shown five factors being traffic, home heating, ozone influenced secondary particles, and two mixed sources I and II, which may represent long range transport and background. The Conditional Probability Function (CPF) plots were drawn to know the directionality of sources. The prevailing wind direction during the campaign were southwest with maximum wind speeds of 7.5 m/s. The CPF plots showed significant contributions to arise from North East, East and South East directions. During the period from 18-22 Jan 2008 we recorded constant wind from southwest direction (225-275 degree) with highest wind speeds, ambient temperature, UV-A,B radiations and high O$_3$ concentrations but with low RH, NOx, CH$_4$, NMHC, THC, SO$_2$ and CO concentrations.

The study was supported by the Grant Agency of Charles University project No. 49707/2007.
9D.03
Source contribution to fine PM in the Los Angeles-Long Beach harbor area. MARIA CRUZ MINGUILLON (1), Mohammad Arhami (1), James J. Schauer (2), Constantinos Sioutas (1), (1) University of Southern California (2) University of Wisconsin-Madison

The Los Angeles - Long Beach harbor is the busiest port in the US, its surrounding area having one of the most polluted and complex atmospheres in the US, since it is affected by multiple PM sources. Size segregated particulate matter were collected at seven sites during a cooler period of higher air stagnation (March-May) and a warmer period of high photochemical activity (July-September) in 2007. Four of the sites were located within the communities of Wilmington and Long Beach, two sites were located at background areas in the harbor of Los Angeles and Long Beach, respectively, and one site was set near downtown Los Angeles, a typical urban area. The samples were analyzed for organic carbon (OC), elemental carbon (EC), organic species, inorganic ions, water soluble and total elements. A comprehensive comparison was made between the two different seasons. Preliminary results showed higher levels of particulate sulfate, ammonium and octadecanoic and hexadecanoic acids in warmer season due to higher photochemical formation.

A source apportionment analysis was carried out using Chemical Mass Balance (CMB). Sources included in the model are: light duty vehicles (LDV), heavy duty vehicles (HDV), road dust (RD), biomass burning (BB) and ship emission (SH), being then the first source apportionment study including vessel emissions. Preliminary results for winter showed that the addition of LDV, HDV and RD account for more than 60% of total OC, whereas ship emissions contribution is lower than 5% of total OC at all sites. In terms of total fine PM, vehicular sources together with road dust explain up to 50% of the mass, whereas ship contribution is lower than 5% of total fine PM mass. This clearly indicates that fine PM in the study area is dominated by the vehicular sources despite the proximity of the studied communities to the largest US harbor.

9D.04
Source Apportionment of Elevated Wintertime PAH in a Northern Swedish Town by Compound Specific Radiocarbon Analysis. REBECCA J. SHEESLEY, ?rjan Gustafsson, Patricia Kreci, Christer Johansson, Martin Krus, Department of Applied Environmental Science (ITM), Stockholm University, Sweden

Atmospheric polycyclic aromatic hydrocarbons (PAHs) are ubiquitous due to their emission from a variety of combustion sources including motor vehicle exhaust and other fossil fuel combustion and biomass burning. Their potential to detrimentally impact human and ecological health makes it vital to apportion these compounds to emission sources. However, the concentrations and molecular fingerprints of PAHs present in the atmosphere are not sufficiently source-specific to apportion to their original emission sources.

Natural abundance radiocarbon analysis offers a trusted method for determining the fraction of modern versus fossil carbon and recent advances in micro-scale techniques have opened the door for compound-specific radiocarbon analysis (CSRA) of organic compounds at the low levels present in environmental samples. In this study, CSRA of PAHs was applied to a set of atmospheric samples collected in Lycksele, a city in Northern Sweden which has frequent episodes of severe atmospheric pollution in the winter. In order to maximize sample collection mass, a high volume total suspended particulate matter (TSP) sampler loaded with quartz fiber filters for PM collection and PUFs (polyurethane foam) for gas-phase species was used in this study. Five different particulate PAH samples were analyzed by CSRA including: phenanthrene, fluoranthene, pyrene, benzo[b+k]fluoranthene and indeno[cd]pyrene+benzo [ghi]perylene whereas phenanthrene was the only compound also analyzed in the gas phase. The percentage wood smoke contribution ranged from 70% for indeno[cd]pyrene+benzo[ghi] perylene to 87% for the PUF phenanthrene and particulate pyrene. There was a distinct molecular-weight trend (r² = 0.68) to the fraction wood smoke contribution with higher contribution for the lower molecular-weight PAHs.
9D.05
Receptor Modeling of Data with Species-Dependent Time Resolution: Results from the St. Louis -- Midwest Supersite.
Yetan Li(1), Philip Hopke (2), Jay Turner(2), (1) Clarkson University (2) Washington University in St. Louis

Recent monitoring technologies have now permitted the measurement of a variety of chemical species in airborne particulate matter with multiple time resolutions (5 min to 1 day). Traditional eigenvalue-based methods used in solving multivariate receptor models cannot analyze a data set which includes parameters with mixed time resolutions because these data cannot form a simple matrix. It is not optimal to temporally average the high time resolution data or temporally interpolate the low time resolution data to generate a time series of uniform time base. The former approach loses valuable temporal information and the latter produces unreliable high resolution series because of the questionable assumption of temporal smoothness needed to interpolate longer period samples to shorter time intervals. In this study, the Multilinear Engine was used to implement a factor analysis model for the multiple time resolution data. The data were analyzed in their original time schedules without averaging or interpolation. The data were acquired at the St. Louis-Midwest supersite, including one week in each of June 2001, November 2001, and March 2002 and including elements (SEAS), OC/EC, sulfate, nitrate, and particle size distributions.

9D.06
Apportionment of the PM2.5 Contribution of Point Sources using Single Particle Mass Spectra and Positive Matrix Factorization (PMF).
David C. Snyder(1), James J. Schauer (1,2), Deborah S. Gross(3) and Jay R. Turner(4), (1) University of Wisconsin-Madison, (2) Wisconsin State Laboratory of Hygiene, (3) Carleton College, (4) Washington University, St. Louis

Integrated single particle mass spectra collected using an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) were analyzed using a factor analysis based source apportionment model, Positive Matrix Factorization (PMF). The results were utilized to assess the contribution of individual point sources to PM2.5 concentrations at the St. Louis - Midwest Supersite during December of 2004. When using each mass-to-charge ratio (m/z) as an input species, a 10-factor solution emerged as the most stable model. The factors produced by this model remained relatively stable when different model parameters, including the cut-off signal-to-noise ratio used to determine which m/z values were included in the model run, were varied. This base-case solution, derived from the positive ion spectra of the ATOFMS, identified four potential point source factors with unique spectral signatures. These factors indicated sources emitting particles enriched in Fe, Pb, Co, and Zn respectively. The remaining factors also contained unique spectral character and included factors enriched in elemental carbon (EC), ammonium nitrate (NH4NO3), organic carbon (OC), and potassium (K). Hourly source contributions for each of the factors were compared with real-time measurements of EC, OC, BC, NO3, and wind direction in order to support the conclusions drawn from the spectral signatures of each factor, i.e. whether factors were indeed represented likely point sources and whether the spectral character of factors correlated with co-located measurements. Hourly PM2.5 mass, as measured by a Beta Attenuation Monitor (BAM), was added to the base-case model in order to apportion fine particle mass amongst the 10 source factors. The results of this analysis indicated that during some hours, as much as 50 percent of PM2.5 mass observed at the St. Louis Supersite could be apportioned to four identified point sources.
9D.07  
Source Apportionment of Total Suspended Particulate. (1) Sandeep Gupta*(2) Arun Srivastava, (3) V. K. Jain, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi.

Source apportionment of total suspended particulate matter (TSPM) and associated heavy metals has been carried out for the city of Delhi using the Chemical Mass Balance Model, Version 8 (CMB8), as well as principle component analysis (PCA) of SPSS (Varimax Rotated Factor Matrix method) in coarse- and fine-size mode. Urban particles were collected using a five-stage impactor at six sites in the winter of 2005-06. The impactor segregates the TSPM into five different size ranges (viz. > 10.9, 10.9-5.4, 5.4-1.6, 1.6-0.7 and < 0.7 um). Four samples were collected from six different sites every 24 hours. Samples were analyzed in five size ranges gravimetrically and chemically for the estimation of SPM and metals. The five different size ranges were divided into two broad categories: coarse (1.6 to > 10.9 um) and fine (< 1.6 um). The CMB8 and PCA were executed separately for both coarse and fine size ranges. Results obtained by CMB8 indicate the dominance of vehicular pollutants (62%), followed by crustal dust (35%) in the fine size range; while in the coarse size range crustal dust dominated (64%) over vehicular pollution (29%). Little contribution from paved-road dust and industrial sources was observed. Results of PCA (or factor analysis) reveal two major sources (vehicular and crustal re-suspension) in both coarse and fine size ranges. The correlations of factors (sources) with the metals show that in the coarse size range the dominant source is crustal re-suspension (68%) followed by vehicular pollution (23%). However, this is reversed in the case of the fine size range factor analysis where vehicular pollution (86%) dominated over crustal re-suspension (10%).

9D.10  
Quantification of organic molecular tracers in urban aerosols collected in Strasbourg (France). Audrey Lottmann (1) Catherine Grand (2) Claire Veilleraud (2) Olivier Delhomme (1) Marie-France Benassy (2) Maurice Millet (1), (1) University of Strasbourg I / CNRS (2) TOTAL France, CRES.

Aerosols in the atmosphere can have a strong importance on the radiative balance of the earth and also some negative effects on human health when toxic pollutants like PAHs are associated. This potential toxicity of atmospheric aerosols has induced the development of monitoring programs. However, in a framework of reduction of particles emissions in the atmosphere, the knowledge of sources of particles is needed and in particular the knowledge of the relative importance of the different sources on the composition of atmospheric particles.

In France, if a survey of the particles concentrations is performed by the atmospheric survey networks, nothing is done for the evaluation of the chemical composition of urban particles, in particular the relative importance of sources like automobile traffic, fossil fuel combustion, wood combustion, meat cooking. In order to evaluate the relative contribution of these sources, a sampling and analysis program was done in Strasbourg (east of France) in 2005. During this period PM10 and PM2.5 were sampled simultaneously in an urban site by using two High-Volume samplers (DA80) on glass fiber filters during 24 hours. Sampling campaigns were performed in winter, autumn, spring and summer. The analytical method is focused on the organic fraction of the aerosols: sampling filters were Soxhlet extracted and extracts were concentrated and purified by flash chromatography. Three fractions were obtained; the first one containing alcanes, the second one PAHs and benzothiazole and the third one metoxyphenols, cholesterol, levoglucosan and monocarboxylic acids.

These fractions were analysed by GC-FID (alcanes), HPLC-fluorescence (PAHs and benzothiazole) and GC-MS after sylilation with MtBSTFA or BSTFA for the polar fraction. Concentrations measured in Strasbourg were generally lower than those observed in other big cities of the world. N-alkanes ratio was in favour of the influence of traffic and domestic heating during winter, while in summer it led to a mixed influence of biogenic and anthropogenic sources. Seasonal variation of levoglucosan concentration is obvious and can be linked to wood heating, even if this compound is still present in summer. The study of phytane and pristane's evolution can lead to questioning about their emission's specificity (vehicular emission vs. whole fossil combustion). Data's interpretation from carboxylic acids was found to be more complex since no real tendencies could be advanced. However, the influence of cooking activities seems to be an important source for these acids together with cholesterol.

First results obtained in France for the molecular characterisation of urban aerosols will be presented and discussed.
9D.11
Characterization of Organic Fine Particulate Matter in Big Bend National Park and Source Apportionment using PMF.
YULING JIA (1), Matthew P. Fraser (2), (1) Rice University, Houston (2) Arizona State University, Tempe

Samples of carbonaceous particulate matter were collected in the Big Bend National Park during the summer of 2007. Organic species including n-alkanes, sugars, petroleum biomarkers, and polycyclic aromatic hydrocarbons (PAH) were quantified to characterize potential sources including wood combustion, mobile sources, and soil resuspension. Secondary organic aerosol formation was determined to be strong in this region based on the quantification of compounds indicative of the photooxidation of biogenic hydrocarbons. Plant wax particles were an important source contributor to ambient concentrations of fine particles (CPI$_{avg}=1.95$), but petroleum sources were also important contributors to the fine PM collected in this remote location. Specific petroleum markers and PAH species concentrations suggests the Big Bend site was directly impacted by local emissions or transport of fossil fuel combustion, and concentrations of levoglucosan measured in PM samples was used to determine that biomass burning particles are present but never the dominant source of carbonaceous particles in Big Bend. By using the PMF modeling technique, source attribution confirmed the above analytical observation by resolving nine source factors that provide similar explanations, and it was estimated the secondary sulfate and mobile sources contributed the greatest fraction of the ambient PM level in Big Bend (43% and 21%, respectively). The PMF modeling also explores the broader ability of the PMF software to model the PM source apportionment using organic molecular markers, and serves as the first example to separate gasoline vehicle emission from diesel vehicle emission using markers other than trace elements in a PMF model.

9D.12
Particulate Matter in Central California: Winter Concentrations and Sensitivity to Emission Controls.
BETTY K. PUN, Rochelle T.F. Balmori, Christian Seigneur, Atmospheric and Environmental Research, Inc.

A wintertime episode during the 2000 California Regional PM Air Quality Study (CRPAQS) was simulated with the air quality model CMAQ-MADRID. Compared with 24-hour average measurements available from CRPAQS, model performance was acceptable. Modeled organic matter (OM) was underpredicted, most likely due to an underrepresentation of emissions, which dominate wintertime OM concentrations, especially in urban areas. In one urban area, modeled daytime nitrate concentrations were low and evening concentrations were high. This diurnal profile was not explained by the partition of nitrate between the gas and particle phases, because gaseous nitric acid concentrations were low compared to PM nitrate. Both measured and simulated nitrate concentrations aloft were lower than at the surface. Heterogeneous reactions involving NO3 and N2O5 accounted for significant nitrate production in the model, resulting in a nighttime peak.

The sensitivity of PM nitrate to precursor emissions varied with time and space. Nitrate formation was on average sensitive to NOx emissions. However, for some periods at urban locations, reductions in NOx caused the contrary response of nitrate increases. Nitrate was only weakly sensitive to reductions in anthropogenic VOC emissions. Nitrate formation tended to be insensitive to the availability of ammonia at locations with high nitrate, although the spatial extent of the nitrate plume was reduced when ammonia was reduced. Reductions in PM emissions caused OM to decrease, but had no effect on nitrate despite the role of heterogeneous reactions. A control strategy that focuses on NOx and PM emissions would be effective on average. Reductions in VOC and NH3 emissions would also be beneficial for certain times and locations.
To quantify emissions from a large sample of on-road vehicles, gas- and particle-phase pollutants were measured separately for a) light-duty (LD) vehicles and b) medium- (MD) and heavy-duty (HD) diesel trucks, during the summer of 2006 at the Caldecott tunnel in the San Francisco Bay area. Aerosol size distributions were measured with a TSI scanning mobility particle spectrometer. In addition, high-time resolution (1 Hz) of total particle concentrations, black carbon (BC), CO, CO₂, and NOₓ concentrations were measured. This presentation will compare number and size distributions measured for both LD and HD vehicles, as well as trends in these measurements over time. For the 2006 particle number emission factors, measured using an ultrafine water-based condensation particle counter, were found to be (3.9 +/- 1.4)10¹⁴ and (3.3 +/- 1.3) 10¹⁵ # kg⁻¹ for LD vehicles and diesel trucks, respectively. Emission factor size distributions (number of particles emitted kg⁻¹ fuel burned vs. Dp) showed that diesel trucks emitted at least an order of magnitude more particles for all measured sizes (10 < Dp < 280 nm). The relative importance of LD vehicles as a source of particles increased as Dp decreased.

Diesel particulate filter (DPF) combined with diesel oxidation catalyst (DOC) has become necessary ingredient of modern after-treatment diesel exhaust system to meet the 2010 PM regulations. Typically, particles are collected on DPF coated with catalytic material during normal operation and then particles are oxidized to regenerate the catalytic surface. Systems utilizing exhaust heat for regeneration are called passive; however, some additional fuel is injected in some systems to regenerate the catalytic surface and are called active regeneration systems. These devices are very efficient in removing PM mass more than 95% during normal operation and PM mass emission during regeneration process depends on the type of regeneration system used. However, these devices emit significant nanoparticles (<50nm) during regeneration process. Therefore, there is a growing concern about PM number emissions and its chemical characteristics due to the deeper penetration of such particles into the respiratory systems and its adverse health impacts.

PM mass, number and size distribution data were collected using Teflo (R) filters, Tissuquartz (R) filters, Dekati Mass Monitor (DMM-230), Engine Exhaust Particle Sizer (EEPS), Condensation Particle Counter (CPC) 3022A and fast-Scanning Mobility Particle Sizer (f-SMPS) along with regulated gaseous emissions using CE-CERT’s Mobile Emissions Laboratory (MEL). Experiments were conducted using two trucks; one with passive DPF (Truck 1) and one with active DPF (Truck 2) on highway roads in California air basin. PM collected on Teflo(R) filters were analyzed for gravimetric mass and then further used for sulfate analysis. Elemental carbon (EC) and organic carbon (OC) analysis were performed on Tissuquartz (R) filters. We will compare the PM mass and number emissions from Truck 1 and Truck 2. A chemical characterization of PM in terms of sulfate, EC and OC will also be discussed. Real-time gaseous and PM emissions will also be investigated to understand the differences in active and passive regeneration.
10A.03  
Toxicity of Particulate Matter from Heavy-Duty Vehicles Retrofitted with Emission Control Technologies.  
(1)University of Southern California, Los Angeles (2)Californian Air Resources Board, Sacramento (3)University of Wisconsin-Madison, Madison (4)University of California, Los Angeles

Diesel exhaust particles (DEP) generally comprise of volatile, semivolatile and non-volatile fractions. Advanced after treatment devices designed to meet stringent mass based US 2007 standards for heavy duty diesel vehicles have relatively less success in controlling volatile and semi-volatile species of PM compared to the refractory fractions. This study investigates the toxic potential of PM from six retrofit technologies (Vanadium and Zeolite based SCRT(R)s, CRT(R), catalyzed DPX filter, CCRT(R), uncatalyzed electric particulate filter [Horizon]) in comparison with a baseline vehicle. The vehicles were tested on a chassis dynamometer at three driving conditions, i.e., steady state cruise (50mph), transient urban dynamometer driving schedule (UDDS) and idle. The consumption rate of dithiothreitol (DTT), as a surrogate measure of redox activity, is determined for undenuded and denuded (at 150◦C) particles collected on filter media. Significant reduction in toxicity (40-100%) was observed as PM is heated to 150◦C for vehicles with retrofit technologies, while particles generated by the baseline vehicle (highly non-volatile) did not demonstrate any changes in toxicity. The toxic potential per unit mass of PM was highest for EPF (DTT-0.14-0.19 nano-mole/min/ug) followed by CRT(R), DPX-idle, SCRT(R)s and Baseline. The introduction of SCR catalysts to CRT(R) has reduced redox activity by four times. In terms of vehicle distance traveled, control devices reduced the net burden of toxicity by 60-90%. Correlation analysis is being performed between toxicity and various chemical constituents such as metals, EC, OC, ions etc. Preliminary analysis suggests that water soluble fraction of OC (R=0.94) is strongly correlated with DTT activity while a week association is observed for total OC (R=0.4).

10A.04  
Distributions of Soot and Ultrafine Particle Emissions from Heavy-Duty Trucks.  
George Ban-Weiss (1), ROBERT HARLEY (1), Melissa Lunden (2), Thomas Kirchstetter (2),  
(1)University of California, Berkeley, (2) Lawrence Berkeley National Laboratory

Previous studies have shown that distributions of vehicle emissions are skewed, meaning that the majority of pollution comes from a small fraction of the in-use vehicle fleet. Of the on-road studies that provide emission distributions in addition to fleet-average emission factors, most have focused on gaseous pollutants from light-duty vehicles. In this study we report emission factors for black carbon (BC) and particle number (N) from 226 individual heavy-duty (HD) trucks driving uphill on a 4% grade through a 1 km-long California highway tunnel. Emission factors (per unit mass of fuel burned) were calculated by carbon balance using 1 Hz measurements of N, BC, and CO2 in the exhaust plumes of individual trucks. BC emissions were log-normally distributed with a mean of 1.7 g/kg and maximum values on the order of 10 g/kg. Corresponding values for particle number emission factors were 4.7E+15 and 4.0E+16 #/kg. The highest-emitting 10% of trucks were responsible for about 40% of total BC and N emissions from all HD trucks. There was minimal overlap among high-emitters of these two pollutants: only 1 of the 226 HD trucks measured was found to be among the highest 10% for both BC and N. These results are consistent with the hypothesis that condensation onto existing BC particle surfaces competes with nucleation of new ultrafine particles, especially when BC emission levels are high. A bootstrap sampling technique is used to assess uncertainty in fleet-average emissions of BC as a function of the number of trucks sampled.
10A.05  
**Ionic and Organic Species in PM Emissions from Advanced Technology Heavy Duty Diesel Vehicles.** ALBERTO AYALA (1), Shaohua Hu (1), Jorn Herner (1), M.-C.Oliver Chang (1), William Robertson (1), John Collins (1), Tao Huai (1), Paul Rieger (1), Constantinos Sioutas (2), (1) Califorinian Air Resources Board, Sacramento/El Monte, CA, (2) University of Southern California, Los Angeles, CA

Meeting the US07 PM and US2010 NOx emission standards for heavy duty diesel vehicles (HDDV) will require advanced engine modification and/or advanced emission control devices such as particle traps and selective catalytic reduction (SCR) technology. The California Air Resources Board (CARB) and the University of Southern California, collaborating with the South Coast Air Quality Management District (SCAQMD) and the California Energy Commission (CEC) have initiated a comprehensive project to characterize the chemical, physical, and toxicological properties of the semi-volatile and non-volatile fractions of PM emissions from these new technology HDDV systems. The after-treatment devices studied in this project were selected from those being tested by various manufacturers for the future California HDDV fleet. Several engine aftertreatment configurations, including vanadium and zeolite based SCRs in combination with continuously regenerating trap technology were compared with a baseline vehicle having no aftertreatment. The vehicles were driven on a heavy duty chassis dynamometer under three driving modes: cruise, transient (UDDS), and idle, at the CARB heavy duty diesel test laboratory in Los Angeles.

Physical properties of PM emissions were characterized by various real-time instruments. Time integrated PM samples with aerodynamic diameter less than 2.5 μm were collected onto Teflon filters for gravimetric mass, water soluble ions, and trace metals analysis. Quartz filters were collected in parallel and analyzed for organic and elemental carbon (OC/EC). Total polycyclic aromatic hydrocarbons (PAH) including particle bound PAH (P-PAH), semi-volatile PAH, and volatile PAH, were collected on a Quartz/PUF/XAD system and analyzed using GC/MS.

EC, OC, ammonium, nitrate and sulfate made up 95% of the PM emissions. Carbonaceous compounds (EC and OC) dominate the PM mass emissions (more than 90%) from the baseline vehicle. The retrofit vehicles showed at least three order of magnitude reduction of the P-PAHs compared to the baseline vehicle. Reduction of OC is less than EC for the retrofit vehicles. Detailed information on the semi-volatile and vapor PAHs, and on the volatile organic species are presented. Sulfate dominates PM mass for some of the retrofit vehicles for certain cycles due to substantial formation of sulfuric acid nucleation mode particles. The molar ratio of sulfate to ammonium on average varied from 0.5 to 0.75 from cruise to UDDS cycle for the nucleating configurations. The effects of driving cycle on aftertreatment technology performance are described.

11A.01  
**Temporal and Spatial Variations of Ultrafine Particles at a Busy Urban Intersection.** YIFANG ZHU, Yungang Wang, Robert Salinas, David Ramirez, Saritha Karnae, Kuruvilla John, Texas A&M University-Kingsville, Kingsville, TX.

A field sampling campaign on ultrafine particles (UFPs, diameter less than 100 nm) was conducted at a busy traffic intersection from December 2006 to June 2007, in Corpus Christi, TX. This traffic intersection consists of South Padre Island Drive (SPID, Highway 358) and Staples Street. Traffic densities on SPID were 9,102 and 7,880 per hr for weekdays and weekends, respectively. Traffic densities on Staples Street were 2,795 and 2,572 per hr, respectively. There were approximately 4 percent of heavy-duty diesel vehicles (HDDV) on both roadways. Peak traffic flows occurred early in the morning and late in the evening during weekdays and around noon on weekends. The average UFP total number concentration collected by a condensation particle counter (CPC 3785; TSI) was 66 thousands of particles per cubic centimeter. A direct relationship between the UFP number concentration and traffic density was observed; but, the HDDV traffic density was found to be a better estimator of the UFP number concentration than total traffic density. A scanning mobility particle sizer (SMPS 3936 with DMA 3081 and CPC 3785, TSI) measuring the particle size distribution from 7 nm to 290 nm was rotated among four corners of the intersection. The upwind and downwind size distributions were both bimodal in shape, exhibiting a nucleation mode at 10-30 nm and a secondary mode at 50-70 nm. The highest and lowest particle concentrations were observed on the downwind, and the upwind side of both roadways, respectively. Wind direction and wind speed played an important role in overall particle concentrations. A negative correlation was observed between particle number concentrations and ambient temperature. The particle number concentration was 3.5 times greater when traffic was idling at red lights than moving at green lights.
11A.02
Characterization of Near-Roadway Air Pollution in Syracuse, NY.
XING WANG (1), K. Max Zhang(1), Jennifer Ehrhardt(2), Philips K. Hopke(2), Thomas Holsen(2), Myron Mitchell(3), (1)Cornell University (2)Clarkson University (3)SUNY College of Environmental Science and Forestry

As part of collaborative efforts to characterize the ambient air quality in Syracuse, NY, we have been conducting field measurements near the intersection of two interstate highways, I-81 and I-690, and selected nearby surface streets in downtown Syracuse. Traffic on I-81 and I-690 are being monitored with machine vision systems to provide traffic counts and speed in five vehicle classes for each highway. At the intersection, particle size distributions and concentrations of various pollutants are measured by analytical instruments on a mobile cart at multiple locations between 10 to 300 meters from the highways. A Mobile Air Pollution Laboratory is employed to measure the air quality on the surface streets. In addition, the ground-level measurements are complimented by continuous monitoring of ambient air quality on two monitoring towers. The measured items include particulate sulfate, OC/EC, black carbon, polycyclic aromatic hydrocarbons (PAHs), PM2.5 mass, and particle size distributions as well as pollutant gases. In this presentation, we will report the results from our field campaigns in March and June, 2008. The seasonal variations of the traffic impact on air quality will be discussed.

11A.03
Characterization of Aerosol at Several Near-roadway Schools in Las Vegas, NV.
STEVEN G. BROWN (1), Paul T. Roberts (1), Taehyoung Lee (2), Jeff L. Collett (2), (1) Sonoma Technology, Inc. (2) Colorado State University

From May 2007 through May 2008 measurements of aerosol and mobile source air toxics (MSATs) were conducted at three schools at various distances near U.S. 95 in Las Vegas, Nevada. Measurements included indoor and ambient Aethalometer (TM) black carbon (BC), ambient CO, ambient NOx, and ambient aerosol scattering via nephelometer. In November 2007, U.S. 95 expanded from four to eight lanes, resulting in increased traffic volume. Traffic count data by vehicle size and speed were also collected near each school to understand the variability of ambient pollutant concentrations with traffic as well as the change in traffic patterns after the expansion. Fyfe Elementary School is located approximately 22 m from the soundwall of U.S. 95; in winter 2007-2008, additional ambient measurements were made using a Sunset OCEC, a particulate polycyclic aromatic hydrocarbons (PAHs) monitor, and an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Basic characterization and ambient concentrations were examined by wind direction (upwind/downwind), wind speed, traffic, and distance from the roadway for both pre- and post-expansion. Detailed aerosol characteristics were further studied using the near-continuous OCEC, PAH and HR-ToF-AMS data collocated with the other ambient data. A strong relationship was observed between primary pollutants and markers throughout the day and with wind direction and speed. Diurnal variations gave insight into how ambient aerosol composition changes with changes in traffic density, speed, and vehicle type.
11A.04
Size-dependent Concentration Gradients of Ultrafine Aerosol in a Near-roadway Community: Effects of a Sound Barrier and Mature Vegetation. MING-YENG LIN, Rawad Saleh, Andrey Khlystov, Duke University

Ultrafine particles (UFP) pose a serious health risk especially to people living and working in near-roadway communities where UFP concentrations are relatively high due to the on-road emissions. Sharp gradients of UFP have been reported near roadways with concentrations rapidly decreasing away from the road. An accurate assessment of population exposure to UFP requires knowledge of spatial distribution of UFP with a resolution of the order of a few meters.

In this study, we investigated spatial distribution of UFP concentrations as a function of particle size on a scale of 10 m near a major urban roadway. The study was located in a neighborhood near US I-440 in Raleigh, NC. The site provides a convenient combination of an open field free-flow region from the highway and a region behind a noise barrier and mature trees. A comparison of concentration gradients in these two regions allows an assessment of the effect of the noise barrier and trees on the dispersion of UFP. Measurements were performed in summer and winter to elucidate the effect of foliage on the near-roadway UFP gradients. It appears that both the noise barrier and trees have a significant reducing effect on the near-roadway concentrations of UFP. The presence of foliage increases the reduction of UFP. Our experiments in a wind tunnel confirm the ability of trees to filter UFP. A summary of the field observations and wind tunnel experiments will be presented.

11A.05
Real-Time Characterization of Pollutant Concentrations and Their Gradients in West and Downtown Los Angeles Using an EV Mobile Platform. Shishan Hu (1), Kathleen Kozawa (1,2), Steve Mara (2), Scott Fruin (3), Suzanne Paulson (1), Arthur Winer (1), 1 University of California, Los Angeles 2 California Air Resources Board 3 University of Southern California

An electric vehicle (EV) mobile platform (MP) was used to measure real-time vehicle-related pollutant concentrations and their gradients in West Los Angeles (WLA) and Downtown Los Angeles (DOLA). The MP has the ability to measure gaseous and particulate pollutants with high spatial and temporal resolution to capture localized high concentrations that cannot be measured by conventional fixed-site monitors. Instruments aboard the MP measured CO, CO2, NOx, black carbon (BC), ultrafine particle (UFP), PM2.5, and particle-bound polycyclic aromatic hydrocarbons (PB-PAH). The MP was driven along fixed routes to identify potential sources of high pollutant concentrations and steep gradients important for human exposure.

WLA and DOLA are traversed by heavily traveled freeways and surface arterials. Field tests were conducted during pre-sunrise, morning, and afternoon periods to determine the key factors affecting pollutant concentrations and gradients, including traffic volume and composition, traffic speed, meteorological factors, time of the day, and weekday versus weekend.

The routes were designed to cover selected major surface arterials, heavily traveled freeways, and the Santa Monica Airport (SMA), as well as residential areas, schools, and commercial sites. The sampled data were analyzed by using video and audio records obtained during each sampling period. Heavy-duty diesel trucks and high-emitting gasoline vehicles were major contributors to elevated concentrations of UFP and BC on, and adjacent to, roadways within DOLA. Concentrations of UFP and BC were elevated throughout the residential neighborhoods surrounded by freeways in DOLA, but were generally lower in WLA even close to the freeways, consistent with the newer and cleaner vehicle fleet in WLA. However, extremely high UFP concentrations were observed in the residential neighborhoods downwind of SMA when jet aircraft took off.
Characterization of Pollution Concentrations On and Near Heavily Traveled Roadways in Communities Adjacent to the Ports of Los Angeles and Long Beach Using a Mobile Monitoring Platform. Kathleen Kozawa (1, 3), Jorn Herner (1), Scott Fruin (2), Arthur Winer (3), (1) California Air Resources Board, Research Division (2) Preventive Medicine, Environmental Health Division, Keck School of Medicine, University of Southern California (3) Environmental Science and Engineering Program, School of Public Health, University of California, Los Angeles

The communities adjacent to the Ports of Los Angeles (POLA) and Long Beach (POLB) are heavily impacted by containerized goods movement, particularly heavy-duty diesel truck (HDDT) traffic. The POLA and POLB combined handle 40% of the container traffic entering the United States; in addition, container volumes are expected to triple in the next decade. Thus, future and existing air quality near roadways and the potential health impacts are of great concern. HDDT traveling through these communities create localized high pollution concentrations often missed by conventional fixed-site monitoring, but are important for accurate exposure assessment in on-road and near-roadway microenvironments. To quantify these impacts, a mobile monitoring platform equipped with real-time instrumentation was driven along fixed routes in these communities to collect spatially- and temporally-resolved data including ultrafine particle (UFP) number concentration and size distribution, black carbon, and particle-bound polycyclic aromatic hydrocarbons. Concentrations of these pollutants were frequently found to be several times higher in 150 meter buffer zones immediately downwind of roadways compared with upwind buffer and ‘non-buffer’ zones, particularly when HDDT traffic volumes were high. On several occasions, UFP number concentrations exceeded one million particles per cubic centimeter when driving on roads heavily trafficked by HDDT, or when driving behind high emitting gasoline vehicles. Pollutant concentrations were also elevated during times of stagnant wind conditions. Overall, in these port communities, near-roadway exposures were significantly elevated for persons living, working or attending school in locations close to heavily diesel trafficked roadways.

Coupling of Positive Matrix Factorization with TOMS to Identify Saharan Dust Transport: Eastern Mediterranean Atmosphere. FATMA OZTURK (1), Ridvan Kirmaz (2), Abdullah Zararsiz (2), Gurdal Tunce (1), (1) Middle East Tecnical University, Environmental Engineering Department, Ankara, TURKEY (2) Turkish Atomic Energy Authority, Saraykoy Nuclear Research and Education Center, Ankara, TURKEY

The primary goal of this study is to differentiate chemical compositions of Saharan Dust and local dust generated in the Eastern Mediterranean region. Data set generated by analysis of approximately 1700 daily PM10 Hi-Vol aerosol samples, collected on cellulose fiber filters (Whatman 41), between 1993 and 2001, at a station located on the Mediterranean coast of Turkey (30.34 degrees E, 36.47 degrees N) were used for this purpose. Major ion content of the collected samples was analyzed by Ion Chromatography (IC) and Colorimetry. Energy Dispersive X-Ray Fluorescence (EDXRF) and Inductively Coupled Plasma Mass Spectrometry (ICP MS) were employed to determine trace element constituents from Li to U. These analytical techniques enable us to measure about 60 ions and elements in each sample. In order to apportion the sources affecting Eastern Mediterranean aerosol composition, Positive Matrix Factorization (PMF) was applied to the generated data set. PMF identified 7 factors, namely, biomass burning, oil combustion, local dust, Saharan dust, general pollution, sea salt and fertilizer use. The scores (or G-scores) of the factor that was identified as the Saharan Dust factor was used to investigate dust transport from north Africa to the Eastern Mediterranean basin. Aerosol Index images provided by Total Ozone Mapping Spectrometer (TOMS) Earth Probe was used to ensure episodes observed in G-scores are indeed due to Saharan Dust transport to the station area. For this purpose, TOMS images were requested for the days that we observed highest G score values. The obtained TOMS images confirmed the Saharan dust transport to Eastern Mediterranean region in these episode days. This allowed us to differentiate chemical compositions of local dust and Saharan dust as sampled at the Eastern Mediterranean atmosphere.
11B.02  
Source Apportionment using Daily Organic Molecular Marker Speciation in Denver. STEVEN J DUTTON (1), Michael P Hannigan (1), Shelly L Miller (1), Jana B Milford (1), Daniel E Williams (1), Sverre Vedal (2), Jessica Garcia (3), (1) University of Colorado, Boulder, (2) University of Washington, Seattle, (3) California Polytechnic State University  

PM2.5 organic molecular markers have been used as tracers for source apportionment in past studies. Due to the relatively large effort required to quantify individual organic compounds, these studies have primarily relied on the Chemical Mass Balance (CMB) model which does not require a long time series of observations like other factor analysis models do. However, multivariate factor analysis becomes more appealing in areas where representative CMB source profiles are not available.

We have collected daily PM2.5 filter samples from a residential receptor site in Denver for the past six years. Organic molecular marker analysis using gas chromatography-mass spectrometry (GC-MS) has been completed on the first 1.5 years of samples. Seasonal and weekday/weekend trends in markers for specific sources will be presented along with Positive Matrix Factorization (PMF) results using the 1.5 year organic molecular marker dataset.

11B.03  

The goal of multivariate receptor modeling such as positive matrix factorization (PMF) is to identify a number of factors that best characterize the total air pollution at a site by decomposing a matrix of ambient data into two matrices - the species profile of each source and the amount of mass contributed by each factor to each individual sample - that need to be interpreted by an analyst to determine what source types are represented. The non-negativity constraint of PMF is sometimes enough to ensure that little rotational ambiguity is in a solution when there are a sufficient number of zero values in the solution. However, in some cases, a priori information about the important sources or the airshed can be used to further constrain the model and reduce rotational ambiguity.

The multilinear engine (ME-2) is a flexible program designed to perform PMF iteratively. In ME-2, several tools are available to incorporate a priori information into the PMF model. Using these tools, certain elements of the output matrices can be 'pulled' toward a fixed value, using the goodness-of-fit parameter (Q) to control how strongly the element is pulled.

Two case studies using PM2.5 speciated data are presented to illustrate the use of rotational tools in ME-2. In the Baltimore case study, constraints were applied to limit excess mass from non-dominant species in the oil combustion factor. In the Allen Park case study, the industrial factor rarely had a zero contribution, leading to an oblique edge on g-space plots. Samples during times when winds were not from the industrial area were pulled to zero. In both case studies, the additional constraints led to a more physically realistic solution: the factor profiles were easier to interpret and the mass apportioned to each factor agreed with expectations based on known local sources.
11B.04
An enhanced understanding of sources in Windsor, Ontario obtained using advanced receptor modeling tools. MAYGAN McGuire (1), Cheol-Heon Jeong (1), Greg Evans (1), Tom Dann (2), Dennis Herod (3), (1) Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Ontario, Canada, (2) Environmental Science and Technology Centre, Environment Canada, Ottawa, Ontario, Canada, (3) Air Emissions Priorities Division, Environment Canada, Gatineau, Quebec

As the southern-most large city in Canada, and home to numerous industrial activities, Windsor, Ontario experiences more poor air quality episodes than any other city in Ontario. In this study, an enhanced understanding of aerosol sources impacting Windsor was obtained in addition to their plausible local and regional geographic origins by applying newly developed receptor modeling tools provided by the U.S. EPA.

Source apportionment of integrated PM2.5 filter samples from the Environment Canada National Air Pollution Surveillance (NAPS) network site in Windsor, Ontario spanning 27 months was interpreted using a new Positive Matrix Factorization graphical user interface entitled EPA PMF 3.0. Geographic origins of sources from the filter data were then investigated using a new EPA platform called APTR 1.0 (Air Pollution Transport to Receptor). A combined local and regional analysis of plausible geographic origins will be presented using the APTR model; the conditional probability function was used to investigate the possibility of local contributions, and then a modified Quantitative Transport Bias Analysis (QTBA) using HYSPLIT backtrajectories was used to investigate regional contributions.

We employed a similar methodology to interpret high time resolution data from an intensive sampling campaign performed in January 2005. Sub-hourly elemental composition information was that was collected using a Semi-Continuous Elements in Aerosols Sampler combined with ICPMS analysis was interpreted using EPA PMF 3.0. Detailed information regarding the chemical composition of the non-refractory aerosol composition was available from an Aerodyne Aerosol Mass Spectrometer. In addition to the analysis methods outlined previously, we exploited the APTR model's non-parametric wind regression analysis capability for the sub-hourly data to better elicit local source origins.

Similar source profiles from the different datasets were evaluated for commonalities, and were then compared to available source profiles from the region. A comparison of plausible local and regional geographic origins was also undertaken to obtain an enhanced understanding of the sources affecting Windsor, Ontario.

11B.05
Identification of Local PM2.5 Sources using Highly Time Resolved Samples and a New Hybrid Receptor Modeling Framework. GARY A. NORRIS (1), Rachelle M. Duvall (1), Joseph R. Graney (2), Jay R. Turner (3), Ram Vedantham (1), Matthew S. Landis (1), (1) National Exposure Research Laboratory, US Environmental Protection Agency, Research Triangle Park, NC USA (2) Geological Sciences and Environmental Studies, Binghamton University, NY USA (3) Department of Energy, Environmental & Chemical Engineering, Washington University, St. Louis, MO USA

The St. Louis Advanced Monitoring Initiative (AMI) project was initiated to provide the States of Illinois and Missouri information to assist in their development of State Implementation Plans (SIP) for fine particulate matter (PM2.5) in the St. Louis non-attainment area. Highly time resolved (30 minute) samples collected using a Semi-Continuous elements in aerosol sampler (SEAS) during the St. Louis-Midwest Supersite study were analyzed to determine the local sources impacting the area. Approximately 600 SEAS samples were extracted using a mixed acid solution (0.2 % HNO3 and 0.1 % HCl)/sonication procedure and analyzed using a high resolution magnetic sector field inductively coupled plasma mass spectrometer (HR-ICPMS). The HR-ICPMS provided a broad suite of species above their method detection limit and no interference corrections to account for analytical artifacts. Local source impacts were identified and quantified using the elemental data in the new EPA Air Pollution Transport to Receptor (APTR) model framework. APTR incorporates statistical receptor modeling tools with meteorological data to identify the type(s) and location of the source(s) through implementation of Nonparametric Wind Regression (NWR) and Sector Apportionment. Local sources contributing to Zn and Pb were identified and quantified and limitations of the NWR approach will be discussed.
11B.06  
Evaluation of Multiple Rotational Controls in Multi-linear Engine-based Receptor Modeling. SHELLY EBERLY (1), Adam Reff (2), (1) Geometric Tools, LLC, Scottsdale, (2) EPA, RTP

Positive matrix factorization (PMF) is a constrained factor analytic approach that has been used extensively to apportion sources of ambient fine particulate matter (PM2.5). Even with non-negativity constraints, PMF models are generally ill-posed meaning there are multiple solutions that fit a given dataset equally well. Selection of the most representative solution requires auxiliary data within an airshed such as locations or concentrations of key species in profiles of sources contributing to ambient PM2.5 concentrations at the receptor site. Such auxiliary information may be directly included in PMF models by formulating additional constraints with the Multi-Linear Engine (ME-2), a script-based program that provides the user with flexibility in specifying both equation-based and parameter-specific constraints for a factor analytic model. There are many approaches for constraining solutions, however the effect on solution accuracy has not been robustly evaluated.

In this work, synthetic datasets are constructed from the PMF solutions of ambient PM2.5 data from ambient monitoring sites at 3 geographically distinct locations: Phoenix, AZ, Washington DC, and Raleigh, NC. PMF receptor modeling is applied to each of these 3 datasets with various constraints using ME-2, and the resulting solutions are compared against the PMF solutions from which the datasets were constructed. Parameter-specific constraints explored include the FKEY, FPEAK, and AUTOPULL options available in the ME-2 script. An equation-based constraint explored is mass closure for resulting factor profiles. Combinations of parameter-specific and equation-based constraints are also investigated. Metrics for measuring rotational ambiguity and the degree to which constraints improve them will be explored, as will the effect of measurement error input into ME-2 with the dataset. Results reported will include those that may be limited to specific data sets and those that likely are generalizable to other data sets.

12A.01  
Intra-community Variability in Ultrafine Particle Number Concentrations in the San Pedro Harbor area (Los Angeles, California). KATHARINE MOORE (1), Margaret Krudysz (2), Payam Pakbin (1), Neelakshi Hudda (1), Constantinos Sioutas (1), (1) University of Southern California, (2) University of California, Los Angeles

Recent evidence links elevated ultrafine particle (UFP) concentrations with adverse health effects, but exposure assessments based upon PM2.5 mass concentrations may be misleading. In order to better understand and quantify intra-community variability in UFP concentrations, a dense network of 14 monitoring sites was set-up in Los Angeles in two clusters - San Pedro/Wilmington and West Long Beach - in communities surrounding the Ports of Los Angeles and Long Beach. Port-related activities - particularly goods movement associated with high volumes of heavy-duty diesel vehicle (HDDV) traffic - represent significant UFP sources. The field study was conducted from mid-February through mid-December 2007 to assess diurnal, seasonal and spatial patterns and intra-community variability in UFP concentrations. Simultaneous UFP number concentrations can vary up to a factor of 10 (<10,000 cm^-3 up to 90,000 cm^-3 for hourly averages calculated by month) for sites within a few km of each other due to the large number and intensity of sources. Specific site locations, particularly proximity to roadways used for goods movement, strongly affects observations. Clear diurnal and seasonal patterns are evident in the data. A diurnal pattern associated with high HDDV volumes and goods movement was identified. Varying factors are shown to influence the observations. Coefficients of Divergence (CODs) calculated for the site pairs suggest moderate heterogeneity overall, but specific site pairs exhibited relatively fixed patterns over a wider range of COD values - from homogeneous to strongly heterogeneous - throughout the study. The intra-urban variability observed in this study is comparable to and exceeds the inter-urban variability observed in a previous study in Los Angeles. A frequency analysis of the concentrations provides some insight into the relative contributions of local and regional aerosol to the observations. UFP concentrations can vary considerably on short spatial scales in source-rich environments which can strongly influence the accuracy of exposure assessments.
The objective of this field study was to evaluate ultrafine particle (UFP) concentration gradients in 5 neighborhoods in Toronto, Canada. Within each neighborhood, 3 Condensation Particle Counters (CPC) were deployed in locations of varying traffic density. In addition, gradients within each neighborhood were measured by walking between sampling sites using P-TRAKs. These field measurements were compared to an identical set of instruments at a downtown central site located on a high traffic road. This study further elucidated how the baseline concentration of UFP within the city changes over time and the degree to which UFP concentrations within neighborhoods are homogeneous.

This study also solidified observations from two previous field studies where UFP concentrations were measured on a short-term basis in areas near and away from traffic. Firstly, although particle number concentrations were significantly higher in areas near traffic, short-duration spikes caused by passing vehicles contributed an estimated 30% to the elevated average concentration. When the spikes were removed, the average UFP concentration was similar to areas away from traffic. Secondly, a constant baseline particle number concentration existed within the city that varied temporally rather than spatially near the downtown core. Thirdly, when clean air masses entered the city from the north, UFP concentrations decreased as a function of distance linearly; however, this relationship did not hold under other meteorological conditions. Finally, in locations furthest away from traffic sources within a neighborhood, UFP particle number concentrations were 40% lower than those measured in areas near traffic.

Analysis illustrates that through all eight campaigns the particle number fluxes exhibit a clear diurnal cycle with a late morning peak coinciding with the morning traffic peak and an early afternoon peak that is closely related to the diurnal sensible heat flux cycle. Pronounced weekday versus weekend differences in the diurnal particle number fluxes could be linked to traffic activity and individual anthropogenic activities associated with sources other than traffic could also be identified. Dependencies on wind direction were identified from the observable relationship between high particle number fluxes and areas of heavy urbanisation.

A simple parameterized model, based on previous work by Dorsey et al. (2002) and Martensson et al. (2006), was found to be satisfactory for predicting the net vertical particle number flux based on traffic activity, friction velocity and sensible heat flux. Predictions have also been made of the concentrations close to street level from the tower level data using the aerodynamic gradient method.
12A.04
Urban and Rural Concentrations of Motor Vehicle Markers in the NY, NJ and CT Airshed. MONICA A. MAZUREK (1), Min Li (1), Claire Belisle (1), Zhiqiang Sun (2), Jessica Sagona (1), Stephen McDow (3), (1) Civil & Environmental Engineering Department, Rutgers The State University of NJ, Piscataway, NJ, (2) Environmental Monitoring Center of Shijiazhuang, Hebei Province, Peoples Republic of China (3) National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC

Motor vehicle exhaust is believed to be a major contributor to ambient fine particle mass in metropolitan NYC. The influence of motor vehicle emissions on rural sites upwind of the NYC area is not well known. Two groups of motor vehicle markers, 1) hopanes and steranes, and 2) 22 PAH compounds were quantified in fine PM at six sites (Chester, NJ; Elizabeth, NJ; Westport, CT; Queens, NY; Bronx, NY; Pinnacle State Park, NY) over a five-year (2002-2007). Urban (n=46) and rural (n=27) composites were compared using simple descriptive statistics and ANOVA tests (2-sided, 95% confidence level).

Total steranes and hopanes for the urban composites ranged from BDL to 6.04 ng/m3, (median = 1.33 ng/m3; average = 1.80 ng/m3). Elizabeth, NJ (NJ Turnpike site) was the only site to exhibit 3 outlier concentrations during summer (4.92 ng/m3), early winter (5.83 ng/m3) and winter (6.04 ng/m3). Rural composites had significantly less total steranes and hopanes with concentrations from BDL to 0.58 ng/m3 (median = 0.08 ng/m3; average = 0.10 ng/m3). The total PAH for the urban composites ranged from BDL to 48.79 ng/m3 (median = 4.32 ng/m3; average = 8.33 ng/m3). The rural total PAH concentrations ranged from BDL to 9.43 ng/m3 (median = 0.64 ng/m3; average = 1.56 ng/m3). Three sites exhibited outlier concentrations: Queens, NYC (early winter, 26.75 ng/m3), Elizabeth, NJ (winter, 48.79 ng/m3), and Westport, CT (early winter, 37.06 ng/m3). ANOVA test results indicated significant differences between urban and rural average year-round ambient concentrations for total steranes and hopanes and total PAHs.

These statistical results indicate strong local influence of motor vehicle fine PM emissions to the urban NY, NJ and downwind CT sites. Upwind sites (Chester, NJ and Pinnacle, NY) had over 10 times less fine PM motor vehicle emissions if median total hopane and sterane ambient mass concentrations are compared.

12A.05
Simulating Airborne Particulate Matter in a Near-Road Environment Using a Source-Oriented Three-dimensional Air Quality Model. Qi YING and Yunlong Zhang , Zachry Department of Civil Engineering, Texas A&M University

In this study, a source-oriented near road air quality model is revised to nest in a regional air quality model to simulate the gases and particulate matter (PM) concentrations and determine their sources in an area of approximately 10x10 km2 near downtown Houston with a spatial resolution of 50 meters. The gas-phase chemistry of the model is a revised SAPRC99 mechanism with additional reactions to simulate the concentrations of air toxic pollutants. The particles are represented using a 15-section representation Emissions from different vehicles categories can be tracked separately to determine their source contributions. Nucleation, coagulation, condensation/evaporation and dry deposition processes are considered for the simulated particles.

The influence of freeway traffic on the turbulent diffusivity of the atmosphere is explicitly simulated using a parametrization scheme that determines the production rate of turbulent kinetic energy due to traffic based on the traffic flow. Emissions of gaseous and particulate matter from on-road vehicles were generated using emission factors from MOBILE6 and traffic flow (vehicle speed, traffic density and fleet composition) from a traffic model. Meteorology for the modeling domain is generated using the Weather Research and Forecast model.

Concentrations and source contributions of EC, OC, secondary nitrate, sulfate, ammonium ion and organic aerosols together with gas phase pollutant concentrations are simulated for a typical summer weekend and typical weekday. Spatial distributions of gases, air toxic pollutants and PM are determined. The predicted concentrations of CO, O3, NOx and PM2.5 are compared with measured concentrations under similar conditions. Regions that are impacted significantly by the freeway traffic are identified using the source-oriented feature of the model. The sensitivity of the predicted pollutant concentrations to the parametrization of the vehicle induced turbulence were investigated. Major processes that influence the PM concentrations in the near road environment are studied using process analysis.
12A.06 Comparing the Toxicity of Fresh and Aged Diesel Exhaust Using a Newly Developed in vitro Exposure System. K. de Bruijne (1), K. G. Sexton (1), S. Ebersviller (1), C. Olenick (1), R. Woodside (1), M. Doyle-Eisele (1), H. Jeffries (1), I. Jaspers (1,2), (1) University of North Carolina Environmental Sciences & Engineering (2) CEMALB

Our previous studies have shown that atmospheric aging of gaseous pollutants modifies the chemical composition of air pollution mixtures, ultimately affecting its toxicological potential. The goal of this current project is to determine whether aging of complex gaseous and particulate mixtures, such as diesel exhaust (DE), in the presence or absence of photochemistry, alters the toxicological potential of that mixture. A second goal was to examine the differences between multiple diesel emission sources, specifically those emitted from a 1980 Mercedes and a 2006 Volkswagen. Each freshly emitted DE sample was injected into a 120 cubic meter outdoor smog chamber and aged utilizing natural sunlight and humidity. Two separate exposure systems, electrostatic aerosol in vitro exposure system (EAVES) and gas in vitro exposure system (GIVES) were used simultaneously to expose human respiratory epithelial cells across an air-liquid interface to particulate and gas-phase components, respectively. We have compared the composition and toxicity of unreacted ‘fresh’ DE, dark-aged DE, and photochemically-aged DE. Atmospheric aging has shown to alter the chemical composition complexity and significantly increases the diameter of the DE particles. Following exposures, cells were analyzed for inflammatory cytokine production (IL-8) using RT-PCR. Both fresh and aged DE from both DE sources increased IL-8 levels as compared to the clean air control, with the Mercedes engine generating a greater response. In addition, our results suggest that aging significantly enhances the responses compared to fresh DE emissions in the particle phase and decreases in the gas phase (when particles are present). This suggests that the gaseous components are partitioning onto the particles during the aging process. Taken together, these results further support the importance of considering engine type and atmospheric aging when examining the toxicity of vehicle emissions.

13B.01 Source apportionment of wintertime secondary organic aerosol during the California Regional Particulate Air Quality Study. Jianjun Chen (1), Qi Ying (2), Robert Griffin (3), Michael Kleeman (1), (1) University of California, Davis (2) Texas A&M University, College Station (3) University of New Hampshire

The UCD/CIT air quality model with the Caltech Atmospheric Chemistry Mechanism (CACM) was used to simulate the formation and perform source apportionment for secondary organic aerosol (SOA) in northern and central California for the period of December 15, 2000 to January 7, 2001, which is part of the wintertime California Regional Particulate Air Quality Study (CRPAQS). Domain-wide maximum 24-hour average SOA concentrations were predicted to reach 9.1 micrograms per cubic meter on certain days. The predicted contribution from SOA to the total organic aerosol (OA) varies with locations. At urban areas such as Fresno, CA and Bakersfield, CA, predicted SOA accounts for approximately 5% of total OA, while at rural areas such as Angiola, CA, predicted SOA contributes as much as 34% of total OA. Stagnant air, the accumulation of SOA precursors, and low temperature favoring partitioning of semi-volatile organics are believed to be the main reasons for substantial formation of SOA in winter.

The model was capable of predicting SOA contributions from catalyst gasoline vehicles, non-catalyst gasoline vehicles, diesel vehicles, combustion of high sulfur fuel, residential wood smoke, other anthropogenic and biogenic sources, and initial/boundary conditions. It was found that other anthropogenic and biogenic sources (e.g., off-road vehicles, running evaporation, solvent use and biogenic monoterpene emissions) were the biggest source to the SOA formation, contributing approximately half of the total SOA formation. Catalyst and non-catalyst gasoline vehicles and wood smoking are the other three sources that contribute to most of the rest SOA formation. In terms of SOA precursors, the major SOA contributor is long-chain alkanes. Other contributors include aromatic compounds and monoterpenes.
13B.02
Modeling of a PM Episode at Santiago, Chile. HECTOR JORQUERA (1), Julio Castro (2), (1) Departamento de Ingenieria Quimica y Bioprocesos, Pontificia Universidad Catolica de Chile, Santiago, Chile. (2) Area Soluciones Ambientales, DICTUC, Santiago, Chile.

The greater metropolitan region of Santiago, Chile (6.5 million inhabitants) is the 7th Latin American city in population, and 40% of the country's inhabitants live there. During fall and winter seasons the meteorological conditions lead to pollutant trapping below the subsidence-based thermal inversion, raising the levels of all pollutants, especially PM2.5.

Steady economic growth in the last 20 years has resulted in a fast increment of car ownership, industrial activity, fuel consumption, etc. As a result of air quality regulations, ambient PM10 and PM2.5 concentrations have been reduced significantly between 1990 and 2005. Nonetheless, the 2006 annual ambient PM2.5 concentration is near 30 (ug/m3), twice the USA standard.

We take a modeling approach to assess the contributions of different emission sources during an intense episode that happened in May 19th-24th 2005. We use the MM5 mesoscale modeling system coupled with the CAMx (V4.40) air quality model to: a) model a base case scenario for 2005; b) improve the emission estimates of primary PM (fine and coarse dust street, elemental carbon, construction dust) and gas tracers such as CO and VOC by means of inverse modeling, using a Kalman filter approach (Rodgers, 2000) and results from receptor modeling analysis (Jorquera and Cifuentes 2007); c) analyze impact of short term contingency measures on the daily emissions.


13B.03
A Technique for Considering Aerosol Dynamics in Size Resolved Near-Road Models at High Spatial Resolution. SANG-RIN LEE, Jay Raife, Charles O Stanier, University of Iowa, Iowa city

Two classes of pollutant components receiving recent attention as causal components for adverse health effects are (a) gases and particulate matter (PM) from combustion sources, particularly from vehicles; and (b) ultrafine particles (UFPs) with sizes less than 0.1 um, which have high pulmonary deposition efficiencies and high surface areas for effective delivery of adsorbed and condensed toxins with associated oxidative stress and inflammatory response. The causal components driving the PM associations, however, remain to be identified. Together with other tools such as concentrated particle exposure studies, exposure models are a useful tool in sorting out the particle component toxicity issue.

The Stanier research group has begun development of a Personal Exposure Aerosol Screening Model (PEASM) having special features: integration of the exposure model with recent health effects studies; simultaneous prediction of UFPs from combustion and from photochemical new particle formation; and allowance of external mixtures created from aerosol dynamical processing of combustion exhaust. One specific aspect of the PEASM is the need to achieve high spatial resolution, while maintaining computational efficiency. This can be achieved by limiting detailed aerosol dynamics calculations to small regions upwind of receptors.

Aspects of model development to be discussed include the selection of emission factors for a near-road emission model, efficient implementation of aerosol dynamics within the CALINE4 roadway dispersion model, and issues arising when multiple roadways or interacting plumes influence a receptor. When typically reported number emission factors of 1-10 x 10$^{14}$ (vehicle-mile)$^{-1}$, are used, the level of agreement with a range of near road and on road number measurements is presented.
Source Apportionment of Particulate Matter Using the Natural Variation of Trace Metal Isotopes. BRIAN J MAJESTIC, Ariel D Anbar, Pierre Herckes, Arizona State University, Tempe

Until recently, measurements of natural isotopic variations in atmospheric aerosols have been primarily restricted to the light elements such as hydrogen, carbon, oxygen, sulfur, and nitrogen. Developments in mass-spectrometry, however, have provided a reliable and reproducible means to measure natural isotope variations (+/- 0.1 %, per mil) in trace-metals using small amounts of sample (4 micrograms of iron). Because isotopic fractionation may occur during biological and non-biological processes, multi collector (MC)-ICP-MS can provide mechanistic clues to atmospheric reactions based on the degree and direction of fractionation, thus providing better clues as to how trace metals cycle in atmospheric media. This talk will focus on some of the exciting possibilities of MC-ICP-MS as well as the limitations of MC-ICP-MS for source-apportionment of atmospheric aerosols. To illustrate the utility of this technique, $\delta^{56}\text{Fe}$ (as $^{56}\text{Fe}/^{54}\text{Fe}$) data will be presented for the coarse and PM2.5 fractions of PM collected at three sites: 1) a parking garage on the campus of Arizona State University, where the PM2.5 iron isotope composition has been observed to be isotopically light relative to the IRM-014 standard ($\delta^{56}\text{Fe} < -0.5 \%$), 2) Nogales, AZ ($\delta^{56}\text{Fe} = -0.2 \%$), a city on the US-Mexico border, and 3) Gilbert, AZ, which is a mixed urban-agricultural site near Phoenix, AZ. The implications of this data will be discussed in the context of how measurements of trace-metal natural isotope variations can be a valuable tool in the source apportionment of aerosols and how this technique can help us better understand aerosol chemistry.

Particulate Air Quality Model Predictions using Prognostic vs. Diagnostic Meteorology in California. Jianlin Hu (1), Qi Ying (2), Zhan Zhao (1), Michael Kleeman (1), (1) University of California, Davis, (2) Texas A&M University

Meteorology is one of the major factors that influence particulate matter concentrations during air pollution episodes (along with emissions and atmospheric chemistry). Accurate meteorology data are necessary for any assessment of source contributions to air pollution and the design of effective emissions control programs using air quality models. The continuous meteorological fields needed by air quality models can either be produced by meteorological models (prognostic fields) or they can be interpolated directly from measurements (diagnostic fields) when analyzing historical episodes. Most air quality studies in the eastern United States are carried out using prognostic fields such as those produced by the Fifth-Generation NCAR/Penn State Mesoscale Model (MM5) or the Weather Research & Forecasting (WRF) Modeling System. In contrast, most air quality studies carried out in California have used diagnostic meteorology fields. Many researchers assume that prognostic meteorological fields are more accurate and therefore produce better air quality predictions. In this presentation we will demonstrate that these assumptions may not hold true for the mountain-valley topography that exists in California.

We evaluate the accuracy of air quality predictions made using prognostic and diagnostic meteorology fields for the central California region during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) 2000 winter episode (Dec 15, 2000 - Jan 7, 2001). The prognostic meteorology fields were predicted by WRF model simulation with 3-nested domains and one-way nesting technique. The discrepancies between the prognostic meteorological fields and measurement will be investigated. The effects of errors in the meteorological fields on airborne particle size and composition distributions will also be examined. Finally, the implication of using prognostic meteorology fields for studies of climate change and future air quality prediction in California will be discussed.
14A.01
Particulate Matter Emissions from Aircraft Engines. PREM
LOBO, Donald Hagen, Philip Whitefield, Missouri University of
Science and Technology

The growth of commercial air traffic has led to an increased
contribution to the local inventory of particulate matter (PM)
from aircraft engines. Until recently PM emissions from
commercial aircraft engines were not well understood. A series
of field campaigns - APEX1, Delta Atlanta Hartsfield Study,
JETS APEX2 and APEX3, were devised and conducted to
address the need for data representative of engines in the
commercial fleet. This paper summarizes the results gathered
from the emissions database associated with these measurement
campaigns and describes them in terms of the physical
characterization of PM emissions by extractive sampling from
several on-wing engines from the fleets of Delta Airlines,
Southwest Airlines, Continental Airlines, Continental Express
and FedEx. Samples were extracted at the engine exhaust nozzle
(1m) as well as locations downstream. The engines studied in
these campaigns ranged from old to new technology and
included CFM56 (B737), JT8D (MD88), RB211 (B757),
AE3007 (EMB 145), and PW4158 (A300). The measured PM
parameters such as emission factors and distribution shape
parameters for each engine type (i.e. JT8D, CFM56, RB211 etc.)
are unique and vary between engine types. These PM parameters
also vary between engine subtypes, e.g. the ratio of mass-based
emission indices for CFM56-3B versus -7B engines at take-off
was found to be 4:1. When emissions were sampled downstream
in the plume condensable exhaust gases were found to convert to
the particle phase by nucleating new particles and by condensing
onto soot. The mass of particles in the plume does not change
within experimental uncertainty as the plume travels downwind
but the number of particles increases by at least an order of
magnitude. The large increase in PM number coupled with
constant PM mass indicates that these newly formed particles do
not contribute significantly to the total PM mass in the plume.

14A.02
The Impact of Alternative Fuels on Aircraft Emissions. B. E.
ANDERSON (1), A. Bhargava (2), A. J. Beyersdorf (1), E. L.
Winstead (1), K. L. Thornhill (1), D. S. Liscinsky (3), J. Souza
(4), C. Wey (5), K. Tacina (6), M. T. Timko(7), Z. Yu (7), T. B.
Onasch (7), R. C. Miake-Lye (7), E. Corporan (8), Robert
Howard (9) M.J. DeWitt (10), and C. Klingshirn (10) , (1) NASA
Langley Research Center (2) Pratt & Whitney, East Hartford (3) United
Technologies Research Center (4) Pratt & Whitney, West Palm Beach
(5) ASRC Aerospace Corp (6) NASA Glenn Research Center (7)
Aerodyne Research Inc. (8) Air Force Research Laboratory (9) AEDC/
ATA (10) University of Dayton Research Institute

We report results of collaborative experiments conducted to
evaluate the effects of alternative aviation fuels on the
performance and emissions of modern gas turbine engines. This
work was motivated by the pressing need to increase available
fuel stocks, reduce U.S. dependence on foreign oil sources,
increase energy security, and understand how fuel parameters
regulate soot and volatile aerosol emissions from aircraft
engines. The tests evaluated a commercially-available, synthetic
fuel produced from natural gas using the Fischer-Tropsch (FT)
process. This fuel was essentially free of aromatic compounds
and long-chain (i.e., > C$_{12}$) hydrocarbons and contained
only small concentrations of sulfur contaminants. In the
primary test venue, 100% FT fuel, a 50:50 blend of FT and JP-8
and 100% JP-8 were alternately burned in a test-stand-mounted
commercial gas-turbine engine typical of those used on small
regional jet aircraft. Gas and aerosol samples were drawn from
inlet probes mounted 1- and 50-m downstream of the engine exit
plane while engine power was varied from idle to about 85% of
maximum thrust. Samples were analyzed for concentrations of
CO$_2$, CO, SO$_2$, NO, NO$_2$, and total hydrocarbons along with
aerosol particle size, number, black carbon mass, composition
and smoke number. Data collected from the downstream
sampling location facilitated an assessment of differences in
plume chemistry and the tendency of each fuel to promote or
suppress formation of volatile aerosols.

In a secondary test venue, measurements of gas-phase species
and particulate composition were performed while the three fuel
types discussed above were burned in a high-pressure flame tube
mounted in a combustion test cell at the NASA Glenn Research
Center. Inlet pressure, temperature and fuel flow were varied
during testing.

The presentation will provide additional experimental details
and examine the ratio of volatile and non-volatile emissions
from the synthetic and blended fuels relative to standard JP-8.
14A.03

The concern of adverse health impacts from exposure to vehicle-emitted nanoparticles has been escalating over the past few years. Fuel sulfur content (FSC) has been cut from hundreds (~400 ppm) to tens of ppm (~15 ppm) across the United States. However, experiments still observed substantial number concentrations of nanoparticles from vehicles running on ultra-low sulfur fuel and equipped with and without diesel particle filters. This study mainly aims at understanding how nanoparticles are formed under those conditions, which is necessary to project future nanoparticle emissions as fuel compositions and after-treatment systems change. Using a detailed composition-resolved aerosol microphysical model with a recently improved H2SO4-H2O homogeneous nucleation (BHN) module, we simulated nanoparticle formation and evolution constrained by two independent experiments both conducted under ultra-low sulfur conditions. The good agreement between model predictions and measurements in terms of particle size distribution and temperature dependence of particle formation rate leads us to conclude that BHN is likely to be the major source of nanoparticles for vehicles equipped with diesel particle filters. We also carried out a comprehensive quantitative assessment of the effects of enhanced sulfur conversion efficiency, sulfur storage/release, and presence of non-volatile cores on nanoparticle formation. We found that the employment of diesel particle filters may lead to a higher nanoparticle number emissions (but smaller in size) for vehicles running on ultra-low sulfur fuel compared to those emitted from vehicles running on high sulfur fuel. We also showed that the sulfate storage/release effect can lead to significant enhancement in nanoparticle production under favorable conditions as well. For vehicles running on ultra-low sulfur fuel but without diesel particle filters, the BHN is negligible; however, the condensation of low volatile organic compounds on nanometer-sized non-volatile cores may explain the observed nucleation mode particles.

14A.04
Measurements of Black Carbon from Diesel and Biodiesel using Thermo-Optical and Other Techniques. Albert Chung (1), and SUZANNE E. PAULSON (2), Dept. of Chemical Engineering, University of California at Los Angeles Dept. of Atmospheric and Oceanic Sciences, University of California at Los Angeles

Particulate emissions from a 4.8 kW diesel generator running on ultra-low sulfur diesel and biodiesel fuels are characterized using a scanning mobility particle sizer (SMPS), transmission electron microscopy and thermo-optical transmission evolved gas analysis (EGA). Characteristics of the generator including load-dependent size distribution, morphology including fractal dimension and primary particle size (for aggregates, and elemental carbon (EC) to organic carbon (OC) ratio (EC/OC), the small generator falls well within the ranges of particles released by much larger engines. Running on diesel fuel, the EC/OC ratio of particle emissions increases from about 0.5 at idle load to 3.8 at 100% load. The use of biofuel (B100) results in emissions of particles that are compact, irregular, and lack the clearly defined primary particles of diesel aggregates, and yet at max load they have similar EC/OC ratios as diesel particles.

The EC/OC ratio measured by EGA is sensitive to the split point that is established by a laser transmission-based correction for charring. A systematic investigation of a series of metals that are commonly found in ambient aerosols were investigated for their effect on the measurement of EC and OC in diesel samples using two EGA temperature programs. Several metal salts were observed to both reduce the oxidation temperature of elemental carbon and increase charring of the OC associated with diesel particles. Copper and calcium catalyzed to the largest shifts in the profiles of evolved material. NaCl enhanced the effect of copper, but dampened the effect of iron. The NIOSH temperature program was much more sensitive to the catalytic effects of transition metals than the temperature program developed by Conny et al. (Aerosol Science and Technology 37 (9): 703-723, 2003).
Nitration of polycyclic aromatic hydrocarbons (nitro-PAH), present in low concentrations in ambient air, are suspected carcinogens and/or mutagens. Therefore, identification and quantification of nitro-PAH emitted from anthropogenic sources are very important.

In this study, nitro-PAH were collected from exhaust of new heavy-duty diesel engines (2007) and Gas Chromatography/Mass Spectrometry (GC/MS) method was used for their analysis. It was expected that emissions of nitro-PAH are significantly lower from modern diesel engines meeting the 2007 US EPA emission standards. Thus, GC/MS method had to be optimized for nitro-PAH analysis in the low concentration range. The aim of this work was identification and quantification of nitro-PAH in the modern diesel engine emissions and determination their distribution between particle and gas phases.

Teflon-impregnated glass-fiber filters and XAD-4 resin cartridges were used for collection of nitro-PAH from gas and particle phases. Samples were extracted with dichloromethane and acetone. Solid-phase extraction (SPE) and normal-phase HPLC fractionation were used for isolation of nitro-PAH to remove interference and thus reduce a matrix effect during GC/MS analysis.

Samples were analyzed with Varian 1200 triple quadrupole gas chromatograph/mass spectrometer (GC/MS/MS) system. GC/MS experiments in negative ion chemical ionization (NICI) and selective ion monitoring (SIM) mode were performed for the quantification of 43 nitro-PAH, while MS/MS measurements were performed to get their structural information. Comparison of MS/MS results obtained for standard mixture and emission samples showed that the most abundant nitro-PAH compounds in diesel emissions are: 1-nitronaphthalene, 2-nitronaphthalene, 3-nitrophenylan, 9-nitroanthracene, 3-nitrofluoranthene and 1-nitropyrene. Quantification of nitro-PAH confirmed that lower molecular weight (MW) nitro-PAH such as 1-, 2- nitronaphthalene, 3-nitrophenylan, 9-nitroanthracene are mostly present in the gas phase while nitro-PAH with higher MW (e.g. 3-nitrofluoranthenf and 1-nitropyrene) are more abundant in the particle phase.
3E.01
Gravimetric measurements of 2007 Diesel engine exhaust: Filter sampling.
JACOB SWANSON, David Kittelson, University of Minnesota, Minneapolis

The Environmental Protection Agency (EPA) and European Union (EU) regulate Diesel particulate matter (DPM) and specify the emission measurement methods and procedures. Prior to 2007, DPM emissions were comprised of 20-90% (by mass) elemental carbon (EC). In 2007 new rules effectively reduced EC to about 1% of the mass. The reduction in the carbonaceous fraction is somewhat offset by an increase in semi-volatile aerosol that is difficult to sample accurately at low concentrations. Using the gravimetric method to measure low mass concentrations of DPM is challenging. Problems are encountered in sampling and mass measurement, and often ineffectively dealt with or ignored. The objective of this presentation is to discuss the sampling aspect of this measurement with emphasis on the semi-volatile portion of the aerosol.

Sampling semi-volatile aerosol is influenced by parameters that do not influence the sampling of solid particles, such as adsorption of gas molecules on the filter, which often leads to an overestimation of the suspended particle mass. In addition, otherwise possibly small effects caused by low emissions levels, laboratory test procedures and filter requirements are magnified by semi-volatile aerosol, leading to irreproducibility issues when determining compliance with 2007 and 2010 DPM emissions regulations. These problems are analyzed using published data, experimental results and simple models. We discuss five factors associated with sampling DPM: dilution air quality, dilution conditions, particle pre-classifiers, filter artifacts, and face velocity. Recommendations are made to improve to reduce the uncertainty of the measurement.

A companion presentation covers analysis of filter mass measurements.

3E.02
JACOB SWANSON (1), David Kittelson (1), David Dikken (2), (1) University of Minnesota, Minneapolis (2) Measurement Technology Laboratories, Minneapolis

The Environmental Protection Agency (EPA) and European Union (EU) regulate Diesel particulate matter (DPM) emissions and specify the emission measurement methods and procedures. The 2007 DPM standard of 0.01 g/bhp-hr represents a 90% reduction of the previous standard and corresponds to roughly 100 micrograms of collected filter mass. In this presentation, we analyze factors that contribute uncertainty to filter mass measurements including the weigh room environmental conditions, filter buoyancy, balance performance (including resolution, precision, linearity, and drift), off-center loading, handling and static charge. We find that filters can be weighed with an uncertainty of about 1 microgram in a best-case scenario but a precision of 3-10 micrograms is more easily achievable and is more likely. These uncertainties are compared in detail with the total uncertainty when calculating brake specific emissions. In most cases, total uncertainty is largely due to the filter mass error. The uncertainty is also compared with the uncertainty arising from the determination of the concentration of suspended particulate matter mass emitted by clean Diesel engines. In this case, the error in filter mass is a small fraction of the total error. Recommendations are made to improve the accuracy and to reduce the uncertainty of the measurement.

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3E.03
Size Distributed Chemical Composition of Fine Particles Emitted from Burning Asian Coals. ZOHIR CHOWDHURY (1), James J. Schauer (2), Lynn G. Salmon (3), David Wagner (4), Adel F. Sarofim (4), JoAnn Lighty (4), Late Glen R. Cass (5,6), Armistead G. Russell (6) . (1) Graduate School of Public Health, San Diego State University, San Diego, CA 92182-4162 (2) Water Chemistry Program, University of Wisconsin-Madison (3) Environmental Engineering Sciences, California Institute of Technology (4) Department of Chemical Engineering, University of Utah (5) School of Earth & Atmospheric Sciences, Georgia Institute of Technology, (6) Department of Civil and Environmental Eng., Georgia Institute of Technology

Much of the energy demand in India and China is met by coal and bio fuel combustion Moreover, residential combustion of coal takes place in homes for heating or cooking purposes and is thought to contribute heavily to global or regional burdens of carbonaceous particles. In order to better quantify the fine particulate emissions for local emissions inventory, it is important to test the emissions from different Asian coals. In this study, we collect diluted exhaust emissions from the combustion of three different Asian coals in a batch underfire air grate furnace using two micro-orifice uniform deposit impactors (MOUDIs). The three Asian coals are from Meghalaya (India), Dinajpur (Bangladesh), and Datong (China). Prior to sample collection, the hot exhaust emissions were diluted in a dilution source sampler. The particle mass distributions from the three coals have a single mode that peaks at 0.18-0.32 micrometer particle aerodynamic diameter. Particles emitted from coal burning were mostly elemental carbon in nature. Organic matter was the next largest contributor. Size distributions from several trace elements (magnesium, aluminum, chloride, arsenic, bromine, cobalt, sodium, mercury, scandium, antimony, lanthanum, and samarium) were measured using instrumental neutron activation analysis. The purpose of these experiments was to examine the emissions that occur when chunks of coal, on the order of 2 inches in diameter, are burned under conditions similar to a small industrial or commercial hand-stoked furnaces. The data obtained from these source tests will prove useful in constructing and evaluating regional emission inventory and assessing source impacts on air quality.

3E.04
Effects of Metallic Additives on Oxidation Characteristics of Particulate Matters Emitted from Diesel Engine. YONGHO KIM, Donggeun Lee, Pusan National University, South Korea

In this study, oxidation characteristics of diesel particulate matters (DPM) including metallic fuel additives such as ferrocene are investigated by using Thermogravimetric analysis (TGA), transmission electron micrograph (TEM), X-ray diffraction (XRD) and etc. The dynamic TGA shows the onset temperature of ferrocene doped samples is decreased dramatically over 130℃. The activation energy is also reduced by doping the fuel additives from 185.34 kJ/mol to 100.08 kJ/mol for 25% engine load and from 219.42 kJ/mol to 117.13 kJ/mol for 50% engine load. Although the engine load effect is appeared to be weak, the samples captured at lower engine load are ignited at lower temperature than higher load samples. From the isothermal TGA results, the catalytic effect of the ferrocene is more pronounced at higher temperature range than at lower temperature range during DPM oxidation. Besides, the added ferrocene has another desirable effect to reduce the primary particle size of DPM from 36 to 26 nm for 50% engine load and from 33 to 23 nm for 25% engine load. The results of XRD reveal that the crystallite size of the DPM is also reduced. The DPMs emitted from 25% engine load condition are composed of the smallest crystallites and primary particles as well. From the chemical mapping, three kinds of Iron-containing species are distributed in particular on the surface of the DPM as forms of oxide, carbide and carbonate (Fe2O3, FeC and FeCO3).
3E.05

Diesel exhaust particles (DEPs) are a health concern because of their complex chemistry, small size, and ubiquitous presence in urban environments. A series of inhalation exposure studies were conducted to relate diesel exhaust properties to cardiopulmonary effects, immune polarization, and trans-generational effects in mice. Three diesel engines [4 cyl. 31 kW engine and air compressor (CDEP), 8 cyl. 134 kW, pickup truck engine and eddy current dynamometer (TDEP), and 1 cyl. 4.8 kW engine and generator (GDEP)] were utilized to generate diesel exhaust for whole animal exposures. During the exposures, gas/particle concentrations and particle size distributions were monitored in real-time. DEP was collected using filters, baghouses, and/or an electrostatic precipitator, and analyzed for organic and elemental carbon (OC-EC), inorganic (non-EC) elements, and organic components. Extractable organic material (EOM) amount was gravimetrically determined and further sub-fractionated with four organic solvents of increasing polarity. When the DEPs were compared between engines, PAHs in the TDEP and GDEP samples were <100 micro-gram/gram compared to >400 micro-gram/gram in the CDEP samples, but particle sizes and other chemical concentrations were with similar ranges regardless of engine and repetition of operations. Geometric mean number diameters of the different DEP samples ranged from 48-102 nm. Sulfur, chlorine, zinc, calcium, and iron were the most abundant inorganic elements, comprising <5% of the mass. OC/EC mass ratios ranged from 0.2-2.0. EOM comprised 10-40% of the DEP mass, and partitioned at 54-77% and 8-13% between the least-polar (hexane) and most-polar (methanol) solvents, respectively. Less than 2.5% of DEP mass of all DEPs was identified and quantified for single organic compounds, and 84-98% of the organics identified were alkanes or organic acids. The overall characteristics placed the three generated DEP samples between the commonly used (but dramatically different) NIST SRM2975 and Japanese (Sagai) reference samples. (This abstract does not reflect EPA policy.)

3E.06
Investigating the Effects of Biodiesel / Diesel Fuel Blends on the Performance of Diesel Particulate Filters. SUSAN KAPETANOVIC; (1), Greg Evans (2), Jim Wallace (1), (1) Department of Mechanical Engineering, University of Toronto, Ontario, Canada, (2) Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Ontario, Canada

Diesel Particulate Filters (DPFs) are an effective means of satisfying the current on-road and upcoming 2012 EPA off-road diesel engine particulate matter emission standards. The DPF under investigation in this study is a commonly encountered wall-flow monolith surface filter composed of porous honeycomb ceramic structures which have alternately blocked channel openings. The filter includes a platinum catalyst which is embedded in the ceramic material to facilitate continuous oxidation of soot / regeneration of the DPFs.

Alongside particulate matter emissions, diesel engine combustion produces undesired and unregulated nanoparticulates (<50nm). Most of this nanoparticulate matter (nano-PM) is a result of the well documented SO2 oxidation mechanism whereby SO2 found in diesel exhaust is oxidized to SO3, which then reacts with water forming sulfur acid nucleating species.

The recent sulfur-content reduction regulations of diesel fuels to 15 ppm (ULSD) have resulted in lowered lubricity properties of diesel fuel. This ULSD fuel has been observed to contribute to a greater consumption of lubricating oil which conventionally contains a greater amount of sulfur than diesel fuel.

Test results have shown that sulfate particulate emissions increase with the use of biodiesel / diesel fuel blends in comparison to traditional diesel fuel. Additionally, particle number emissions were shown to be greater with biodiesel fuel blends than with ULSD, and that this was further increased with the use of catalyzed-DFP filters at high engine loads.

The implications of these results will allow for an enhanced assessment of the impacts of biodiesel fuel blends on the sulfur content in the exhaust as well as the effects of these fuels with respect to DPFs on nano-PM formation.
3E.07
Electrostatic Removal of Diesel Particulate Matter. Ali Farnoud (1), Chenbo Huang (2), Al Armendariz (2), (1) Trinity Consultants, (2) Southern Methodist University

Diesel Particulate Matter (DPM), a probable human carcinogen, is one of the largest contributors to ambient PM pollution in urban areas around the world. Emission standards for DPM are becoming more stringent, and likely cannot be met well-into the future with only with modifications to the fuel and engine. The objective of this study was to design and construct an electrostatic precipitator (ESP) with an innovative design to capture DPM from diesel exhaust. A compact laboratory system for the generation, sampling, and analysis of diesel particulate matter was constructed to test the performance of the ESP. DPM was produced by a 4.5 kW diesel-powered electric generator and directed to the ESP through a short section of galvanized steel pipe after the muffler. Number and mass removal efficiencies were measured with a condensation particle counter (CPC) and by sampling through a stainless steel cassette and collecting the DPM on Teflon filters. Removal efficiency of the ESP was tested under two different engine load conditions: idle and medium load. The results show that the ESP provides 60-80 percent reductions in both DPM mass and number concentration with very low power consumption of 25-60 Watts.

3E.08
The Effect of Changing Gas Composition on Emission Factors Measured from the Combustion of Natural Gas in Residential Appliances. Toshifumi Hotchi, Douglas Black, Brett Singer, MELISSA LUNDEN, Lawrence Berkeley National Laboratory, Environmental Energy Technology Division, Berkeley

Current standards for natural gas in California are under review in preparation for new LNG supplies that differ in composition (e.g., lower fraction of methane, higher fraction of ethane and other non-methane hydrocarbons) and properties (e.g., higher heating value and Wobbe index). Many in-use natural gas combustion devices were designed and/or tuned for current fuel formulations, and emission from industrial, commercial, and residential appliances may change as fuel composition changes. We have been conducting an investigation of pollutants emitted from common residential appliances, including ovens, ranges, furnaces, and hot water heaters. Appliances were selected to represent a significant cross section of burner technologies. Experiments to measure emission factors were conducted on both as-installed appliances in homes and selected appliances in the laboratory. The measurements focused on NOx, CO2, CO, formaldehyde, and particle number. We will present emissions measured from appliances burning as delivered line gas as well as from gas mixtures designed to test the range of compositions that may be encountered from future LNG suppliers.

A novel benchtop diesel exhaust simulator has been developed that produces a consistent engine-like exhaust over an extended period of time. Exhaust is generated using pyrolysis of syringe-fed diesel fuel in a tube furnace. This simulator can be used in place of a diesel generator to deliver aerosol and gas-phase diesel combustion products that reasonably simulate the output of a large diesel engine. Control of combustion temperatures and oxygen concentration allows emission characterization over a range of combustion conditions. This simulator can produce controlled concentrations of exhaust at a specified rate, by controlling fuel injection rate and carrier air flow, eliminating the need for dilution and reducing hazardous vapor and particle mitigation. A TSI Scanning Mobility Particle Sizer Spectrometer (SMPS) Model 3975L and a TSI Ultra-violet Aerodynamic Particle Spectrometer (UV-APS) Model 3314 were used in conjunction to measure particle size distributions from the exhausts with the simulator set to temperatures ranging from 250 degrees C to 1200 degrees C. Aerosols ranging in particle size from about .01um to 12um were collected and compared to aerosols collected from the exhaust of a Mitsubishi tractor. The emission products from these two sources were compared in terms of size, concentration and mass and found to be in reasonable agreement, although the particle concentration of the tractor exhaust decreased as a function of size relative to the benchtop source, probably due to the long sampling line used in the tractor studies. Exhausts were also collected for analysis by GC-MS and were found to be compositionally similar.

Effect of Boiler Loads on the Particle Extinction Coefficient at a Coal-Fired Power Plant with Flue Gas Desulphurization. Wen-Fu Tu(1), Jenn-Der Lin(1) and Yee-Lin Wu(2), (1) Department of Mechanical Engineering, National Chao Tung University, Hsinchu, Taiwan. (2) Department of Environmental Engineering, National Cheng Kung University, Tainan, Taiwan.

Generally, the particulate mass concentrations emitted by coal-fire power plant are measured by opacity in the continuous stack monitoring system. The stack opacity is significantly affected by the water moisture after flue gas desulphurization (FGD) by the wet scrubbing method. The purposes of this study are to investigate the effect of various boiler loads on the particle opacity after accounting for the effects of water moisture. The boiler loads are operated at the main stream flow of 42.5 to 50.2 tons/hr for full capacity of 70 tons/hr. In order to compare the empirical results with theoretical estimations, the stack opacity, particle concentration, water moisture, the particle size distribution, particle density, particle index of refraction, gaseous SO2 and NOx concentration are all measured. The empirical equation for the relationship between stack opacity and particle concentration is determined by using Lambert-Beer's law with minimum least square method. Finally, in order to illustrate the discrepancy in the empirical estimate and theoretical value of particle extinction, theoretical particle coefficient is analyzed with the Mie theory by the computational BHMIE program and compared to the experimental value. The results will provide useful information for investigation on the coal-fire power plant with wet scrubbing FGD.
Pilot-scale experiments were conducted in a pulverized coal combustor at the Energy and Environmental Research Center (EERC) burning a Powder River Basin (PRB) subbituminous coal. A Scanning Mobility Particle Sizer (SMPS) and an Electrical Low Pressure Impactor (ELPI) were used in combination to measure the particle size distributions (PSDs) in the range of 10 nm to 10 um at both the inlet and outlet of the Electrostatic Precipitator (ESP). At the ESP inlet, high number concentrations of ultrafine particles were observed with the mode around 75 nm. The mass concentrations at the ESP inlet followed a bimodal distribution with one mode at 90-200 nm and the other at 10 um. The collection efficiency of the ultrafine particles of the ESP decreased dramatically as particle size decreased below 55 nm. Injection of nanoparticle sorbents for capture of toxic metals in the flue gas caused high penetration of the ultrafine particles through the ESP. Insufficient or partial charging of the ultrafine particles caused the decrease in their collection efficiency. The conventional ESP was modified to enhance charging using soft X-ray irradiation. A slipstream of flue gas was introduced from the pilot-scale facility and passed through this modified ESP. At moderate electrode voltages (-8.5 kV), the soft X-ray significantly enhanced particle charging and collection efficiency. Increasing the voltage to -10 kV also resulted in much higher particle removal.

Recent introduction of condensation particle counters (CPCs) utilizing water as the working fluid has given researchers an alternative to the traditional butanol based CPCs. Consistency in performance has been verified, but only with very limited aerosol compositions in controlled laboratory settings. This work compares the performance of multiple CPC models operating with both water and butanol when used in a Scanning Mobility Particle Sizer (SMPS) configuration. A total of 5 CPCs are compared, TSI models 3786, 3782, 3010, 3025, and 3775. Two of which operate with water as the working fluid. Instruments with similar lower size limits are compared by examining aerosols that have significant concentrations near the instrument's fifty percent counting efficiency point. The test aerosol is generated by a turbo charged, direct injection, passenger sized diesel engine running at constant speed and load. A two stage micro-dilution system is employed to keep aerosol concentrations within the acceptable limits of the instrumentation. Both low sulfur diesel and neat biodiesel are used as test fuels to illustrate performance consistency. The tests are executed using a single SMPS platform and switching CPCs for each set of tests. In addition, the tests are repeated with long and nano DMA columns. To ensure constant aerosol generation, engine and dilution conditions are closely monitored and an Engine Exhaust Particle Sizer (EEPS) is used to continuously monitor the particulate matter in the exhaust.
4D.03
Particle Emissions of Small Non-Road Engines Fueled by Ethanol Blends. TERESA L. BARONE, John M. Storey, Brian H. West, John F. Thomas, Tim J. Theiss, Oak Ridge National Laboratory, Fuels, Engines and Emissions Research Center, Knoxville, TN

Approximately one third of U.S. gasoline contains up to 10% ethanol. Increasing the fraction of ethanol in fuel has been suggested as a strategy to meet the President's plan to reduce gasoline consumption by 20% in 10 years. The effect of low-level ethanol blends on the performance of small non-road engines is of interest to the U.S. Department of Energy. This is because ethanol fuel blends may elevate engine operating temperature, and because the effect on emissions is unknown.

In this work, particulate emissions were characterized for one field-aged and three new portable power generators (5.5 - 25 hp). The generators were fueled by gasoline (E0), and gasoline blended with 10% (E10) and 20% ethanol (E20). Particle mass, total number concentration, and number-size distributions were compared for gasoline and the low-level ethanol blends. For the field-aged device at manufacturer rated load, the total particle number concentration was reduced by approximately one order of magnitude with E10 and E20. In addition for two of the three new generators, the total particle number concentration substantially decreased with increasing ethanol blend content.

With E0, the particle number size distribution for the field-aged generator shows a sharp peak near 15 nm at rated load. Its number size distributions did not change significantly for various speeds and loads. With E10 and E20, the number size distributions of the field-aged generator were broader and changed shape for varying speeds and loads; the geometric mean diameter ranged from 9 to 28 nm. Weighting factors based on typical usage of a speed and load condition were applied to calculate an overall geometric mean diameter. The weighted geometric mean diameter for three of the four generators increased with E10 and E20. The weighted total particle mass based on filter samples, decreased with E10 and E20 for two of the generators.

4D.04
Fine Particle Emissions From Engines Operating on Biodiesel Derived From Different Feedstocks. MARISSA MIRACOLO (1), Eric Lipsky (2), Frederik Betz (1), David Archer (1), Allen Robinson (1), (1) Carnegie Mellon University, (2) Penn State Greater Allegheny

In recent years, there has been a surge of interest in biofuels due to concerns about climate change, air quality, and energy security. Widespread adoption of biofuels may have significant, but unforeseen, environmental consequences. One concern is the impact on urban and regional air quality. The problem is that changing fuels inevitably changes emissions. It is important to assess the potential impacts of the introduction of biofuels into the transportation fleet before widespread adoption of these fuels.

This research characterizes emissions from diesel engines operating on either pure biodiesel (B100) or standard petroleum based diesel. Separate testing was done with biodiesel fuels derived from soy- and animal-based feedstocks. Testing was performed on 4.5 kW diesel engine and a grid-connected 30 kW diesel generator operating at three different loads (50, 75, 100%). Emissions of CO, NOx, and unburned hydrocarbons were measured. Fine particle emissions were measured using a dilution sampler to account for changes in gas-particle partitioning as the exhaust is cooled. Physical and chemical composition of particulate matter emissions were characterized using an SMPS and a quadrupole AMS. PM2.5 filter samples were collected to determine particle mass organic and elemental carbon emission factors.

Preliminary results show reductions in PM2.5 mass emission for operation with both biodiesel fuels, with greater reductions demonstrated for animal-based biodiesel. Biodiesel reduces concentrations of particles greater than 50 nm and reduces accumulation mode number and volume concentrations. Particulate matter emitted from biodiesel combustion contains less elemental carbon and more volatile organic carbon than standard diesel exhaust. Emissions of compounds such as benzene, chlorobenzene, and chloroform are lower in biodiesel exhaust. The use of biodiesel fuel is shown to have the potential to reduce emissions of pollutants that affect human health and air quality.
6D.01
Characterizing PM10 emission profiles for various kinds of coal-fired power plants. Y. Yue, Q. Song*, S. Q. Li, Q. Yao, Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing, 100084, CHINA

In China mainland, the PM emission from coal-fired plants is totally 3.81 million ton per year, which accounts for 44.6% of total amounts. In this work, a comparative studies on characterizing PM10 and trace elements from various representative plants, e.g., pulverized coal boiler (PCB), circulating fluidized bed boiler (CFB), coal-water mixture fired boiler (CWM) and chain-grate stoker boiler (CGB) were conducted. A distinct peak in range of 1-10 um of particle size distributions (PSD), known as the coarse mode that forms the particulate matters, was confirmed for all different plants. In the PCB and CWM, this peak is steep and occurs at 9 um, however, it becomes flat in a wide range of 4-10 um as far as CFB is concerned. The PM10 emissions, in a term of the mass concentration of PM10 to that of total fly ashes, increase from PCB/CMW, to CFB and then to CGB. Remarkably, the ratio of PM1/PM10 in CFB is only half of that in PCB. The explanation for all that was given in the last part.

6D.02
Modelling residence time distribution of oxidising soot particles in a laminar flow reactor. MANISH SHRIVASTAVA(1,2), Ashok Gidwani (3), Heejung Ju (1,2) , (1) Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, CA 92521 (2) Department of Mechanical Engineering, University of California, Riverside, CA 92521 (3) CFD Research Corporation, 215 Wynn Drive, Huntsville, AL 35805

This talk describes the simulation of high temperature soot oxidation in a laminar flow reactor using research version of Computational Fluid Dynamics software CFD-ACE+. The kinetics of freshly generated size-selected soot particles were measured using tandem differential mobility analyser (TDMA) by Higgins et al. (2002). Monodisperse soot particles from ethylene diffusion flame were oxidised in a tube reactor over the temperature range 800C-1100C. Size distribution of particles coming out of the tube reactor was measured using a second DMA. Particle size distribution spread over smaller sizes as monodisperse soot particles oxidised to form smaller particles. In addition, convective diffusive transport of particles in the tube reactor combined with changing diffusivities of particles due to oxidation and size reduction caused a distribution of residence time profiles of particles.

We modelled the residence time distribution of oxidised soot particles within the flow reactor incorporating effects of fluid drag, Brownian diffusion, thermophoresis, and particle size reduction due to surface oxidation. The temperature and flow field within the reactor were solved using the Eulerian finite volume approach in CFD-ACE+. Effects of buoyancy causing flow recirculation were also incorporated using Boussinesq approximation. Particles were introduced with the spray module in CFD-ACE+ and tracked using the Lagrangian approach. Brownian diffusion of particles was verified against the Einstein's equation. We modified the research version of CFD-ACE+ to model reduction in particle size due to oxidation using the size-dependent kinetic parameters derived by Higgins et al. (2002). Simulation results were evaluated qualitatively and quantitatively against experimental data. This analysis enables us to better understand the effects of each of the parameters: Brownian diffusion, soot oxidation and thermophoresis, on evolution of particle size distribution within the reactor. Knowledge gained from this analysis is valuable to design better flow reactors through control of residence time and diffusion and thermophoretic effects with respect to convective transport of particles.
6D.03  
**Comparison of Emissions from Back Up Generators Operating on different Fuels.** Varalakshmi Jayaram (1,2), Aniket A Sawant (3), Sandip D Shah (4), Kent C Johnson (1,2), J. Wayne Miller (1,2), David R Cocker III (1,2), (1) University of California, Riverside, (2) CE-CERT, Riverside, (3) Currently at Johnson Matthey, Philadelphia, (4) Currently at Ford Motor Company, Detroit

Back Up Generators (BUGs) fall under the class of stationary heavy duty diesel engines. Emissions from these sources are of great concern since they are generally located in highly populated areas. This research focuses on the effect of fuels on the emissions from BUGs. Several different fuels ultra low sulfur diesel, 10% ethanol, lubrizol, JP8, yellow grease A, yellow grease B were tested on a series of BUGs. Each of these BUGs were tested using UCR/CE-CERT’s Mobile Emissions Laboratory (MEL) which consists of a full-scale primary dilution tunnel with direct exhaust hookup and CFR-quality secondary dilution system for integrated species collection as well as real-time instrumentation. The tests were performed based on the ISO 8178 type D2 5-mode steady state cycle. Criteria pollutants nitrogen oxides, carbon monoxide and particulate matter were measured. Also speciated PM (elemental and organic carbon) and carbonyls were sampled. A comparison of each of these species across different fuels is presented.

6D.04  
**Ammonia Emission from Forest Prescribed Burning: Contribution from Wildland Fuels and Soil.** L.-W. ANTONY CHEN (1), Judith C. Chow (1), John G. Watson (1), Paul Verburg (2), (1) Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, (2) Division of Earth and Ecosystem Sciences, Desert Research Institute, Reno, NV

Secondary ammonium sulfate and nitrate aerosols represent a major challenge for many states to comply with the Regional Haze Rule. Much effort has been made to reduce emissions of precursor gases sulfur dioxide (SO2) and nitrogen oxides (NOx) from point and mobile sources as criteria pollutants, but effect of these controls on regional haze cannot be accurately assessed without an understanding of ammonia (NH3) availability in the atmosphere. Biomass burning may account to ~20% of global NH3 emission. Forest biomes and natural soil are important reservoirs of nitrogen (N), which can be mobilized into the atmosphere, mostly in the form of NOx and NH3, through wildfires and/or prescribed burning. The change in NOx/NH3 ratio due to burning conditions (e.g., temperature and moisture) should be investigated for forest fuels alone as well as with natural soil (organic layer) underneath. Not only is this important for the development of NH3 emission inventory, it may also impact the decisions regarding the use of prescribed burning for forest fuel management, e.g., more intense and centralized pile burns versus moderate underburns with prolonged smoldering combustion.

A laboratory combustion chamber has been constructed to simulate open burning conditions including wildland fuels and soil from the Lake Tahoe Basin. Smokes are conducted into a dilution tunnel and analyzed for N components in both gaseous (NOx, NOy, NH3) and particulate phase (nitrate and organic N). Fuel and soil moisture and N content are determined before and after burns to determine the N loss and the degree of conversion to NH3 as a function of fuel/soil conditions. This experiment is coordinated with the prescribed burning activities in the Lake Tahoe Basin during spring through fall, 2008. Results of NH3 emission factors and implications of prescribed burning on NH3 emission and deposition in the Lake Tahoe Basin will be discussed.
Combustion-Based Parameterizations of Biofuel Emissions.
Christoph A. Roden, Yanju Chen, Yue Fong Abel Lau, and
TAMI C. BOND, University of Illinois at Urbana-Champaign

Burning of traditional biofuel is one of the largest contributors to primary organic aerosol worldwide. Aerosol emissions from these sources are highly variable, resulting in a wide range of aerosol composition and optical properties depending not only on the fuel, but also the manner of burning. We present some steps toward constraining biofuel emissions by parameterizing them in terms of observable variables such as wood size, wood type, heating rate, and temperature.

We generate laboratory aerosol using a controlled combustor at different temperatures, with flaming combustion encouraged or suppressed. We use these experiments to bound the emission properties and quantities, and to identify the variables that govern those properties. Emitted particles are measured with real-time measurements of absorption, scattering, and particle size. Simultaneous measurements of carbon monoxide and carbon dioxide allow calculation of instantaneous emission factors. Bulk samples of smoldering aerosol are taken for organic and elemental carbon measurements, and are extracted for UV-Visible spectroscopy. Temperature and residence time within the wood make the biggest difference to increased absorption by organic carbon. Samples are extracted more effectively with methanol or acetone than with water or hexane. The additional carbon extracted by the semi-polar solvent also absorbs more light than the remaining carbon.

Finally, we compare the real-time optical data between controlled combustion, laboratory tests of simulated cooking with wood, and real, in-use combustion by cooking stoves. While controlled combustion spans the range of emission factors observed for in-use cookstoves, the simulated cooking tests do not. Simulated cooking tests should include fuel of larger diameter with higher pitch content to make emission factors and properties more representative.
3F.01
Quantitative Analysis and Design of Spray Inhaler Mouthpieces Based on a Concurrent CFD and Experimental Approach. P. WORTH LONGEST and Michael Hindle, Virginia Commonwealth University

Current development and design of mouthpieces (MPs) for spray inhaler systems relies heavily on trial-and-error based empirical testing. In contrast, implementation of concurrent CFD and in vitro analyses can be used to better relate design variables, transport characteristics, and MP performance. In this study, concurrent CFD and in vitro testing is used to establish quantitative correlations that relate transport characteristics arising in a spray inhaler system compared with MP performance criteria. The developed quantitative correlations are then used to optimize MP performance. As a model system, a handheld capillary aerosol generation (CAG) spray inhaler is considered. Results indicate that highly predictive correlations can be established between transport characteristics, such as turbulence intensity, and aerosol deposition in the MP. These correlations are then implemented to quantitatively guide modifications that include changes to the MP geometry and flow pathways of dilution air. In vitro and CFD evaluations of the modified design indicate that MP deposition can be reduced by up to an order of magnitude based on simple geometric changes of the inhaler system. Moreover, performance results of the modified MP are in good agreement with predictions from the developed correlations. As a result, quantitative analysis and design of spray inhalers based on concurrent CFD and in vitro analyses is shown to be a highly effective approach to control and engineer MP performance.

3F.02
Comparison of Different Aerosolization Methods for Inhalatory Delivery of Nano-sized Drug Carriers. SATYANARAYANAN SESHADRI, Taewon Han, Olga Garbuzenko, Tamara Minko, and Gediminas Mainelis, Rutgers University, New Brunswick, NJ

Treatment of lung diseases such as lung cancer could be enhanced by using inhalatory delivery of drugs which can potentially enhance retention of active ingredients by the lung cells and minimize adverse side effects. Delivery of drugs into the lungs could be achieved using nanoscale carriers such as liposomes, polymers, dendrimers, and nanoparticles. However, it is unclear how different aerosolization methods affect the mass and size characteristics of aerosolized drug carriers. Therefore, the present study was aimed at comparing different aerosolization methods for pulmonary delivery of nanocarriers. A single jet Collison nebulizer (BGI Inc.), a Sparging Liquid Aerosol Generator (SLAG) and an ultrasonic inhalator (Mabis Healthcare Inc.) were used to generate particles from water based suspensions of neutral and cationic liposomes, cationic liposomes bonded with SiRNA and also lung surfactant in order to identify the most suitable drug aerosolization and delivery parameters. The size distributions of the aerosolized drug carriers were obtained using a Scanning Mobility Particle Sizer (TSI Inc.).

The mean diameter of the liquid-borne neutral and cationic liposomes was 136nm and 80nm, respectively, as measured by a 90 Plus size analyzer (Brookhaven Instruments Ltd.). For neutral liposomes, the mean airborne particle diameter obtained from Collison, SLAG and ultrasonic nebulizers was 139, 120 and 326 nm, respectively, while for cationic liposomes, the sizes were 90, 94 and 346 nm. It was observed that the mechanical forces in the Collison nebulizer led to the degradation of SiRNA bonded liposomes and the surfactant. The higher mean particle sizes from the ultrasonic inhalator might have been due to formation of multiplets, but the generator did not degrade the lung surfactant. Maximum concentration of liposomes in aerosol was obtained from the ultrasonic nebulizer while SLAG provided the lowest concentration. The SLAG, however, could be used for prolonged aerosol delivery at a constant rate.

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**3F.03**

**Biodistribution and Effects of Gold Nanoparticles after Inhalation Exposure.** Suresh Kumar Balasubramanian (1), Wei-Yi Ong (2), Lanry Yung L.Y. (3), Liya E. Yu (4), (1) Environmental Science & Engineering, National University of Singapore, Singapore, (2) Anatomy & Office of Life Sciences, National University of Singapore, Singapore, (3) Chemical & Biomolecular Engineering, National University of Singapore, Singapore, (4) Environmental Science & Engineering, National University of Singapore, Singapore

Massive synthesis and applications of nanotechnologies worldwide increase potential exposure of humans to airborne nanoparticles (NPs) during production, usage and disposal processes. Systematic investigation on health effects of NPs is required to properly protect workers and public, as well as to sustain development of emerging nano-industries. In this study, 20 nm gold NPs were aerosolized and introduced into an inhalation exposure chamber. Number concentrations and size distribution of NPs in the exposure chamber were monitored throughout animal exposure experiments. Airborne NPs in the exposure chamber had an average concentration of around \(8 \times 10^6\) NPs/cm\(^3\) with a peak diameter of around 62 nm. More than 80% of the airborne NPs were smaller than 100 nm. Mice were exposed to airborne NPs in the chamber for 6 hours per day and for 15 days. To quantify accumulated gold in individual organs, fourteen organ tissues were harvested followed by quantification using microwave digestion coupled with ICP-MS analysis. Similar to previous studies using a rat model, lungs - the first entry portal of inhaled particles - showed the highest accumulation of gold NPs (155 ng Au/g), followed by tongue (56 ng Au/g) and skin (40 ng Au/g). Accumulation of gold in other organs, such as heart, demonstrate translocation of inhaled gold particles to other organs. More effects on tissue samples will be discussed.

**3F.04**

**Nanoparticle Agglomerate Dispersion in Biologically Relevant Fluids.** DAVID G. NASH, Owen R. Moss, and Brian A. Wong, The Hamner Institutes for Health Sciences, RTP, NC

Nanoparticles released into the atmosphere will likely begin to agglomerate due to their high diffusivity. The state of agglomeration upon inhalation and the potential to deagglomerate back into nanoparticles upon deposition onto biological fluids may affect the distribution and subsequent toxicity of the inhaled particles. Visualization of the deposition and deagglomeration of nanoparticles will be essential to understanding the mechanisms of toxicity of nanoparticles. A system was set up to generate agglomerates of aerosol particles. The particles, composed of zinc, were generated using zinc rods in a spark generator (Palas GFG-1000, Karlsruhe, Germany). An aging volume and tube furnace (Carbolite HST, Derbyshire, UK) were used to modify the agglomeration process. Zinc agglomerates formed at room temperature were deposited on TEM grids and exposed to either DI water or lung serum simulant. TEM images were taken before and after exposure. Initial measurements suggest that the zinc agglomerates were undergoing both dissolution of the primary particles and deagglomeration.
3F.05
Aerosolization and Characterization of Multi-Walled Carbon Nanotubes for Inhalation Studies. BEAN T. CHEN, Walter McKinney, Diane Schwegler-Berry, Vincent Castranova, David G. Frazer, NIOSH, Morgantown

Carbon nanotubes (CNTs) are among the most promising nanomaterials in the emerging industry of nanotechnology. They are being produced globally in increasing quantities because of high interest in applications resulting from their unique physicochemical, electrical, mechanical and thermal properties. However, because of their extremely small sizes (few nanometers in diameter) and remarkably large specific surface areas, concerns have been raised that these particles may present a risk to occupational workers via potential respiratory exposures during production and handling. At NIOSH, animal inhalation studies using multi-walled carbon nanotubes (MWCNT) are being conducted to determine potential toxicity. A generator was developed to produce a respirable aerosol for animal exposure. Bulk powder was placed on a diaphragm of the generator and particles were aerosolized as a result of the vibration of the diaphragm using acoustic energy generated from an audio speaker. MWCNT concentration within the exposure chamber was monitored in real time with a Data RAM to allow feedback control of the generator. Gravimetric samples were taken to determine the actual mass concentration. Particle size distribution was determined by using a MOUDI. For a target concentration of 10 mg/m³, the mean concentration determined from the gravimetric samples was 10.0 mg/m³ with a standard deviation of < 0.3 mg/m³. Based on the results from the MOUDI, the mass mode aerodynamic diameter was approximately 1.3 micron and count mode aerodynamic diameter was approximately 0.42 micron, indicating that the system is ideal for generating a respirable MWCNT aerosol for inhalation toxicological studies.

3F.06
In-vitro Selection of DNA Aptamers for (1->3)-beta-D-Glucans. SWEE YANG LOW, Jordan Peccia, Yale University

(1->3)-beta-D-glucans are non-allergenic structural cell wall components of fungi, plants, and some bacteria and have been linked with respiratory symptoms following aerosol exposure. A clear interpretation of the health impact of (1->3)-beta-D-glucans is partly limited by the high cost and uncertainties associated with current glucan quantification methods. The objective of this research is to develop DNA aptamers for the measurement of (1->3)-beta-D-glucans. Aptamers are synthetic DNA functional binding molecules that fold into unique conformations through traditional Watson-Crick base-pairing, allowing them to bind specifically to their target analyte. They can be produced in-vitro at costs 10-50 times less than antibodies, and can be readily labeled with reporter molecules for use in common assays or functionalized for immobilization onto microarrays. Through the in-vitro selection process SELEX, we have produced aptamers that are able to bind with micromolar affinity to curdlan, a linear unbranched form of (1->3)-beta-D-glucans, with dissociation constant values in the range of 1 micro-molar to 10 micro-molar. The aptamers also display high selectivity to curdlan and do not bind to chemically and structurally similar targets including the polysaccharide dextran and the monosaccharide glucose. The DNA aptamers produced here will enable the production of more cost effective, less ambiguous assays and sensors for the environmental measurement of (1->3)-beta-D-glucans.
Study of nanoparticle agglomerate dispersion in biologically relevant solutions. DAVID G. NASH, Owen Moss, Brian Wong, The Hamner Institutes for Health Sciences

Nanoparticles released into the atmosphere will likely begin to agglomerate due to their high diffusivity. The state of agglomeration upon inhalation and the potential to deagglomerate back into nanoparticles may affect the toxicity of the inhaled particles. A system was set up to generate agglomerates of aerosol particles. The particles, composed of zinc, were generated using zinc rods in a spark generator (Palas GFG-1000, Karlsruhe, Germany). An aging volume and tube furnace (Carbolite HST, Derbyshire, UK) were used to modify the agglomeration process. For the initial conditions used in this study, zinc agglomerates formed at room temperature were deposited on TEM grids and exposed to either DI water or lung serum simulant. TEM images were taken before and after exposure and suggest that de-agglomeration and dissolution are occurring. These results will be instrumental in understanding the toxic nature of nanoparticles, and have led to the development of a study where BEAS-2B cells will be exposed to nanoparticle agglomerates at an air-liquid interface and the level of cytokines such as IL-8 will be measured as an indicator of the relative toxic effect of agglomerates.

Characterization of TiO2 Nanoparticles for In Vitro Models of Toxicity. ZHICHENG WEI, Lupita D. Montoya, Rensselaer Polytechnic Institute, Troy NY

The possible health effects of nanoparticles are of increasing concern as they are being used more ubiquitously. However, little is still known about the specific mechanisms and possible effects of nanoparticles on cells and tissues. Part of the difficulty in doing rigorous research on this topic is that it is difficult to reliably characterize nanoparticles, and therefore to determine which characteristics of nanoparticles produce effects in biological systems. The aim of our study is to develop a comprehensive methodology to isolate highly characterized TiO2 nanoparticles for subsequent use in in-vitro models of toxicity and other health outcomes. An electrospray aerosol generator and an electrostatic classifier were utilized to produce monodisperse nanoparticles from a polydisperse particle source (primary particles, ranging from 3 nanometer (nm)-55.5 nm). A condensation particle counter was used to determine the size distribution of the generated aerosol. A nanoparticle surface area monitor estimated the equivalent surface area of these particles and an atomic force microscope was used to verify size and shape. Monodisperse nanoparticles (secondary particles, 5.52 nm) were collected by a midget impinger. Two collection liquids, nanopure water and 0.1M ammonium acetate, were selected as solutions potentially compatible with the chosen biological assays. The collection efficiency of the impinger was also investigated and results showed a cutoff diameter of about 6nm, below which the collection efficiency sharply decreased. The secondary nanoparticles collected in water produced a wider distribution in solution. However, the ammonium acetate buffer helped to narrow the distribution of particles compared to that of the primary particles. The geometric standard deviation for water was 1.75 and 1.30 for ammonium acetate. Once the secondary nanoparticles were generated, they were delivered into appropriate media for use in in-vitro tests of cell proliferation and viability.
Chemopreventive effect of aerosolized drugs on lung tumorigenesis in A/J mice. Huijing Fu, Ruth Chen, and Da-Ren Chen, Washington University in St. Louis

Chemoprevention is an effective approach to inhibit the development of lung cancer in high-risk group like smokers. Investigation has been carried out to find effective chemopreventive agents with lower systemic toxicities and adverse effects. Green tea is a potent inhibitor of carcinogenesis of lung. Polyphenon E (Poly E) is the recommended form of green tea for clinical chemoprevention trials and has been used in several clinical studies. Polyphenon E is a mixture of five different catechins, among which epigallocatechin gallate (EGCG) is the most abundant. Meanwhile, compared to other means of administration (intravenous, oral, or intraperitoneal), aerosol inhalation directly administering the compound to target organ could reduce the dose level, and thereby reduce systemic toxicity. For example, aerosol delivery of budesonide resulted in more than 80% inhibition of pulmonary tumor formation in female A/J mice (Lee W. Wattenberg, 1997). Aerosolized Poly E decreased lung tumor load by 59% while EGCG failed to inhibit lung carcinogenesis. (Ying Yan, 2007). At the present no experiment shows the chemopreventive performance of the components in Poly E other than EGCG. The objective of this study is to access the chemopreventive effect of Poly E without EGCG.

In this study, Poly E and Poly E without EGCG were dissolved in distilled water and ethanol solution and then atomized by a special designed atomizer. After passing through silica gel and active carbon, the resulting particles were introduced into a nose-only exposure system, custom-built for this animal exposure study. The delivery system could achieve a 12.5% drug deposition rate in mice lungs. Female A/J mice were given a single intraperitoneal dose of B(a)P. Two weeks after carcinogen treatment, mice started to receive aerosol treatment 8 minutes per day, 5 days per week for 18 weeks. Mice were sacrificed 20 weeks after exposure to B(a)P and lungs from each mouse were fixed and evaluated to obtain tumor count and tumor load. The result of this study will be present in the conference.

Estimation of Regions of Sensitivity to Smooth-Muscle Agonists Inhaled by Balb/c, B6C3F1, and AJ mice: Impact of Pulmonary Morphometry. Owen Moss (1), Michael Oldham (2), (1) The Hamner Institutes for Health Sciences, (2) University of California, Irvine.

When airway hyperresponsiveness is used as a measure of allergic asthma in patients, between-patient differences in genetically-based pulmonary morphometry can cause an overestimation of differences in underlying molecular sensitivity: -- the test for hyperresponsiveness predicts a difference in airway-cell function when the only difference is target-tissue dose (Moss and Oldham, 2006, JAMed 19(4)555-564). For the methacholine challenge, this overestimation was demonstrated with B6C3F1 and Balb/c mice -- whose airway diameters differ, respectively, by the ratio 1.6:1. The comparison was limited to typical path airway dimensions (average airway dimensions for generations 1 through 6) with the most-sensitive region being airway generations 4, 5, and 6. Our current research accounts for the dimensions of each individual airway and expands the comparison to include the AJ mouse. We compare, airway-by-airway, the change in resistance to air flow due to methacholine dose at the surface of airway smooth muscles. For 6 week old male B6C3F1, Balb/c, and AJ mice (n=3 per group), in-situ lung casts were prepared and measured for airway diameter, length, gravity angle, and branch angle. The NCRP (1997) aerosol dosimetry code was used to calculate the deposition (Xdep) in each airway for 22 particle diameters from 0.1 to 10 microns. The calculated change in resistance to air flow was based on the change in airway circumference (which was assumed to be directly proportional to the number of methacholine molecules (Xdep) that are distributed on the inner surface of the airway). For the AJ mouse we found that the diameters of the first three airway generations were similar to the B6C3F1 while generations 4 to 6 were similar to the Balb/c. For all three varieties of mice we found that the region of sensitivity was independent of whether surface dose is based on typical-path airway dimensions or individual airway dimensions.
4C.01
Do Nanoparticle Activity and Toxicity Depend upon Size?
JINGKUN JIANG (1), Gunter Oberdorster (2), Pratim Biswas (1), (1) Washington University in St. Louis, (2) University of Rochester

Nanoparticles are in the same size range (<100 nm) as ambient ultrafine particles, and lessons learned from epidemiological, clinical, and animal studies with ultrafine particles indicate that exposure to these particles is associated with and can cause significant adverse health effects. Data about the potential toxicity of some nanoparticles have been reported. However, there is still uncertainty in the current understanding of the correlation between nanoparticle physico-chemical properties and potential toxicological effects, due to the lack of (a) well controlled samples for toxicological studies, (b) the use of appropriate dose metrics, and (c) simple assays to predict in vivo toxicity. In this study, gas phase aerosol synthesis methods that allow for strict control of nanoparticle properties were used to prepare 9 different sized anatase TiO2 nanoparticles (4-195 nm). These samples were well characterized both as synthesized and as administrated. The reactive oxygen species (ROS) generating capacity of these particles was measured. An S-shaped size dependent ROS activity was established after normalization by particle surface area. In vivo experiments evaluated the pulmonary inflammatory responses in rats of these samples. Expressing the observed responses per unit of particle surface area demonstrated a similarly S-shaped inflammatory potential of different sized TiO2 nanoparticles. These data indicate that significant correlation between TiO2 nanoparticle size and toxicological potentials exists, and it is possible to predict the acute inflammatory potential in vivo with cell-free assays by using nanoparticle surface area based dose and responses metrics.

References:

4C.02
Generation of Reactive Oxygen Species by Urban Particulate Matter.
Chuautemoc Arellanes (1) Daniel Curtis (2) and SUZANNE E. PAULSON (2), (1) Now at Environ Corp. (2) Atmospheric and Oceanic Sciences Department, University of California at Los Angeles, CA

Size-segregated measurements of the generation of reactive oxygen species, specifically hydrogen peroxide (H2O2), in both the gas- and the aerosol-phase have been made at several sites around the Los Angeles Air basin. Particles were collected downstream of a virtual impactor on filters and are extracted with a small amount of an aqueous solution adjusted to a pH between 1.5 and 7.5. Measured aerosol-phase hydroperoxide levels ranged between 0.5-40 ng m-3, and are generally higher in more aged air, even when normalized to particle mass. The particle-associated H2O2 corresponds to aqueous concentrations of 10-3-10-1 M in the aerosol liquid water, several hundred times that expected from gas-liquid partitioning. These levels are well above the levels necessary to induce lung epithelial cell damage in laboratory studies and to induce oxidative stress-related physiological changes in vivo. The rate of peroxide generation by particles in aqueous solution decays with time, dropping by 90% in about four hours. The ability to generate peroxide is retained in aerosol samples collected on filters for several days, decaying by about 90% over the course of a week. Peroxide production by particles is sensitive to components in the extraction solution, including the pH and ionic strength. Dependence on these parameters is different for the coarse (> 2.5 um) and fine (< 2.5 um) size fractions. Limited measurements of the relationship between peroxide production and metal ion content reveals only modest correlations, suggesting that peroxide production is the result of more than chemical pathway.
Simulated Transport and Deposition of Ellipsoidal Fibers with Application to Human Breathing. KEVIN T. SHANLEY (1), Goodarz Ahmadi (1), Philip K. Hopke (2), and Yung-Sung Cheng (3), (1) Department of Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY (2) Department of Chemical and Biomolecular Engineering, Clarkson University, Potsdam, NY (3) Lovelace Respiratory Research Institute, Albuquerque NM

Numerous industrial applications expose human beings to a variety of airborne particulate matter not all of which are spherical in shape. Fibers in particular are known to cause serious health hazards. Fibers have a strongly anisotropic geometry causing kinematics which markedly departs from that of spheres. Commercially available codes typically include a second phase model that can handle spherical particles. However, none of the available commercial codes can handle fiber transport and deposition processes. In this study, a series of user defined functions have been developed to augment the discrete phase model of the FLUENT(TM) code enabling the tracking of ellipsoidal fibers. This augmentation expands the capabilities of an already widely tested and accepted discrete phase model. The augmented code has been applied to the real world application of fiber transport and deposition in human nose for different breathing conditions. MRI scans of the left passageway of an anonymous, adult, male, human subject have been used to construct a flow volume. Steady, laminar, inspiratory flow was used to simulate the inhalation process. Both spherical and ellipsoidal particulate matter was tracked via a Lagrangian approach. Deposition predictions agree favorably with the available experimental data.

Hybrid Modeling for Respiratory Dose Estimation of Inhaled Particles. CHONG S. KIM (1), Shu-Chieh Hu (2), Jung-II Choi (3), (1) USEPA National Health and Environmental Effects Research Laboratory, RTP, (2) IIT Research Institute, Chicago, (3) North Carolina State University, Raleigh

Accurate estimation of respiratory dose of inhaled particles is a difficult task because multiple factors intricately affect airway flow and particle transport in the lung airways. Traditionally, human data measured in vivo under controlled breathing conditions are used as a basis of dose estimation. Over many decades experimental database has been expanded for a wide range of particle size and breathing pattern, and now the size of the database, particularly total lung deposition, is sufficiently large so that empirical modeling may be achieved to the extent nearly comparable to mathematical models. On the other hand, mathematical models have been markedly improved with more realistic morphological designs and refined analytic processes of aerosol transport in the dynamic lung airways. Recent advances in CFD simulation studies have shown an opportunity of microdose analysis not only in a small segment of airways but also in the entire airway structure, thus offering an alternative or complementary approach to mathematical modeling. In the present study we attempted to link three different modeling approaches, empirical, mathematical and CFD such that for a given exposure condition deposition values may be assessed for total, regional and local airways at a desired level of details. Empirical equations of total and regional deposition were obtained using in vivo human data compiled from EPA studies. A single-path dynamic mathematical model based on Weibel's lung morphology and a 3-dimensional CFD scheme for 15-generation airway models were used for inter-comparison of models. We found a reasonable agreement among the models under a few typical breathing conditions. The linkage between models thus may provide a convenient way of assessing respiratory dose with multiple levels of resolution.
Determination of Parameters for Single-Point Particle Sampling in a Nuclear Stack. HONGSEOK KIM (1), Jae Hee Jung (1), Sang Bok Kim (1), Gak Hyeon Ha (2), Sang Soo Kim (1), (1) Korea Advanced Institute of Science and Technology, South Korea, (2) Korea Electric Power Research Institute, South Korea

Radioactive particles exhausted from nuclear stacks are dangerous materials for human. So monitoring these particles is important but sampling and analyzing these particles are difficult. In many of nuclear power plants in Korea, sampling and detecting of radioactive exhaust particles have been conducted by following ANSI/HPS 13.1-1969. But in 1999, ANSI/HPS 13.1-1999 was released and this standard states that a single-point sampling can make representative sampling if some conditions of sampling are satisfied. The conditions regulates that the location of sampling point in the nuclear stacks. The COVs (Coefficient of Variation) of gas velocities and concentrations of particles shall not exceed 20% over center region of 2/3 stack area. In this paper, we designed and made the stack that reproduces the aerodynamic characteristics of real stacks. And measuring the velocity of gas and the concentration of particles and comparing the results of concentrations for the cases of multi-point sampling and single-point sampling were performed. The velocities are measured at z=4D and z=7D, and at totally 41 points over the cross section of the stack. The COVs of the velocities are 19.79% and 11.52% respectively. The concentrations are measured by APS (3310A, TSI) and at totally 17 points over the cross section. And the COVs of concentrations are 29.4% and 16.1% at z=4D and z=7D respectively. Finally the penetration ratios of the case using shrouded probe are measured and results are 68.5% and 72.1%. So this result can satisfy the condition of ANSI/HPS 13.1-1999 which states that the penetration ratio of single-point sampling should exceed half of that of multi-point sampling. According to these results, it is confirmed that the stack we designed can reproduce the characteristics of real stacks. And single-point sampling using the shrouded probe can be a representative sampling of the particles from the stack.

Dispersal of Coarse Aerosol from Explosive Blast: Field Measurements. PETR SKREHOT (1), Michaela Havlova (2), Jan Hovorka (3), (1) Occupational Safety Research Institute, Prague (2) T-soft, Prague (3) Charles University in Prague

An explosive blast in the ambient air, besides the direct destructive impact, is also distinct source of an aerosol. Such aerosol, co-emitted or formed by explosion, may have strong impact to human health due to high aerosol concentration, biological activity or radioactivity. To measure dispersal of aerosol by explosion, we conducted series of explosive blast tests at grass-covered runway of the field airport during two seasons. Several types of explosives were employed to blow up the test quartz powder of 16.3 micrometer mass median diameter of the grain size. An aerosol cloud was formed immediately after the explosion. Then the cloud have moved over passive samplers and nefelometres (DustTrack) positioned in the Cartesian grid. The cloud size, rate of the cloud movement and the test particle concentrations were determined by this way. Both the types of detectors were localised at the breathing height above the runway. Collection efficiencies of the passive samplers for the test aerosol were determined in a closed-circulation wind tunnel using an aerodynamic particle sizer (APS 3321). The collection efficiency was in the range of 0.005-0.2 depending on wind speed of 0.2-10 ms⁻¹. The cloud rate of movement were in the range of 0.5-10 ms⁻¹ and particle mass concentration measured in distance of 60 meter from the blast center ranged from micro-grams to tens of milligrams per cubic meter. The test aerosol concentrations were strongly dependent on wind speed/direction and local air thermal instability.
5C.03
Assessment of heavy metal pollution in air and surface waters. AFRIM SYLA (1), Agron Veliu (2), Bajram Kafexholli (2), (1) University of Prishtina -Kosova, (2) NewCo Ferronikeli Complex L.L.C, Department: Laboratory

This research paper discusses about the status of some selected heavy metals (Fe, Pb, Cd, Zn, Ni, Co and Cr) in surface and ground waters that discharging in river Trepca from Lead smelter of Kosovo, using the field study data during the year 2007. As result of production process of lead-zink applied in lead smelter the following heavy metals are expected: iron, lead, cadmium, zink, nickel, cobalt and chrome. Measurements indicated the concentration of heavy metals and TSS in river and urban air.

The length of river Trepca is 14 km. It is a tributary of the river Sitnica that it joins at the West of Mitrovica. The catchments area of the river is 108.35 km². This river is running all seasons. Visually, water quality of the Trepca looks poor.

Heavy metal concentrations have been investigated for groundwater close to slag landfill site and surface water flowing close to smelter site. The concentrations of these heavy metals were then compared with the relevant guidelines value for a class II river. The results indicated that the extent of pollution of groundwater and surface water by heavy metals can be considered low.

5C.04
Association of fine particles (PM2.5) from different sources with daily mortality in Seoul, Korea. JONG-BAE HEO (1), OkHee Yi (2), BoRa Choi (1), Ho Kim (2), Seung-Muk Yi (1), 1. Department of Environmental Health, School of Public Health, Seoul National University 2. Department of Public Health, School of Public Health, Seoul National University

Environmental health problems due to fine particulate matter (PM2.5) have been raised recently as regional issues in many parts of Korea. Lacking systematic approaches in the study of PM2.5, however, its management based on scientific results is yet to be accomplished. In this study we examined the chemical constituents of PM2.5 samples collected on the ambient air monitoring site (School of Public Health building of Seoul National University) and conducted a time-series study to investigate the relationship between PM2.5 constituents and source apportionments and daily mortality in Seoul.

PM2.5 and chemical speciated samples were collected every third day from March 2003 to December 2006 using a 4-channel system consisting of Annular Denuder System (ADS) and filter packs (URG). We obtained daily count of non-accidental deaths among residents in Seoul from 2003 to 2006. We examined association of PM2.5 mass, components, and source contributions with daily counts of several mortality categories: all non-accidental, cardiovascular, and respiratory mortality. Poisson regressions incorporating LOESS were used to control for time-varying covariates.

PM2.5 mass and several constituents were associated with multiple mortality categories, especially cardiovascular deaths. For example, for a 2-day lag, the cardiovascular mortality increased by 3.1, 3.6, 3.0, 2.4, 4.7, and 3.8% for PM2.5, OC, EC, sulfate, nitrate, and ammonium based on interquartile ranges of 28.6, 6.4, 2.1, 6.0, 6.1, and 4.7 micro-gram per cubic meter, respectively. Using PMF for source apportionments, we identified nine sources including secondary nitrate, secondary sulfate, gasoline vehicle, biomass burning, diesel emission, soil, industry, incinerator and road salt, and aged sea salt. For the nine sources identified in Seoul, we found the strongest increase in daily mortality associated with diesel emission sources. The results of this study can be used for the establishment of an effective management strategy related to air quality and adverse health effects of PM2.5 in Korea.
Two Years of Data on Changes of Potential Danger to Humans of Culturable Bacteria in Atmospheric Aerosol of Southwest Siberia. ALEKSANDR S. SAFATOV (1), Irina S. Andreeva (1), Boris D. Belan (2), Galina A. Buryak (1), Elena K. Emel'yanova (1), Ruprecht Jaenicke (3), Mikhail V. Panchenko (2), Natalya I. Pechurkina (1), Larisa I. Puchkova (1), Aleksandr N. Sergeev (1), (1) Federal State Research Institution State Research Center of Virology and Biotechnology "Vector", Novosibirsk Region, Koltsovo, Russia, (2) Institute of Atmospheric Optics SB RAS, Tomsk, Russia, (3) Johannes Gutenberg - Universitat Mainz, Institut fur physik der atmosphere, Mainz, Germany

Recently the method for quantitative estimation of potential danger for human of culturable bacteria in atmospheric aerosol was presented using four groups of tests. Firstly, these bacteria must be pathogenic or potentially pathogenic for humans. Secondly, bacteria in aerosol are the more dangerous the higher the concentration of viable microorganisms and the larger the portion of bacteria pathogenic or potentially pathogenic for human they contain. Thirdly, the bacteria hazard increases when they display high resistance to unfavorable environmental factors causing their inactivation. Fourthly, when potentially pathogenic bacteria affect humans, these being drug resistance represent the greatest danger.

Bacteria potential pathogenicity was determined in vitro by erythrocyte hemolysis and plasmacoagulation reactions and other characteristics that were used for determination of potential pathogenicity integrated index. Concentrations of different bacteria determined with standard culturable method was used for determination of the second integrated index. Resistance to environmental factors was characterized by the ability of bacteria to grow at high salt concentration, the presence of various enzymatic activities such as lipolytic, phosphatase, etc., the presence of restriction nucleases, plasmid DNAs, etc. These characteristics were used for determination of the third integrated index. Drug resistance was evaluated by resistance to a number of antibiotics. These data were used for determination of the fourth integrated index. All four indexes normalized multiplication gave integrated index of potential danger for human of cultivable bacteria in atmospheric aerosol.

Carrying out experimental evaluation of bacteria characteristics, which were discovered in atmospheric aerosols samples, allows one to draw a valid conclusion about their potential danger for human.

Data on changes of four integrated indexes described above in Atmospheric Aerosol of Southwest Siberia during two years are presented. It was shown that the maximum potential danger for human had bacteria in springtime.

The work was partially supported by ISTC, project #3275.
5C.07
A Comprehensive Ambient Air Sampling and Characterization Study. JEROME GILBERRY, Shanna Ratnesar, Jason Quizon, Neal Baker, Christopher Bare, Joshua L. Santarpia, Johns Hopkins University Applied Physics Laboratory

Time-resolved characterization of the ambient aerosol background, including bio-aerosols, is important both for understanding environmental processes that affect bio-aerosols and for determining realistic test conditions for the evaluation of bio-aerosol detection systems. Current data is limited. There exist very few data-sets with the resolution to meet the testing needs of cutting-edge biological agent detection systems and test facilities or to provide an understanding of the temporal fluctuations in aerosol concentration and bio-aerosol concentration. In order to provide a more comprehensive picture of the ambient environment, a suite of air samplers has been assembled in one station. A TSI Scanning Mobility Particle Sizer (SMPS) is used to measure size distribution and concentration of submicron particles while a Grimm Portable Aerosol Spectrometer is used to measure size distribution and concentration of supermicron particles. Together, the two particle counters cover a size distribution spectrum from 0.014 to 32 um. A TSI Ultraviolet Aerodynamic Particle Sizer (UV-APS) is used to measure fluorescence intensity and can provide information on the fluorescent and possibly biological nature of the aerosol. An Air Trace slit-to-agar sampler by Biotrace is used to provide time-resolved, culturable bio-aerosol data. Microorganisms are identified based on morphology or through a range of more in-depth microbiological biochemical analysis. The data obtained from the sampling suite, once compiled and analyzed, can be used to re-create ambient conditions in a laboratory for extensive testing and evaluation of current and future aerosol detection technologies.

5C.08
Design and Characterization of a Sequential Cyclone System for the Collection of bulk PM. Ana M. Rule (1); Alison S. Geyh (1); Juan P. Ramos-Bonilla (1); Jana Mihalic (1); Jared D. Margulies (2); Jana Kesavan (3); Patrick N. Breysse (1), (1) Johns Hopkins University, Dept. of Environmental Health Sciences. (2) Goucher College. (3) Aerosol Sciences Team, RDECOM, Edgewood Chemical and Biological Center.

The National Research Council, in its 2004 publication, identified the need to better understand the relationship between toxicity and the size and composition of PM as an important research priority. Testing for toxicity and composition requires a method for the collection of bulk ambient PM. We have designed and manufactured a sequential cyclone system that collects size segregated PM at ambient concentrations.

The first stage of the system consists of a high volume PM10 inlet. We designed the second stage cyclone to have a cut point of 2.5 micrometers. The third stage is commercially available. We characterized the second and third stage cyclones at 1000 L/min with monodisperse fluorescent aerosols, using outlet filters to determine penetration efficiency.

Laboratory characterization of the cyclones resulted in a D50 cut size of 2.33 micrometers for the second stage coarse fraction cyclone, and 0.3 micrometers for the third stage fine fraction cyclone. The fine cyclone collects between 30% and 50% of particles with 0.1 micrometers in diameter.

The major limitation of this system is that cyclone technology does not allow for the collection of ultra-fine particles. Recovery of the ultrafine particles was considered in the developmental stages of the design process. However, the mass of particles smaller than 0.1 micrometers, if collected, would not have been adequate for toxicological tests and characterization evaluations. Based on published results, the cyclone system collects ~ 85% of fine PM mass >0.1 micrometers. Consequently, the design of this system allows for the collection of bulk quantities of PM in size fractions that have regulatory significance.

The system has been deployed in the field and collocated with PM10 and PM2.5 Harvard impactors. As compared to the expected mass estimated from the Harvard Impactor results, recoveries were approximately 65% for both fractions.
5C.10 Evaluation of Airborne Nanoparticle Release: A Comparison of A Conventional Fume Food and The Air-Curtain Isolated Hood. SU-JUNG TSAI*, Earl Ada(1), R.F. Huang(2), Michael J. Ellenbecker(3), *University of Massachusetts Lowell, One University Avenue, Lowell, MA  (1)Campus Materials Characterization Laboratory, University of Massachusetts Lowell, One University Avenue, Lowell, MA (2)Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, ROC (3)Toxics Use Reduction Institute, Department of Work Environment, University of Massachusetts Lowell, One University Avenue, Lowell, MA

The magnitude of airborne nanoparticle exposure would be minimized as long as the toxicity of nanoparticles is uncertain. Test results by Tsai et al. found that the handling of dry powders consisting of nano-sized particles inside laboratory fume hoods can result in a significant release of airborne nanoparticles from the fume hood into the laboratory environment and the researcher's breathing zone. The turbulent airflow formed in the worker wake region interacts with the vortex in the conventional fume hood; this can cause nanoparticles to be carried out with the circulating airflow. An evaluation was performed to examine the performance of the newly-designed air curtain isolated hood (developed by Huang et al.) compared to the conventional hood. The air curtain hood induces a push-pull air curtain on the face of the hood. The air curtain is generated by a narrow planar jet issued from the double-layered sash and a suction slot located on the floor of the hood just behind the doorsill.

Experiments were performed to measure airborne particle concentration while handling nanoalumina particles in these two hoods. The handling tasks were performed by transferring and pouring nanoparticles from beaker to beaker. A TSI Fast Mobility Particle Sizer (FMPS) was used to measure airborne particle concentration from 5 nm to 560 nm. Air samples were also collected and characterized. Measurement locations were the room background, the researcher's breathing zone, and the handling location inside the hood. Room airborne particle concentration increases of greater than 2,000 particle/cm³ were measured when handling nanoparticles in the conventional fume hood, while a concentration increase was barely identified when using the air-curtain hood. The particle concentration increase peaked at 200 nm, due to the presence of agglomerated nanoalumina particles. Complete results of the evaluation will be given and fully discussed in the presentation.

5C.11 Occupational Monitoring of Carbonaceous Nanomaterials. DOUGLAS E EVANS, M. Eileen Birch, Bon Ki Ku and Toni Ruda-Eberenz, The National Institute for Occupational Safety and Health Division of Applied Research and Technology Cincinnati OH

Carbon nanotubes and nanofibers (CNTs/CNFs) are one of the most mass-produced engineered nanomaterials. Annual global production of CNTs is over 100,000 tons; CNF production and use are increasing at a similar pace. Industrial, high volume production of CNTs/CNFs presents the potential for worker exposure, especially for those who handle these materials. Carbon nanotubes and nanofibers may be especially toxic when inhaled because of their fibrous structure, composition, and insolubility. Workplace investigations to evaluate potential exposures are important because the toxicological properties of CNTs/CNFs are not yet understood, manufacturing processes are rapidly changing, and exposure data are lacking.

Recent studies were conducted at a facility that produces and processes CNFs. Different areas of the facility were monitored for particulate carbon [1]. In addition, air samples for analysis by transmission electron microscopy were collected, and multiple, direct-reading instruments were used for on-site monitoring. Contamination of workplace air by CNFs and manufacturing byproducts was found throughout the facility. Approaches, results and findings from these studies will be presented.


Disclaimer: The findings and conclusions in this abstract have not been formally disseminated by the National Institute for Occupational Safety and Health and should not be construed to represent any agency determination or policy.
5C.12
Wind tunnel and Numerical Simulations of the Fate of Nanoparticles Released into a Work Environment.

NICHOLAS STANLEY (1), David Y.H. Pui (1), Thomas Kuehn (1), Christof Asbach (2), Thomas Kuhlbusch (2), Heinz Fissan (2), (1) Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA (2) Institute of Energy and Environmental Technology, Duisburg, Germany

Nanoparticle toxicity has become a major issue in recent years as the potential for human exposure has risen. A leak in nanoparticle production equipment can cause large quantities of nanoparticles to be emitted into a work environment. These nanoparticles can cause adverse health affects, and toxicologists have proposed using nanoparticle surface area as a health relevant measure to assess worker exposure. However particle properties can change as these particles traverse from the leak and undergo physical and chemical reactions. The particle properties need to be examined by looking at changes in chemical composition, particle morphology, and number and surface area concentrations.

Nanoparticles of different materials are injected through an experimentally simulated leak into an ASHRAE 52.2 - 1999 classified wind tunnel. Measurements are then taken with various instruments to determine the fate of the injected nanoparticles. Lung deposited surface area is measured using an NSAM and size distribution is measured with an SMPS. Particle morphology and chemical composition are determined using TEM analysis after sampling. By adjusting the experimental parameters (such as particle material, particle concentration, and pressure drop across the leak) the effect of various conditions on the fate of nanoparticles can be studied. However measurements can only be taken at discrete locations throughout the wind tunnel, so a numerical simulation must be used to show a more in depth look at the fate of these nanoparticles and to allow predictions for other practical situations.

Results from initial experimentation and modeling will be presented including: velocity measurements, dispersion tests, burner classification, and initial burner injection tests.

This project is sponsored by NSF G2006-Star-F2 (Fate/Transport). The financial support is gratefully acknowledged.

5C.13
Cumulative Growth of Mainstream Tobacco Smoke In the Human Lung.

CONOR McGRATH, Colin Dickens, John McAughey, British American Tobacco

Tobacco smoke is a complex and dynamic matrix consisting of gaseous compounds and particulate material. Smoke particles are sub-micron (150-250 nm) and are present in high concentrations (up to 109 particles/cc). Despite the small diameter of the smoke particles, deposition efficiencies of 60 - 80% in the airways have been reported where deposition efficiencies of 20-30% might be expected from ICRP & NCRP models. Smoke particles in the respiratory tract may grow by coagulation, condensation and hygroscopic growth and the aerosol may exhibit cloud properties. The particles may also shrink by evaporative losses of semi-volatile soluble species. We report measured cumulative growth factors for cigarette smoke in the human lung by direct measurement of exhaled smoke and by replicating measured smoking behaviour parameters to measure inhaled smoke.

Particle size was measured by fast electrical mobility spectrometry at 10 Hz resolution. Particle size measurements for exhaled smoke in seven volunteer subjects smoking 3 different products were conducted in triplicate, in real-time, via an open-tube sampling system. Inhaled particle size was measured by re-smoking cigarettes, in triplicate, at 12.5 Hz resolution, to the measured smoking profiles from the triplicate exhaled smoke experiments, using a Smoking Cycle Simulator with fast electrical mobility spectrometry.

Inhaled and exhaled particle diameters ranged from 138-180 nm to 215-275 nm count median diameter (CMD) respectively, with an average growth factor of 1.56 (1.36-1.92). Growth factors for each individual were more consistent than between volunteers. Analysis of the time-resolved exhaled measurements showed no significant difference in exhaled diameter with inhaled depth, implying all growth processes were complete in the course of the breathing cycle. It was noted that 95% of all inhaled or exhaled particles were < 500 nm CMD implying all deposition behaviour will be driven by Brownian Motion.
5C.14
Comparison of Particle Size Distribution in the Mainstream Smoke Aerosols of the Narghile Waterpipe and Cigarette.
ALAN SHIHADHEH, Hiba Sheheitli, Nancy Daher, American University of Beirut

Prompted by the global resurgence of the narghile waterpipe (WP) as a tobacco smoking device, recently conducted studies (Shihadeh and Saleh, 2005; Sepetjian et al, 2007) have found that WP smoke contains large quantities of lung carcinogens, nicotine, tar, aldehydes, and CO. For example, a typical 1-hour smoking bout using a popular flavored tobacco mix has been found to deliver approximately 50 times the carcinogenic PAH as a single cigarette.

While the large quantities of carcinogens indicate the potential for negative health consequences, lung dosimetry assessment is hampered by the lack of information on the particle size distribution. Due to differing combustion conditions, residence times, and varying transport phenomena in the WP, there are strong theoretical grounds for why the particle size distribution could significantly differ from that of cigarette smoke. The aim of the current study was to measure and compare the particle size distribution of the WP and a common cigarette brand.

Mainstream smoke particles were sized using a QCM cascade impactor, equipped with a sliding valve dilution sampler. The effective dilution ratio was estimated at 83, with a residence time prior to dilution of less than 0.5 seconds. Because WP smoke exhibits high volatility in ambient air, the dilution stream was generated from HEPA-filtered mainstream WP smoke vapors.

It was found that the WP aerosol was largely composed of sub-micron particles, with a greater MMAD (0.55 versus 0.33 micrometer), and greater per-puff delivery of respirable PM (0.74 versus 0.21 mg/puff) than cigarette smoke. The measured cigarette smoke MMAD was consistent with previous studies (e.g. Chang et al, 1985). According to the ICRP deposition model, circa 10% of the inhaled WP aerosol will deposit in the alveoli, indicating that WP smoking is likely associated with significant exposure of carcinogens to sensitive regions of the human lung.

5C.15
Tobacco Smoke Delivery System for Respiratory Research.
Vladimir B. Mikheev (1), Alec K. Hitchman (1), Bruce R. Westerberg (1), David J. Hesse (2), (1) Battelle Toxicology Northwest, Richland, WA (2) Battelle, Columbus, OH

Testing of the tobacco products under wide range of smoke concentration requires simultaneous maintaining stable constituents concentration, stable critical ratios (such as CO/WTPM, CO/nicotine, etc), and stable environmental conditions (such as relative humidity and temperature).

Most of the currently used tobacco smoke exposure systems have some limitations, such as:

a) Widening of the smoke concentration range may lead to constituents ratios instability,
b) Loss of Wet Total Particulate Matter (WTPM) is often observed during the smoke delivery,
c) Control of environmental parameters (such as temperature and relative humidity) needs to be more accurate.

Redesign and test of some of the key components of the tobacco smoke exposure system (such as smoke mixing-dilution-delivery system, temperature and relative humidity control) is required in order to improve system performance.

CFD simulations along with experiments were conducted in order to investigate how different smoke mixing-dilution-delivery configurations may affect overall smoke exposure system performance.

Acknowledgement: This work was supported by Internal Battelle R&D funding.

This study in was conducted in 11 U.S. retail pharmacies to assess the potential health risks for pharmacy staff and customers arising from airborne pill dust generated by robotic dispensing machines. Aerosol particle count and mass measurements were taken in pharmacies employing the two most commonly found pharmacy robots and compared to measurements taken in a pharmacy that manually filled prescriptions.

The study was suggested by the fact that some robots use compressed air and/or vacuum (differential) pressure to dispense prescriptions in a retail pharmacy (Parata RDS Robotic Dispensing System). The dust was subjected to re-aerosolization using a TSI 3034 Small Scale Powder Dispenser. A TSI 3321 aerodynamic particle sizer (APS) and a TSI 3034 scanning mobility particle sizer (SMPS) were then used to measure the particle size distribution. These instruments showed that the dust contained a substantial population of particles less than 0.5 micron in diameter and a large mass fraction of particles in the size range less than 2.5 microns (PM-2.5 particles). The log-normalized particle size distribution had a mass median diameter of 2.82 microns and a geometric standard deviation of 1.65 microns.

The most common particle size (modal particle size) found was 0.626 microns. 94.4% of the particles by number (61% of the particle mass) in the respirable size range (less than 10 microns) were PM-2.5. It is widely accepted that PM-2.5 particles present health risks because they penetrate the lungs deeply and are rapidly absorbed by the bloodstream. Such particles are also believed to contribute to cardiac events such as increased heart rate variability and triggering of myocardial infarction (heart attacks). This dust was chemically analyzed using high-performance liquid chromatography/mass spectroscopy (HPLC/MS) and shown to contain active pharmaceutical compounds including Acetaminophen (analgesic), Levofloxacin (Fluoroquinolone antibiotic), Mirtazapine (antidepressant), Methocarbamol (muscle relaxer), Carisoprodol (muscle relaxer), Loratadine (anti-allergy drug), Diazepam, and Valacyclovir (antiviral). Analysis of drug mixtures containing excipients and environmental dust is a complex procedure. Undoubtedly, other compounds were present in the dust that were not extracted using the particular method chosen for this screening.

The effect of nanoparticles on human health is not well understood and is a rapidly emerging research topic. It has been shown that nanoparticles can pass directly into the bloodstream from the lungs, then directly into individual cells of the body. Nanoparticles are implicated in blood clotting, and are suspected of causing carotid artery thrombosis. Subsequently, 24-hr sampling was conducted at all eleven pharmacies for aerosol particles between 0.2 microns (200 nm) and 20 microns to see if respirable particles could be attributed to robotic and/or manual dispensing. The results of this sampling showed spikes in respirable particles compared to measurements taken in pharmacies that manually filled prescriptions.

Airflow and Particle Deposition in Airway Models of the Combined Human Nasal-Oral-Tracheobronchial Regions. ZHE ZHANG, Clement Kleinstreuer, North Carolina State University

In this study, inhalation and deposition of both micron- and nano-size particles are numerically simulated for a combined human upper airway model, including the interconnected nasal cavities, oral airway, and the first four generations of asymmetric tracheobronchial airways. Using a commercial finite-volume software with user-supplied programs and an in-house, parallelized particle trajectory code as solvers, validated solution approaches, i.e., Euler-Euler (for nanoparticles) and Euler-Lagrange (for micron particles), are employed with a low-Reynolds-number k-omega model for laminar-to-turbulent airflow transition. Validated computational results are obtained in terms of airflow structures as well as particle distributions and deposition patterns, deposition fractions, efficiencies, and deposition enhancement factors. Effects of human breathing patterns, i.e., oral breathing, nasal breathing, and simultaneous nasal and oral breathing, on airflow and particle deposition are discussed as well. This study may provide useful information for both health assessments of inhaled toxic particulate matter as well as optimal drug aerosol delivery via inhalation.
Development of a CFD Model to Simulate the Effects of Aerosol Number Density and Hydrodynamic Interactions on Deposition. P. Worth Longest (1), Guoguang Su (1), Michael J. Oldham (2), (1) Virginia Commonwealth University and (2) PM USA Research Center

At high number concentrations, significant hydrodynamic interactions can occur between aerosol particles or droplets. The net effect of these hydrodynamic interactions may be a reduction in aerosol drag or an increase in particle mobility compared with individual particles of the same size. As a result, the net settling velocity and deposition by impaction may increase for high concentrations of aerosols, i.e., the aerosol cloud effect. A classic example of this effect is cigarette smoke deposition in the upper respiratory tract. Cigarette smoke particles (CSPs) are known to have a MMAD in the range of 0.3 to 0.7 micrometers. However, these submicrometer aerosols occur at high concentrations in mainstream smoke and deposit like much larger aerosols in the upper airways. The objective of this study is to develop a framework for a CFD model that can simulate the effects of concentration dependent hydrodynamic interactions on the transport and deposition of submicrometer aerosols in the respiratory tract. The effects of particle concentration density on deposition will be evaluated in a representative model of the mouth-throat geometry on a local and regional basis. Deposition will be presented as a function of submicrometer aerosol concentration, with number density values ranging from $1 \times 10^5$ to $1 \times 10^9$ particles per cubic centimeter. Finally, predicted mouth-throat deposition will be compared with in vitro deposition values of CSPs available in the literature. These findings will have a significant impact on predicting the transport and deposition of high concentration aerosols, like mainstream CSPs, in the respiratory tract.

A Sampling System for Rapid Measurement of Regional Lung Deposition. Kuan-Nan Chang (1), Sheng-Hsiu Huang (1), Yu-Mei Kuo (2), Chih-Chieh Chen (1), (1) National Taiwan University, (2) Chung Hwa University of Medical Technology

The serial bolus delivery method was commonly used to measure the regional deposition of inhaled particles in the human respiratory tract. This technique is versatile and can provide important data, such as fraction of lung deposition and morphological dimension of the airways. However, the process is time-consuming because only one aerosol size and regional deposition rate can be measured each time. Therefore, the principal objective of this study was to develop a sampling system for rapid measurement of regional lung deposition.

The main sampling train consisted of a mouthpiece, a flow meter, and a particle counter. The mouthpiece was attached to the pneumotachograph in line with a minimum dead space. In the present study, condensation particle counters (CPC) were used to measure the number concentrations of particle with diameter less than 1 micro-meter. During respiration, the aerosol was sampled continuously into a CPC via the sidearm port attached to the mouthpiece. By using the TSI AIM software (Aerosol Instrument Manager Software), the CPCs can measure particle number concentration at a frequency of 10 Hz. In order to optimize the experimental system, combinations of three different models of TSI CPC (Model 3010, 3022A, and 3025A) with three pneumotachograph flow meters (Fleish No1, 0, and 00) were compared for response time and flow rate fluctuation at different pressure drop conditions. Moreover, a homemade cylinder-piston breathing machine, which can be adjusted for breathing flow patterns (breathing frequency and tidal volume), was used to generate a series of 'standard' breathing patterns.

The results showed that under the high flow mode (1.0 L/min for CPC3010; 1.5 L/min for 3022A and 3025A), the response time (0-95%) was ~1 s, 3.7 s, and 10 s for 3025A, 3010, and 3022A, respectively. The sampling train has a maximum volume of 23 cm$^3$ when equipped with No. 1 pneumotachograph and caused a ~1 s lag for CPC 3025A to respond. Furthermore, during the breathing cycle, the change of pressure drop in the sampling train caused the flow rate of the CPC to fluctuate. When the static pressure changed from 0 to -0.35 inch H$_2$O in 2.5 s (tidal volume of 500ml, breathing frequency of 12 breath/min), the flow rate fluctuation of CPC 3025A was within +/- 10%.
Transport and Deposition of Ellipsoidal Fiber in Human Tracheobronchial Tree with a Multi-level Bifurcation Computational Model. Lin TIAN (1), Goodarz Ahmadi (1), Philip K. Hopke (1) and Sung-Yung Cheng (2), (1) Clarkson University, Potsdam (2) Lovelace Respiratory Research Institute, Albuquerque

Transport and deposition of ellipsoidal fibers in the upper tracheobronchial tree were analyzed using a multi-level asymmetric lung bifurcation model. The first three generations (G0-G3) of tracheobronchial tree were included in the model study and asymmetric lung bifurcation models were considered. The laryngeal jet at the trachea entrance was modeled as an effective turbulence disturbance, and the study was focused on how to accurately simulate the airflow and predicate the dynamic behavior of the inhaled aerosol fibers in the upper lung. Downstream in the lower level of the bronchial region that smoother flow condition was expected, a laminar flow model was used. The study showed that the multi-level asymmetric lung bifurcation model was flexible, easy to use and highly efficient computationally. It was also found that the use of anisotropic Reynolds stress transport turbulence model (RSTM) was appropriate, and the enhanced two-layer model boundary treatment was essential for the simulation of the turbulent airflow conditions in the upper airways. Lagrangian simulation of ellipsoidal fiber transport and deposition was performed. The hydrodynamic drag and torque, shear induced lift, gravitational sedimentation, turbulence diffusion and the coupling between the fiber’s translational and rotational motions were accounted for in the model. The deposition patterns of ellipsoidal fibers in the human tracheobronchial tree are compared with those of the spherical particles, and their differences are discussed.
5F.06
Fiber deposition in realistic human lung bifurcation model.
PHILIP HOPKE, Zuocheng Wang, Clarkson University

The adverse health effects of man-made vitreous fibers (MMVF) have drawn attention in recent years because their specific elongated shapes cause them to act as so-called physical carcinogens. Knowledge of specific regional and local deposition sites is important because the toxicity of these fibers is often more dependent on the number deposited at a specific site than on the total quantity of particles that are inhaled.

In this study, a three-generation, asymmetric bifurcation was developed based on Hofmann's definition [Heistracher and Hofmann, 1995]. The basic geometric sizes of the model were acquired from measurements on a human airway cast. Stereolithography was used to construct the airway model. A glass fiber aerosol generated using an electrical fiber classifier was used to challenge the model. Spherical particles were also used for comparison. The deposition efficiencies of both glass fibers and spherical particles within the lung bifurcations were determined. It was found that the deposition efficiency increases with increasing Stokes number for these particles investigated in this research. Generally the fiber length has a positive influence on the deposition efficiency.

Reference:

5F.07
Simultaneous Effects of Coagulation and Hygroscopic Growth on the Deposition of Particles in Human Lungs.
Bahman Asgharian, Owen T. Price, CIIT at The Hamner Institutes for Health Sciences

Particle deposition in the lung depends on variables such as particle aerodynamic properties (size, shape, density, and interaction with airflow), lung properties (structure, dimensions, and volume) and breathing parameters (tidal volume and breathing frequency). At very high concentrations and immediately after production, the processes of coagulation and hygroscopic growth may significantly alter the size of the particles and influence lung deposition on inhalation. To study the effect of these parameters on deposition, an existing model of particle deposition in the lung (Asgharian et al., 2001: Aerosol Sci. Technol. 34:332-339) was modified by including particle size change due to coagulation and hygroscopic growth. Lung deposition of particles with diameters between 0.001 nm to 10 micrometers was calculated at typical breathing scenarios for cases of no coagulation or hygroscopic growth, only coagulation, only hygroscopic growth, and when both hygroscopic growth and particle coagulation are present. Computed results indicated a distinct deposition pattern for each mechanism. When both mechanisms were present, the contribution of coagulation to particle deposition in the lung was significant only for concentrations above 10 billion particles per cubic centimeter.
6C.01
In Vitro Nasal Airway Deposition in Infants. WARREN H. FINLAY, John Storey-Bishoff, Michelle Noga, University of Alberta

Inhaled aerosol delivery to infants and young children is primarily through the nasal airway. In order to better understand the filtration of aerosols by the nasal airways, in vitro experiments on nasal replicas of 11 infants aged three months to 18 months were performed. Aerosol particles ranging in aerodynamic diameter from 0.8 micrometers to 5.3 micrometers were used in combination with various periodic, physiological breathing patterns in order to measure individual nasal filtration curves over a wide range of impaction parameters. Nasal filtration at the same impaction parameter was found to vary widely among subjects modeled. Nasal filtration was well described for all individuals by a function of the flow Reynolds number and the particle Stokes number defined with a subject specific length scale given by the nasal airway volume divided by the nasal airway surface area. The filtration data was captured even more closely if an additional dependence on the subject specific length scale was combined with the Reynolds number and Stokes number dependence. Various subject specific length scales were attempted including the minimum cross-sectional area, trans-nasal pressure drop and average cross-sectional area. The best results were obtained using nasal volume divided by nasal surface area. This length scale is similar to a hydraulic diameter since it can be expressed as average cross-section divided by average perimeter.

6C.02
Particle Deposition In Oral Airway Models At High And Low Flow Rates And Moving Boundary. Zheng Li (1), Ali A. Rostami (2) and Clement Kleinstreuer (3), (1) ClearPoint Resources, Inc., Virginia Biotechnology Research Park, Richmond, VA, (2) Philip Morris USA, Center of Research and Technology, Richmond, VA, (3) Department of Mechanical and Aerospace Engineering and Department of Biomedical Engineering, North Carolina State University, Raleigh, NC

Considerable progress has been made on modeling particle deposition in the oral-tracheal airway at high airflow rates corresponding to different breathing conditions, i.e., resting, light activity and moderate exercise. Low airflow rates have not been addressed in these studies. It is known that particle deposition in the oral-tracheal airway is greatly influenced by flow and particle inlet conditions. Particle deposition is numerically investigated in three oral-tracheal airway models, i.e., circular, elliptic and realistic oral-tracheal airway models. Both micro- and nano-particles are considered. Results show that airflow rate greatly influences the particle deposition. At relatively low flow rates, for ultra-fine particles, the oral deposition is enhanced due to longer residence time in oral cavity and stronger Brownian motion. However, for larger particles, less particle deposit in the oral-tracheal airway due to the weaker impaction. The highest deposition fraction could be in either circular or realistic models depending on the particle property and the geometric characteristic of oral cavity.

Another important factor is the periodical expansion and contraction of the mouth cavity. In published numerical works, the oral cavity model is generally assumed as non-moving, which is not realistic. In this work, the moving boundary effect on the flow field and the particle deposition is considered. As a first step for a complex computational analysis, particle deposition in circular oral airway models is investigated. The result shows that both the flow field and the particle deposition are greatly influenced by the moving boundary effect.
6C.03
Particle Deposition Efficiency in Defined Regions of a Human Nasal Replica. EARL W. TEWKSbury, Jeffry D. Schroeter, Julia S. Kimbell, and Brian A. Wong, The Hamner Institutes for Health Sciences, RTP, NC

The human nasal airways contain several distinct anatomical regions of interest for toxicological or pharmaceutical reasons. Specific regions such as the olfactory region or nasal turbinates may be vulnerable to a toxic material or the target for a pharmaceutical compound. The objective of this study was to determine the efficiency of deposition of inhaled particles in the different regions in order to provide information that can be used to predict localized effects of inhaled materials.

Stereolithography was used to construct a human nasal replica that could be disassembled into several pieces. Boundaries of these pieces were designed to delineate regions of interest: the nasal vestibule, the nasal valve area, the anterior turbinates, the turbinates, the olfactory, and the nasopharynx region. Particle deposition was measured by generating a monodisperse aerosol of fluorescein (Vibrating orifice aerosol generator, TSI, Inc., St. Paul, MN, aerodynamic diameter ranging from 2.6 to 14 micrometers) and passing the aerosol through the nasal replica at a constant flow rate. Impinger traps were used to capture aerosol that passed through the model. The model was disassembled and the deposited fluorescein in each region washed out and quantified using a fluorescence spectrometer.

The total deposition fraction in the nose was calculated by determining the amount of aerosol that deposited in all regions of the nose and the amount collected in the impingers. The measured total deposition efficiency results were similar to results from our previous studies conducted in single-piece nasal replicas. The experimentally determined deposition fraction in the various regions was compared with computational fluid dynamics calculations in a mathematical model having the same regional areas. At a particle diameter of 14 micrometers, the experimental and computational results were consistent. Further studies with additional particle sizes are being conducted.

6C.04
Deposition of MMVF’s in Human Respiratory Airway Casts. WEI-CHUNG SU, Yung Sung Cheng, Lovelace Respiratory Research Institute, Albuquerque

In this research, experiments of fiber deposition in the human respiratory airway were conducted by delivering aerosolized man-made vitreous fibers (MMVF’s) into human respiratory airway casts. Man-made glass fiber and titanium dioxide (TiO2) fiber with relatively thin fiber diameters (about 0.6 um) were used as the test materials. Two different human respiratory airway casts made from conductive silicon rubber were used for investigating the variability of the deposition results. The airway casts consist of the oral cavity, oropharynx, larynx, trachea, and tracheobronchial tree up to the third generation. The deposition studies were carried out at constant inspiratory flow rates of 15, 43.5, and 60 l/min. Fiber deposition patterns and regional fiber deposition efficiencies in the airway cast were acquired by measuring the length distribution of the deposited fibers in every region of the airway. The results showed that the deposition patterns and deposition efficiencies were similar between the two human airway casts. Very few fibers were found to deposit in the casts, which is significantly different from the results previously obtained in our laboratory using carbon fiber (fiber diameter: 3.7 um). This result implies that the inhaled thin fibers behaved similarly as did the small spherical particles which can easily enter the human lower tracheobronchial tree, causing possible lung diseases.
6C.05
Bolus dispersion as a measure of lung function in rats.
PRAVEEN K. SRIRAMA, DongYoub Lee, Anthony S. Wexler, Edward S. Schelegle, University of California, Davis

Dispersion of aerosol boluses in human lung is a non-invasive, functional diagnostic for measuring convective mixing of gases in the lung and predicting any irregularities in the lung structure due to diseases. Typically aerosol bolus dispersion experiments have been performed on humans, while many other hypotheses of pulmonary health effects employ murine models. The much smaller inhalation and expiration volume for rats and their rapid respiration rate requires not only small dead space in apparatus but also the use of real time data acquisition and control instrumentation for accurate and reliable measurements. A condensation monodisperse aerosol generator (CMAG, TSI) generates 0.5 micrometer particles, a laser photometer measures the particle concentration in inhaled and exhaled air, and the entire apparatus is operated and monitored by a real time controller. The talk presents details of the aerosol bolus apparatus and dispersion experiments performed using healthy and diseased rats.

7C.01
Indoor Air Bio-aerosols in varying Micro-environment: Prevalence of Bacteria, Fungi and Thermophilic Actinomycetes in Mumbai. RAKESH KUMAR(1), Varsha Kelkar (2), (1) National Environmental Engineering Research Institute (NEERI), Mumbai, (2) Department of Life Sciences, University of Mumbai, Mumbai

Bioaerosols, a group of organic aerosols ranging from ~10 nm to 100 um airborne particles or large molecules that are either alive, carry living organisms or are released from living organisms (e.g., bacteria, fungi, virus, pollen, cell debris, and biofilms). The presence of various types of bioaerosols in indoor air, in the troposphere and even in the stratosphere has long been established (Gidlen, T., Biological Reviews, (1948) 23, 109-126).

India being a tropical country, experiences several changes in the atmosphere, brought about by the meteorological factors. The climate in given region also signifies the composition of microbes existing within that environment. In urban areas due to over crowding, insufficient spaces are available for dwelling units leading to improper ventilation. Due to poor ventilation, people are exposed to various pollutants and as a result increase in respiratory diseases.

The present study delineates the nature and composition of the microbes in the given environment so that it would finally help to undertake measures to prevent and control diseases arising due to such exposures. Microenvironments which have been investigated are Shopping Mall, Temple, Household, Canteen and Sewage Treatment Plant. Prevalence of bioaerosols suggests diurnal variation with activities and the hour of the day of sampling. Seasonal variations were also noticed. Exposure risk of population in each of the microenvironment has been assessed.
Influenza is transmitted from person to person by multiple pathways, which may include inhalation of small aerosol particles generated when infectious individuals sneeze, cough, speak or breathe. However, the relative importance of airborne transmission compared to other routes of infection is unknown and is the subject of considerable debate. To assess the amount of potentially infectious airborne influenza virus in typical healthcare settings, we collected size-fractionated aerosols in a hospital emergency department and a student health clinic during influenza season. Aerosols were collected using a novel two-stage cyclone sampler with a first-stage cutoff diameter of 4 micrometers, a second-stage cutoff diameter of 1 micrometer, and a filter to collect particles less than 1 micrometer. At 3.5 liters/minute, the novel sampler conforms to the ACGIH/ISO criteria for respirable particle sampling. Sampling was conducted on 8 days for 3 to 5 hours per day during influenza season. Fourteen healthcare workers were equipped with personal samplers, and 98 samplers were mounted on stands in waiting rooms, exam rooms and reception areas. RNA in the collected material was isolated, reverse-transcribed and amplified using real-time PCR with primers specific to an Influenza A matrix protein. Preliminary results indicate that influenza virus was detected in 3 of 14 personal samplers and 10 of 98 stationary samplers, and that 50% of the viral particles were detected in the respirable aerosol fraction. The results suggest that a measurable amount of airborne influenza virus can be found within a typical healthcare facility, and that the amount of airborne virus varies considerably both spatially and temporally.
7C.04  
**Assessment of Recreational Exposure to Aerosols Containing Microcystin.** YUNG SUNG CHENG (1), Yue Zhou (1), C. Mitch Irvin, Barbara Kirkpatrick (2), Lorraine Backer (3), (1) Lovelace Respiratory Research Institute, Albuquerque, (2) Mote Marine Laboratory, Sarasota, (3) Centers for Disease Control and Prevention, Atlanta

Toxic blooms of cyanobacteria are ubiquitous in both freshwater and brackish water sources throughout the world. One class of cyanobacterial toxins, called microcystins, is cyclic peptides. In addition to ingestion and dermal, inhalation is a likely route of human exposure. The purposes of this study were to evaluate sampling and analysis techniques for microcystin aerosol, produce aerosol droplets containing microcystin in the laboratory, and deploy the sampling instruments in field studies. A high-volume impactor and an IOM filter sampler were tried first in the laboratory to collect droplets containing microcystins. Samples were extracted and analyzed for microcystin using an ELISA method. The laboratory study showed that cyanotoxins in water could be transferred to air via a bubble-bursting process. The droplets containing microcystins showed a bimodal size distribution with the mass median aerodynamic diameter (MMAD) of 1.4 and 27.8 um. A field study was conducted to assess the exposure levels of people at risk for swallowing water or inhaling spray during recreational activities (water skiing, jet skiing, and boating) during a Microcystis aeruginosa bloom in a small recreational lake in Michigan on August 4 to August 6, 2006. Two high-volume air samplers, each including a filter sample or a cascade impactor (Model SA235; Andersen Instruments), were placed on a motor boat that circulated in the lake to collect aerosol samples in the area. Personal samplers (IOM Inhalable Dust Sampler; SKC, Inc) were worn by human volunteers recreating on the lake to assess personal exposure levels. This field study demonstrated that we can detect very low levels of microcystin aerosol in areas with blue-green algae. Both high-volume and personal samplers show microcystin concentrations between 0.02 to 0.08 ng/m3. This confirmed our laboratory results.

7C.05  
**Active Pharmaceutical Ingredients Released by Dispensing Robots.** DAVID ALBURY (1), Pamela Murowchick (1), Andrew Page (2), (1) AlburtyLab, Inc. (2) Page Applied Research, LLC

We conducted a study in U.S. retail pharmacies to assess the potential health risks for pharmacy staff and customers arising from airborne pill dust generated by robotic dispensing machines. Aerosol particle count and mass measurements were taken in pharmacies employing the two most commonly found pharmacy robots (Parata RDS and ScriptPro SP 200) and compared with measurements taken in a pharmacy exclusively filling prescriptions manually.

The study was suggested by the fact that some robots use compressed air and/or vacuum (differential) pressure in the dispensing process. Pill dust can be readily observed on and around these machines and is likely also to be in the air.

The study was begun by taking a sample of dust from a robot that had employed both compressed air and vacuum pressure to dispense prescriptions in a retail pharmacy. The re-aerosolized dust contained a substantial population of nanoparticles (less than 0.5 micron in diameter) and a large mass fraction of particles in the size range less than 2.5 microns (PM-2.5 particles). The dust was analyzed and shown to contain active pharmaceutical compounds.

Subsequently, a screening study of 3 pharmacies was performed to determine test methods for the pharmacies. This was followed by 24-hr sampling at a total of 11 pharmacies. Sampling was conducted using the TSI 3321 APS and replicate quartz fiber reference filters.

Dust samples collected using air filters placed at Parata RDS sites were analyzed using HPLC/MS and were determined to contain hundreds of peaks that could be active pharmaceutical compounds. A limited set of the largest peaks were identified as the active pharmaceutical ingredients acetaminophen, ibuprofen, isosorbide, and trazodone, confirming that aerosols present in those pharmacies were partially composed of pill dust that could be attributed to operation of the robots. Dust samples collected at the pharmacy using the ScriptPro SP 200 and the pharmacy using manual dispensing contained active pharmaceutical ingredients that were attributed to generation during manual dispensing.
Examination of Simulated Workplace Aerosols for Nanoparticle Contamination Using Transmission Electron Microscopy. NANCY JENNERJOHN (1), Arantza Eiguren-Fernandez (2), David C. Fung (1), William Hinds (1), Nola J. Kennedy (1), (1) Environmental Health Sciences Department, UCLA, (2) Center for Occupational and Environmental Health, UCLA

It is uncertain which characteristics of airborne engineered nanoparticles encountered in workplace air are the best predictors of potential adverse health effects. The objective of this study is to develop a robust collection of transmission electron microscopy (TEM) techniques to measure aerosol properties of engineered nanoparticles. Many aerosol properties can be evaluated using TEM including morphology, crystal structure, surface area, particle size distribution and chemical composition. The ability of air monitoring instruments to correctly report aerosol properties can be evaluated by comparing measured properties to those found using TEM techniques.

A simple versatile electrospray aerosol generator is used to aerosolize single-walled carbon nanotubes and quantum dots. Since those who work with nanoparticles also encounter other airborne pollutants, we aerosolize these nanoparticles with varying amounts of two NIST SRMs, urban dust and diesel particulate matter. Altering the proportion of pollutant to nanomaterial allows the simulation of atmospheres containing nanoparticles and the evaluation of limits of detection of aerosol monitoring instruments and techniques. Numerous TEM images have been obtained. The TEM methods used permit quantitation of engineered nanoparticle concentration among the airborne particulates deposited onto TEM grids. Samples were also taken from two campus research labs, one where carbon nanotubes are in heavy use, and one where quantum dots are synthesized. These two labs serve as test sites for the evaluation of instruments and techniques that may prove efficacious in quantifying worker exposure to airborne nanomaterials in the industrial setting.

There is a long history of using microscopy in occupational health studies. Phase-contrast microscopy (PCM) is used to quantify asbestos exposure, and TEM complements PCM using selected area electron diffraction (SAED) for identification of crystal structure and energy-dispersive x-ray (EDX) for chemical analysis. UCLA is home to several TEMs in its Electron Imaging Center for NanoMachines (EICN) capable of performing SAED and EDX, as well as three-dimensional electron tomography. Progress to date in establishing this TEM performance baseline at the EICN for the evaluation of instrument performance will be reported.
8C.02
Controlling the Size Distribution of Bioaerosol Droplets by Modifying the Viscoelastic Properties of Mucus. M A Hasan (1), G. Zayas (2), M King (2) and C F. Lange (1), (1) Department of Mechanical engineering, University of Alberta, Edmonton, T6G2G8, Alberta, Canada (2). Pulmonary Research Group, University of Alberta, Edmonton, T6G 2V2, Alberta, Canada

We present recent in-vitro results on the effect of viscoelastic properties of mucus on the size distribution of bioaerosol droplets exhaled during coughing. The issues addressed include the effects of viscosity and elasticity of artificial mucus simulant gels on the size distribution of droplets generated during a simulated cough using artificial cough machine. Mucus simulant gels having similar viscoelastic properties as real human airway mucus [King, 1987] were used. The gels were prepared by mixing various proportions of 0.5% ~ 1.5% Locust bean gum solution and 0.1 M sodium tetraborate (XLB) solution. A Bohlin Gemini (Malvern) nano rheometer was used to measure the viscoelastic properties of the mucus simulant samples. An artificial cough machine was used to simulate human cough, generating aerosol droplets in a model trachea attached to the front of the cough machine. The model trachea had a simplified model throat attached at its other end to filter out larger droplets. The characteristics of the generated droplets were measured using a laser diffraction particle sizer (Malvern SprayTec). The cough machine experiments showed a dual mode particle size distribution comparable to that of a real human cough (Edwards, 2004). The elementary results confirm that the viscoelastic properties of mucus have substantial effect on the size distribution of particles generated during coughing.

8C.03

To better evaluate the health effects caused by nanoparticles generated by laser printers, measurements were made to characterize the number concentration, size distribution, morphology, and chemistry of the emitted nanoparticles at various printer and room locations, as well as the likely generation mechanism and possible emission control strategies.

Experiments were conducted using an HP LaserJet4100, a common office printer in the same series previously reported to be high emitters of nanoparticles [1], in both a small office conference room environment and in a stainless steel chamber of similar size. Particle concentrations and size distributions were monitored using two real time optical particle counters and a Scanning Mobility Particle Sizer. Aerosols were collected using both an electrostatic precipitator and a magnetic passive sampler, and toner particles from the LaserJet printer cartridge were collected to reveal the composition of the source material for the generated particles. Collected particles were characterized using several different techniques, including FTIR spectroscopy, TGA, SEM/EDS, and TEM/EDS. The magnetic sampler was used to concentrate any iron oxide particles aerosolized from the toner.

Repeated measurements revealed that the LaserJet printer emitted nanoparticles: (1) with a concentration of 104-105 #/cc and 30-150 nm peaks, depending on the number of printed pages and aerosol age, (2) emitted primarily during the cold power up of printer and at the start of printing, but only if the LaserJet has been idle long enough for the internal surfaces to cool (about 30 minutes), (3) likely generated from condensation of vapor-phase polystyrene acrylate compounds, which are released from the toner powder during the rapid heating of internal printer surfaces. Preventing the cool down of the internal printer surfaces or increasing preheating time before printing may be helpful for reducing the generation of these polymer nanoparticles, which may represent a human exposure health concern.

Specific properties of viral aerosols - ultrafine size range of aggregates and shielding effect of aggregates/encasement - along with the presumed low infective dose of viruses are of great concern from the perspectives of dosage assessment and inactivation treatment for viruses. An investigation of the distribution of infectious and noninfectious viruses in the size fractionized aerosols will provide information critically important to evaluating the shielding effect of aggregates/encasement.

As test microorganism, MS2 bacteriophage was used as a surrogate for human pathogenic viruses. The viral suspension with and without tryptone was atomized using a Collison nebulizer, and aerosols certain sizes (i.e., 30, 60, and 90 nm) selected by electrostatic classification were collected by a SKC BioSampler. Tryptone was used to preserve the infectivity of viral aerosols and simulate the substances in the air inducing the encasement of viruses. The collected viruses were subsequently analyzed by infectivity assay for infectious viruses and polymerase chain reaction (PCR) for total viruses including both infectious and noninfectious viruses. The results were compared to the concentrations of the same aerosol sizes measured by Scanning Mobility Particle Sizer.

The number of viruses in a given particle size was theoretically calculated with the assumption that the particle is composed of only viruses. The observed infectious viruses were much lower than the calculated values for 30 and 60 nm; however, no significant difference was observed between the observed and theoretical values for 90 nm, indicating the effective shielding of aggregates. Experiments for the encasement of viruses and PCR analysis are underway and the results will be presented at the conference.

8C.05
Relationship between aerodynamic and mobility diameters of single- and multi-walled carbon nanotube aerosols.
PRAMOD KULKARNI, Gregory J. Deye, Bon-Ki Ku, and Paul A. Baron, Centers for Disease Control and Prevention National Institute for Occupational Safety and Health Cincinnati, OH

Relationship between aerodynamic and electric mobility diameter of aerosol particles of single- and multi-walled carbon nanotubes (CNT) were investigated. Aerodynamic diameters of mobility classified CNT aerosols were measured in the diameter range of 100 - 1200 nm using a DMA- electrical low pressure impactor (ELPI) setup. A procedure was developed to obtain mean, number-weighted aerodynamic diameter of the CNT aerosol from ELPI measurements and was validated using polystyrene microspheres over the entire range. Various aerosolization techniques were used to obtain CNT aerosols from bulk dry phase and aqueous suspensions. Morphology of CNT aerosol particles was studied using TEM analysis, and showed that multi-walled CNT agglomerates had high-aspect ratios and fiber-like morphologies while the single-walled CNT agglomerates generally exhibited low-aspect ratios with open, complex structures made up of entangled web of nanotubes and nanoropes.

Measurements show that at large mobility diameters, aerodynamic diameter of multi-walled CNT particles were much smaller than their mobility diameters. Effective density and dynamic shape factors were deduced from these measurements, which showed very low effective density and high dynamic shape factors. The effective density of CNT aerosol particles was then used to infer their deposition characteristics in the respiratory system over the submicron size range.
9C.01
Assessing PM Exposure from Woodsmoke in Guatemalan Kitchens Using CO Concentrations. Amanda L Northcross(1), Zohir Chowdhury (2), John McCracken (1), Ryan Johnson(3), Eduardo Canuz(4), Kirk R Smith(1), (1) University of California Berkeley (2) San Diego State University (3) California Air Reseouces Board (4) Univesity del Valle Guatemala

In the developing world the use of inefficient stoves for cooking exposes large numbers of people to high concentrations of smoke from biomass fuels. The health implications of such large and continuous exposure to toxic gases and particulates has been estimated to be responsible for 1.4 million premature deaths per year. In an attempt to more precisely quantify the health effects of biomass smoke exposure, a randomized improved stove intervention trial was conducted in the rural highlands of Guatemala. Of 568 homes studied, a chimney stove was randomly given to half at the start and the other half (control group) continued to use the traditional open woodfire for cooking until the end, when they received the improved stoves. To quantify exposure to smoke, CO, PM1.0, PM2.5, PM10.0 were measured in 1/8 of the homes. CO was measured in all of the study homes, as well as personal CO measurements on mothers and children were made. A host of health measurements were also conducted.

Homes with improved stoves had large reductions in smoke levels. Mean 48-h kitchen concentrations of CO were 8.8 +/- 4.2 (+/- SD) ppm and 1.0 +/- 1.4 ppm for open fires and improved stoves respectfully. PM2.5 kitchen concentrations were 931 +/- 1490 and 81 +/- 181 ug/m3 for open fires and improved stoves respectfully. PM1.0 kitchen concentrations were 1083 +/- 906 and 75 +/- 93 ug/m3 for open fires and improved stoves respectfully.

As wood burning is the major source of smoke in these homes, the ratio of CO to PM should be stable, at least over 48h, as previously described by Naher et al, for PM2.5 (2001). We will further investigate the CO/PM relationship using PM1.0 and PM10.0 to quantify their effect on the smoke reductions by the improved stoves and the overall estimated PM exposures.


9C.02
A Typical Day's Exposure to Ultrafine and Fine Particulate Matter in Toronto, Canada. KELLY SABALIAUSKAS (1) Greg Evans (1) Dave Stieb (2) Amanda Wheeler (2) Jeff Brook (3) Monica Campbell (4), (1) Department of Chemical Engineering and Applied Chemistry, University of Toronto (2) Health Canada (3) Environment Canada (4) Toronto Public Health

The objective of this study was to determine an individual's exposure to ultrafine particles (UFP) and fine particulate matter (PM2.5) on a typical day through personal monitoring. This work was composed of three field campaigns where pollutants were measured directly alongside an individual and indirectly through a study of microenvironments and activities. For the microenvironment study, emphasis was placed on locations and activities where individuals had control and choice. For example, commuting to a place of work had a variety of options; however, an individual had very little choice or control over their workplace exposures to these pollutants. Activities such as cooking were performed under controlled laboratory settings and in the field. Time-activity patterns were used in conjunction with the microenvironment measurements to reconstruct a typical day's exposure in Toronto. The reconstructed values were then compared to the measurements collected alongside an individual.

The second component of this study evaluated the effect of following the advice issued to the public during air quality advisories by various health and environmental agencies. Two types of advice were evaluated. The first describes how an individual can reduce their exposure to air pollution by staying indoors. The second describes ways where an individual can 'spare the air' or 'do their part' to improve their air quality by riding public transportation or cycling instead of driving. Two scenarios were run simultaneously where the study participant behaved as normal and a second technician followed a script in which all exposure reduction and 'spare the air' advice was adhered to. This study showed that individuals following the exposure reduction advice were exposed to significantly higher concentrations of both UFP and PM2.5 in transportation-related microenvironments and during activities such as cooking.
9C.03
Personal Exposure to Indoor PM2.5 from Woodsmoke in the CRECER Study Using Inexpensive Datalogging Sensors for Time-Activity and Particle Pollution. Ilse Ruiz-Mercado (1), Nick Lam (1), Amanda Northcross (1), Gian Allen-Picollo (2), Eduardo Canuz (3), Kirk Smith (1) (1) University of California, Berkeley (2) EME Systems, Berkeley (3) Universidad del Valle, Guatemala

Monitoring exposure to indoor air pollution from burning solid fuels is critical to quantify the effectiveness of interventions and to further understand the health effects of the pollutants. Most of the premature deaths attributed to indoor air pollution (1.6 million each year) happen in developing countries. Measuring personal exposure to indoor aerosols in these environments on populations that are large enough to obtain statistically significant results can become challenging because of cost, intrusiveness or lack of appropriate technology.

Our group has developed 2 instruments that are inexpensive, reliable, non-intrusive and that have been deployed on a routine basis for several years by field personnel in the CRECER (Chronic Respiratory Effects of Early Childhood Exposure to Respirable Particulate Matter) study. The UCB-Particulate Monitor is based on a commercial photoelectric smoke detector that has been modified to log real-time PM2.5 levels, along with temperature and humidity. The UCB-Personal Locator consists of an ultrasonic receiver placed in the room of interest and several ultrasonic transmitters worn by the people to record a minute by minute account of the presence/absence of each participant in the microenvironment.

Merging the time-activity outputs of the personal locators with the microenvironment concentration readings from the particle monitors, we are able to quantify personal exposure to PM2.5. We present an analysis of 24-hr exposure records for about 60 study participants that were monitored 10 times in a 2 year period including before and after receiving the chimney-stoves.

9C.04
Contribution of outdoor and wall fungus to indoor airborne fungus in residents. Ning Huang (1) Yahui Hsu (1) Chunchieh Tseng (2) Chihchieh Chen (1) Yueliang Leon GUO (3) (1) Institute of Occupational Medicine and Industrial Hygiene, National Taiwan University (1) Department and Graduate Institute of Public Health, Tzu Chi University (2) Department of Environmental and Occupational Medicine, National Taiwan University College of Medicine and NTU Hospital (3)

OBJECTIVE: The objective of this study is to determine the contribution of outdoor and wall fungus to indoor airborne fungus in residents.

METHOD: From a birth cohort of 1000 mother-infant pairs followed from the third trimester between December 2003 to December 2005, we selected 28 residents of children with asthma, allergic rhinitis, or atopic dermatitis, and 14 residents of children with none of the above diseases for evaluation of airborne fungus in indoor environment. The environmental monitoring was conducted in the city of Taipei, Hsinchu, Yunlin, Chiayi, Tainan, Kaohsiung, and Taitung. For indoor samples, Andersen Single Stage Sampler was used to collect air samples in the living room and child bedroom. Outdoor samples were taken from the main gate outside. In addition, the indoor surface samples were taken from the vertical wall, floor and ceiling tile with obvious molds. Finally, both airborne and surface samples were stained by lactophenol cotton blue for fungal species identification.

RESULT: The identified microbial genera in indoor include Cladosporium spp., Penicillium spp., Aspergillus spp., Geotrichium spp., Yeast, and Verticillium spp. The total concentrations of outdoor airborne fungus was highly related to indoor fungus (R²=0.54). Moreover, the relationship between the concentrations of outdoor and indoor fungus was depended on the fungal species, the R-squares for Verticillium, yeast, Geotrichium, Cladosporium, Penicillium, and Aspergillus were 0.97, 0.69, 0.59, 0.44, 0.27, and 0.18 respectively. In most evaluated residents in our study, wall fungus did not demonstrate a significant contribution to the indoor fungus, except in one room, in which outdoor concentration of Aspergillus spp. was low, but wall growth of Aspergillus spp. showed a significant contribution to the indoor Aspergillus spp.

CONCLUSION: Our study demonstrated the main contribution of indoor fungus was outdoor fungus. The relationship between the concentrations of outdoor and indoor fungus was highly depended on the fungal species.
Microbial Particles in Confinement Animal Buildings Measured Using a Six-stage Impactor. JONGMIN LEE, Yuanhui Zhang, University of Illinois at Urbana-Champaign

Airborne microbial particles are highly associated with health problems. Bioaerosols have been considered as living and non-living biological pollutants exist as single, unattached microorganisms or as aggregates. An Andersen six-stage impacting viable particle sampler was used for seasonal collection of airborne bacterial particles in various types of livestock buildings, and the collected particles were cultivated for counting of colony. Each colony represents a single bioaerosol. This sampler collects both respirable and inhalable particles with six different particle-cutoff sizes: 0.65, 1.1, 2.1, 3.3, 4.7, and 7.0 micro-meter. In addition, total suspended particles (TSP) were collected, and the relationship between bioaerosol number concentration and particle mass fraction with aerodynamic particle size was investigated. The major objectives of this study are: (i) determine the concentration and the size distribution of bioaerosol in various animal buildings with season; (ii) evaluate the fraction of respirable bioaerosol concentration that caused respiratory diseases; (iii) identify the relationship between bioaerosol concentration and TSP mass concentration.

Measurement of endotoxin and aeroallergens in PM10 and settled dust in the homes and school rooms of asthmatic children. Suresh Raja, Ying Xu, Andrea R. Ferro, Peter A. Jaques, Philip K. Hopke, Clarkson University, Center for Air Resources Engineering and Science, Potsdam, NY

Prior studies have shown that inhaled endotoxin and allergens, such as from dust mites and cockroaches, and from dog and cat dander, cause inflammatory reactions in humans, including fever, flulike symptoms, cough, headache, respiratory distress and asthma. Increases in the relative concentrations of these endotoxins and allergens in different micro-environments are hypothesized to trigger asthma symptoms. To assess daily exposures, a field study was conducted to collect settled dust and resuspended PM10 samples from the homes and schools of asthmatic children (ages 9 to 16). Samples were analyzed for dust mite and cockroach allergens, dog and cat dander (Der p 1, Der f 1, Bla g 1, Can F 1, and Fel d 1, respectively) and endotoxin. Settled dust was collected over a 1m2 area from the living room, bedroom, and classroom on a single day for each child using a vacuum pump with a DUSTREAM (TM) Collector. Airborne particulate matter (PM10) was collected using BGI 400 personal sampling pump connected to a Personal Exposure Monitor (PEM). The PEM is a single-stage impactor (impactor cut size - 10 um aerodynamic diameter) loaded with a pre-weighed 37mm teflon filter. The airborne particulate matter and settled dust samples were weighed and then extracted into phosphate buffered saline and stored at -20C prior to analysis. Endotoxin was analyzed using PyroGene (R) Recombinant Factor C Endotoxin Detection System and allergens were detected and quantified using Enzyme-Linked ImmunoSorbent Assay (ELISA).
9C.07
Number Size Distributions of Ambient Sub-micrometer Particles Inside and Outside a Hospital. Ya-Wen Jhang, Cheng-Hang Sie, Yi-Ting Wang, LI-HAO YOUNG, China Medical University, Taiwan

The number size distributions of ambient particles, between 0.01 - 1 micrometer, were measured inside/outside a hospital to assess personal exposure to and penetration characteristics of ultrafine particles. We used a sequential mobility particle spectrometer and condensation particle counter (SMPS/CPC) to measure the particle size distributions every 3-min at the adjacent road, the entrance and a number of floors of the hospital, including the lobby, admission office, surgery, newborn center, and general inpatient areas. The outdoor (roadside/entrance) concentrations averaged $7.4 \times 10^4$ cm$^{-3}$ and the inter-connected first/second floor averaged $4.0 \times 10^4$ cm$^{-3}$. The concentrations on the upper floors (5F/7F) ranged from $1.2 \times 10^4$ to $2.1 \times 10^4$ cm$^{-3}$, where the lowest concentrations were measured at the surgery floor. The ultrafine particle contributions to the measured number concentration decreased from the outdoor (85%) to the lower floors (82%), and to the upper floors (75%). The geometric mean diameters, on the other hand, increased from the outdoor environment (0.043 micrometer) to the lower floors (0.046 micrometer), and to the upper floors (0.057 micrometer). As oppose to those measured outdoor, the indoor number size distributions showed little variability, with the mode diameters consistently in between 0.05 and 0.08 micrometer. The I/O ratios for the lower and upper floors were 0.54 and 0.21, respectively. With respect to size, the I/O concentration ratios have a maximum (I/O = 3.9) at 0.6 micrometer, and the ratios decrease with decreasing/increasing particle sizes. This strong enrichment of 0.6 micrometer particles was likely due to the aging (growth) process. The highest exposure concentrations for workers and patients inside the hospital occurred at around 0.06 micrometer, despite its I/O ratios averaged only 0.5. Finally, it is worthwhile to note that the number concentrations of sub-micrometer particles inside the hospital are comparable to those measured at US urban background sites.

9C.08
The impact of different type of heaters on indoor PM2.5 and gases concentrations: A study in Santiago, Chile. Pablo Ruiz (1) Claudia Toro (1) Pedro Oyola (1) Jorge Caceres (1) Petros Koutrakis (2), (1) Centro Mario Molina Chile (2) Harvard School of Public Health

In Santiago, Chile people are exposed to high levels of air pollution, especially during winter months, because of high outdoor air pollutant concentrations, which usually exceed air quality standards, and of the extended use of indoor heaters, which may lead to even higher concentrations in the indoor environment. In Santiago, Chile most usual heaters use kerosene and gas; either liquefied petroleum gas (LPG) or compressed natural gas (CNG). To study the contribution of these different types of heaters in a real setting, we measured air pollutants in 16 homes in Santiago. Homes were sampled in 4 sessions, with 4 homes sampled simultaneously in each session together with an exterior site. To compare the impact of heaters, in each session we compared homes using kerosene heater, CNG heaters, LPG heaters and a home using only electrical devices as a control. Homes were sampled for 8 or 10 straight days. Pollutants sampled were PM2.5, continuously and by integrated samples collected every 48-hours; and NO2, SO2 and BTEX collected during the whole period. For PM2.5 samples, mass, elemental and organic carbon, elements and polyaromatic hydrocarbon were determined. We present preliminary results comparing concentrations of NO2, SO2, PM2.5 and PM2.5 components in homes using different type of heaters. The use of tracers to determine the contribution of outdoor air on indoor levels is explored.
Redistribution of Semivolatile Organics Associated with Airborne Particles as a Consequence of Outdoor-to-Indoor Transport. CHARLES J WESCHLER, William W Nazaroff, (1) Environmental & Occupational Health Sciences Institute, UMDNJ & Rutgers, (2) University of California, Berkeley

Numerous studies have reported associations between outdoor particles, measured at central monitoring sites, and both morbidity and mortality. Refined interpretation of such findings requires better understanding of the ways in which indoor particles of outdoor origin differ physically and chemically from their outdoor counterparts, since a large fraction of exposure to particles occurs indoors. One potential chemical difference involves semivolatile organic compounds (SVOCs) that are associated with particles. SVOCs partition between the gas phase and particles; indoors, they can also partition to room surfaces. Factors that govern this partitioning, in addition to the airborne concentration of particles and the vapor pressure or octanol-air partition coefficient of the SVOCs involved, include these three: (i) temperature, (ii) fraction of organic matter that comprise airborne particles, and the (iii) respective concentrations of the SVOCs in outdoor and indoor air. This study uses material balance models to examine, in a systematic fashion, the changes that occur in the SVOCs associated with airborne particles when they are transported from outdoors-to-indoors. Seven cases are examined. In the first three, only one key factor is allowed to vary between outdoors and indoors. In another three cases, two factors are allowed to vary. In the final case all three factors have different outdoor and indoor values. The factors are varied over the ranges of conditions expected to prevail, based on empirical evidence. Classes of SVOCs included in the simulations include dioxins, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), phthalate esters, and pyrethroids pesticides.

PM2.5 and heavy metal measurements in residential areas of Agra, India. AJAY TANEJA, Aditi Kulshrestha, David Massey and Jamson Masih, School of Chemical Sciences, Department of Chemistry, St. John

The current interest in atmospheric particulate matter is mainly due to its effect on human health and its role in climate change, particulate matter especially those with small diameter (d<2.5um) are among the pollutants highlighted for adverse health effects. Thus detailed investigations of the chemical characteristics of PM2.5 are important for elucidating the particle toxicity. The study purpose is investigation of pollutant levels in urban residential area, of the city Agra, characterization of PM2.5 and finding correlation structure among particulate concentrations, heavy metal content and secondary particulate expressed as NH4+, SO4-2 and NO3-. Sampling was carried out inside and outside urban residences. PM2.5 samples were collected by medium volume sampler for 24 hours on 47 mm diameter Teflon filter paper and each sample is analyzed by AAS techniques for heavy metals and secondary particulate was analyzed on UV visible spectrophotometer. The mean 24 hour PM2.5 concentration in the sampling period ranged from 316.7 ugm-3 to 78.0 ugm-3 indoors and 295.1 ugm-3 to 104.1 ugm-3 outdoors with average concentration 149.2 +/- 81.4ugm-3 indoors and 172.60 +/- 50.4ugm-3 outdoors. Measurements of mass concentration of heavy metals lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), chromium (Cr) and of total fine particulate matter (PM2.5) were conducted from October 2007 to February 2008. Zn and Cr were most abundant heavy metals measured followed by Cu, Ni and Pb. The spatial distribution, indoor-outdoor relations and the correlation between PM2.5 levels and metal concentration as well as secondary aerosols will be discussed during presentation.
9C.11
Personal Exposure Measurements from the Traditional Household and Commercial Scale Stoves in Rural Areas of Orissa, India. MANORANJAN SAHU (1), Gautam Yadama (2), Jagdeesh Puppala (3), Pratim Biswas (1). (1) Aerosol and Air Quality Research Laboratory, Washington University in Saint Louis. (2) Brown School of Social Work, Washington University in Saint Louis. (3) Foundation for Ecological Security, India

Around 3 million people in developing countries use biomass as their main source of energy. Biomass used as cooking fuel in rural areas causes adverse health effects like chronic diseases, lung cancer, respiratory infection and global climate change. The objective of this study is to investigate the emissions characteristics from the traditional biomass stoves used in rural households and commercial scale stoves used in small restaurants in India and to understand the impact of emissions from these sources with the aim of designing an improved biomass cook stoves suitable for the rural India.

In this study the emissions characteristics based on mass concentration, size distribution and surface area of the emitted aerosols will be presented for both traditional stoves used in rural household and commercial scale stoves used in restaurants. Preliminary emissions measurements by personal aerosol monitor (TSI, Model AM510 SIDEPAK) indicate that the average mass concentration of the emitted PM10 particles can be as high as 3.5 mg/m$^3$ in traditional household stoves and 4.8 mg/m$^3$ in the commercial scale stoves based on the operating conditions of the stoves. The emission from the biomass stoves varies depending on the location of the stoves in household, ventilation system, behavioral pattern and meteorological conditions. Average concentration of 0.382 mg/m$^3$ was observed in a rural household using LPG gas stove. Exposure measurements inside a secondary school campus, where biomass stove is used to cook mid day lunch, indicate students can be exposed to emissions from the stoves depending upon the location of class rooms and other environmental factors.

9C.12
Mass and Number Concentrations of Size Segregated Aerosol in a Large Sport-Hall. MARIN BRANIS, Jan Hovorka, Charles University in Prague, Faculty of Science, Institute for Environmental Studies, Prague, Czech Republic

Exercise in high ambient particle conditions may increase risk of lung and vascular damage, since total particle deposition increases in proportion to minute ventilation and deposition fraction nearly doubles from rest to intense exercise. Information about aerosol concentration during sport events is therefore of high importance. We performed air quality measurements in a large sport-hall during a top national sport event - Czech 2008 Indoor Athletic Championship on 23 and 24 February 2008. A pair of photometers (DustTrak) and meteorology sensors were used to measure indoor and outdoor PM$_{10}$, temperature and relative humidity. A set of indoor SMPS 3936L25 and APS 3321 was deployed to measure 3 minute integrates of aerosol size distributions in the range of 15 nm-10 micro-meter. Five minute data on ozone and NO$_x$ were monitored indoors by Horiba equipment. Our measurements confirmed a well-known feature, that concentration of coarse aerosol well reflects the presence and movement of people documenting resuspension. Regarding fine aerosol, we observed seven, short-time (10 min) bursts of ultrafine particles (<50 nm) during which number concentrations reached $8.5 \times 10^4$ cm$^{-3}$. Such bursts appeared around mid-day and near 3 PM and were clearly not associated with any specific human activity indoors. For instance, three bursts which appeared on the first day (23 Feb) were recorded around mid-day, i.e. one hour before the beginning of the competition when no indoor source could be active. A slow condensational particle growth, lasting for three hours after the bursts, indicates rather new particle formation process than direct aerosol emission from an unknown source could be the cause. The results are discussed in terms of potential sources of fine aerosol in similar large indoor spaces and their potential to adversely influence the athlet's performance or health.
9C.13
Resuspension of Indoor Particles From Floor Due to Human Walking. Xinyu Zhang, Jing Qian, Goodarz Ahmadi, Andrea Ferro, Clarkson University

A model for resuspension of indoor particles from floors due to human walking was developed. Both the hard floor and the carpet-covered floor were included in the study. The foot stepping down and up processes were treated as the motion of an effective circular disk toward or away from a stationary surface. The airflow generated from this squeezing film was assumed to be laminar and the corresponding gas velocity inside the foot range was evaluated. The squeezing flow outside the foot range was also evaluated based on the radial wall jet theory. The surface roughness effect and the adhesion and drag forces were included in the analysis. The particle cloud deposition, dispersion and transport were taken into account in the analysis. The resuspended PM concentrations for different particle sizes due to human walking in the room were evaluated. The effect of various factors affecting the resuspension process was discussed. The model predictions were compared with the experimental data and good agreement was obtained. The results show that shoe bottom roughness, foot size as well as foot stepping down and up velocities and frequencies affect the PM concentrations.

9C.14
Estimation of PM Exposure from Human Activities on Real Floorings. SASIKALA MANTHENA (1), Jing Qian (2), Andrea R Ferro (3), Department of Civil and Environmental Engineering, Clarkson University, Potsdam, NY

Resuspension of indoor particles accounts for a significant portion of human particulate matter exposure. Resuspension rates and environmental factors that affect resuspension require more accurate characterization. This study was conducted to characterize the resuspension from human activities from real floorings in a controlled environment. Experiments were conducted in the Indoor Particle Transport Chamber (IPTC) at Clarkson University. For each experiment, a participant walked on seeded flooring inside the chamber. The floorings were seeded with house dust particles with a known composition and size distribution. The environmental conditions were controlled by the chamber settings. Factors that were varied include flooring type (carpet and hard flooring), particle type (Arizona test dust and real indoor dust), and relative humidity (in a wide range from 30% to 80% RH). Size-resolved resuspension rates were estimated from an air-surface compartment model using real-time particle concentration data. The impacts of various factors were evaluated. The resuspension rates of specific pollutants that cause adverse health effects, including metals and allergens, were determined.
9C.15
Droplet Transport and Deposition in a Room. Mazyar Salmanzadeh Goodarz Ahmadi, Clarkson University

Transport and deposition of droplet in a room is studied using a computational modeling approach. Coughing and sneezing by a person in a room leads to emission of droplets that could carry viruses and bacteria and could lead to transmission of diseases. A computational model for simulating the airflow, the thermal and the humidity condition in room was developed and the distributions of evaporating droplet in the hospital room with two beds were studied. The turbulence model was used for continuous fluid phase calculations and the trajectories of the evaporating droplets were evaluated with a Lagrangian method. The particle equation of motion included the viscous drag, the Brownian, the Saffman lift and the gravity forces. Mixing and displacement air distribution systems were considered and trajectories of particles in the range of 1 to 500 microns were simulated. The simulation results suggested that the chance of disease transmission was higher when the mixing ventilation system was used. In addition, the air distribution system does not affect the large particle trajectories.

9C.16
Nonspherical Particle Adhesion and Removal in Turbulent Flows. Goodarz Ahmadi, Shiguang Guo, Clarkson University, Potsdam

Adhesion and detachment of compact irregular shape particles from surface are studied. An earlier developed bumpy particle model is first described. The effect of electrostatic and capillary forces on particle adhesion and removal is studied. The JKR theory is used and the increase of adhesion by the capillary force is accounted for. The effects of electrostatic forces and nonlinear hydrodynamic drag under in turbulent airflow conditions are included in the analyses. The criteria for incipient rolling and sliding detachments and electrostatic lifting removal are evaluated. A turbulence burst model is used for evaluating the peak air velocity near the substrate. The critical shear velocities for detaching particles of different sizes under different conditions are evaluated. The electric field strength needed for electrostatic removal of particles with different charges is also estimated. The results are compared with those obtained in the absence of the capillary force. Comparisons of the model predictions with the available experimental data are also presented.
10C.01

A Spatial and Seasonal Profile of Fine Particle Nickel in New York City: Estimating Exposures For Health Research. RICHARD E PELTIER, Morton Lippmann, NYU School of Medicine, Department of Environmental Medicine

Recent toxicological studies have suggested a link between exposure to fine particle nickel (Ni) aerosol and decreases in heart rate variability in a mouse model of atherosclerosis. A significant source of ambient fine particle Ni within the New York City (NYC) metropolitan area derives from combustion of fuel oils for space heating and large ship vessel bunkering purposes. NYC, a highly populous region, has been shown to have mortality rates that are higher than in other large metropolitan regions. Using data from the EPA Chemical Speciation (CSN) and IMPROVE networks, and NYC has been shown to have elevated concentrations of Ni. This is especially evident during the heating season, where winter Ni concentrations are six times higher than summer concentrations (~60 ng m\(^{-3}\) compared with ~10 ng m\(^{-3}\), respectively), which is consistent with fine particle Ni being associated with increased residual fuel oil combustion for wintertime space heating. However, NYC has only 3 aerosol CSN sites, and thus spatial resolution for Ni is likely inadequate for epidemiological surveillance. We report results of a pilot study in which Ni (along with ~33 other elements), PM2.5 mass, and elemental carbon were measured at 11 sites across the metropolitan NYC region. Weekly samples were collected during both the winter months and summer months at each site and the data are presented as a spatial profile of Ni across NYC. Together with the CSN and IMPROVE data, they demonstrate that considerable spatial and seasonal variability in ambient fine particle nickel concentration was observed, with highest concentrations measured in NYC, and lower concentrations in the surrounding regions. We also provide seasonal concentration estimates at most of 190 zip codes in NYC. These findings may provide important insight into a better understanding of ambient nickel aerosol exposures in large cities.

10C.02


Companies and other organizations that plan to use or make nanoscale materials in manufacturing processes and/or final products will be faced with intense scrutiny over environmental fate and transport of airborne emissions, as well as occupational safety and health issues. Risk Management tools, in particular the Nano Risk Framework developed by the Environmental Defense Fund and DuPont, require information for evaluating risks and guiding decisions. In order to investigate these issues and obtain information to enable effective risk management, data on nanoparticle airborne emissions from various processes were gathered through carefully designed air sampling with multiple aerosol measurement instruments, including traditional industrial hygiene standards, as well as more complex sampling methods. Nanoparticle releases from various handling and workplace operations are characterized, and changes in nanoparticle size distribution and morphological properties are monitored with time after initial release and/or distance from release point. The removal efficiencies and lifetimes of typical air abatement systems for nano-sized materials, such as baghouses and incinerators, are evaluated. Proper measurement techniques and instrumentation necessary for facility and worker exposure monitoring and/or technology evaluation are investigated and developed.

The work presented here is intended to support development of environmental, occupational, safety, and health protocols for evaluating workplace process and engineering control designs and to determine effective practices for protecting workers and the environment from accidental or incidental nanoscale material releases. Data is also used for estimation of fate and environmental concentrations for exposure assessments, as required for the commercialization of products, and to assess the applicability of current atmospheric environmental fate and transport models to nanoscale materials.
10C.03

Institute of Energy and Environmental Technology (IUTA), Division Air Quality & Sustainable Nanotechnology, Duisburg, Germany (2) Div. Aerosol Technology (EAT), Lund University, Sweden (3) Div. Occupational and Environmental Medicine, Lund University, Sweden

Health effects of fine and ultrafine particles have raised increased interest over the recent years. Welding fumes are one of the major sources of nanoscale particles leading directly to the exposure of workers. Those fumes are known to contain high particle number concentrations and toxicologically relevant metals. Despite this relevance only very few studies investigating the nanoscale fraction of welding fumes in detail in real work areas are known.

In the study presented here, particle number size distribution and lung deposited surface area were measured in a real workplace environment in a welding workshop in southern Sweden. The welding activities were intermittent, with welding periods and breaks, each lasting from a few seconds to approximately one minute. The resulting quick fluctuations for particle concentrations and size distributions as well as the associated particle dynamics required a high time resolution of the measuring devices. Instruments involved in this study included a Fast Mobility Particle Sizer (FMPS, TSI Model 3091, 1 s time resolution) measuring particle size distributions and a Nanoparticle Surface Area Monitor (NSAM, TSI model 3550) delivering the surface area concentration deposited in the alveolar region with 10 s time resolution.

Measurements were conducted either approximately 5 m away from the welding activity to measure how the background is affected by welding activities or directly in the plume. Measurements in the plume were subject to very high particle concentrations. Therefore a two stage ejector dilution system (combined ratio 1:150) was used in order to minimize coagulation upon sampling and to reduce particle concentrations.

Results show that FMPS and NSAM could both follow the dynamics well and are in good agreement. Regression analysis of total lung deposited surface area concentration versus particle number concentration during background measurements showed that different particle generation processes can quite clearly be distinguished by the slope.

10C.04
Effectiveness of Air Cleaner on reducing indicators of airway inflammation in asthmatic children. Ying Xu (1), Suresh Raja (1), Andrea R. Ferro (1), Peter A. Jaques (1), Sean McMahon (1), Yang Qi (1), Philip K. Hopke (1), Cheryl Gressani (2), Larry E. Wetzel (2), (1) Clarkson University, (2) Air Innovations, Inc, North Syracuse

Poor indoor air quality has been linked to the exacerbation of asthma symptoms in children. Clarkson University has partnered with Air Innovations (AI) and the Canton-Potsdam Hospital in a study aimed to examine the reduction of asthma symptoms by improving residential air quality. Thirty-two children (ages 5-16 years) previously diagnosed with asthma were randomly split into two groups. As a control, one-half started without an air cleaner for the first 6 weeks. Then, the air cleaning/ventilating unit (HEPAiRxTM) was installed in the bedroom of each of these participants and operated for 12 weeks. In the second group, the HEPAiRx was installed initially and operated for 12 weeks, after which it was switched off for 6 weeks. As a measure of pulmonary inflammation, exhaled breath condensate (EBC) was collected every sixth day from each participant and analyzed for nitrate and pH. As a control, peak expiratory flow (PEF) was measured. Analysis of variance was performed on the EBC nitrate concentrations and z-score normalized PEF data. Results show statistically significant reduced levels of EBC nitrate concentration and increased PEF rates when the HEPAiRxTM was operating, versus when it was not. These results indicate that use of the HEPAiRxTM in the children's bedrooms reduced these markers of respiratory inflammation.
Indoor chemistry can be initiated by ozone, which reacts with surfaces and other gas-phase pollutants. Research has established that ozone readily reacts with terpenes commonly found indoors to produce secondary organic aerosol (SOA) in the ultrafine (<0.1 micro-meter) and fine (0.1-2.5 micro-meter) range. Most indoor SOA formation research focuses on the products of gas-phase ozone/terpene reactions. However, during experiments that investigated SOA formation in a 27 cubic meter residential room with varying ozone (achieved with an ion generator) and terpene concentrations (from plug-in air fresheners), we noticed different levels of SOA formation depending on the floor surface (either carpet with padding or sealed/stained concrete). We hypothesize that ozone surface reaction products with terpenes adsorbed to indoor surfaces can influence gas-phase SOA formation. To investigate this hypothesis, we conducted small chamber (28 and 56 L) experiments at identical air exchange rates and gas-phase ozone and terpene concentrations so that any difference in SOA formation in the two chambers could be attributed to surface reaction products. Investigated surfaces include the stainless steel chamber walls, activated carbon, carpet with padding, and painted gypsum board. The results suggest that surfaces have a strong impact on the amount and size distribution of formed SOA. A possible mechanism for increased formation of SOA is the volatilization of ozone/terpene surface reaction products. This research allows insight into SOA formation in real environments and suggests strategies for passive indoor air chemistry control.

Many studies report that adverse health effects are most strongly correlated with fine particulate matter (< 2.5 um in diameter), originating from ambient emissions mainly derived from fossil fuel combustion. This study examines the infiltration of ultrafine (0.055-0.7 um) into indoor environments including typical office space and elementary schools in an urban location, Denver, and a more rural location, Boulder. With the use of an Ultra High Sensitivity Aerosol Spectrometer and an Aerosol Mass Spectrometer, the size and chemical speciation of ultrafine particulate matter were measured as a function of time. Results showed that indoor particle levels were highly correlated with outdoor levels (0.65-0.85). Inside and outside number concentrations in Denver where higher than those concentrations in Boulder. The highest number concentrations occurred during the summer and fall. The ratio of indoor-to-outdoor (I/O) ultrafine particulate matter was weakly dependent on the amount of ventilation provided to the indoor environment. The I/O did not vary much with particle size and ranged between 0.47 and 0.57. The I/O was similar for each period of the week (weekend vs. weekday, night vs. day). The lag time, which is an estimation of the time it takes for outdoor particles to come indoors, and on average ranged from 10 to 90 minutes. The majority of the particles were organic in nature. During high nitrate episodes, the indoor nitrate was reduced due to transformations from particle to gas phase. This study provided important data needed to understand exposure associated with inhalation of fine particulate matter, and to improve understanding of filtration requirements in mechanically ventilated buildings. The correlation of indoor to outdoor particulate concentrations can be used to evaluate the performance of HVAC systems in conditioning indoor environments with an air quality perspective.
**11C.02**

Size Fractionated Mass Concentration of Aerosol in a School Gym. MARTIN BRANIS (1), Jiri Safranek (2), Adela Hytchova (1), (1) Charles University in Prague, Faculty of Science, Institute for Environmental Studies, Prague, Czech Republic (2) Charles University in Prague, Faculty of Physical Education, Department of Outdoor Sports, Prague, Czech Republic

Twenty-four hour mass concentration of size segregated aerosol was measured simultaneously in a school gym and in its outdoor vicinity in a central part of Prague (Czech Republic). The air was sampled by means of two five-stage Personal cascade impactor samplers (PCIS). The concentrations were assessed by gravimetry. Eight campaigns 7 to 10 days long were performed between December 2005 and August 2006. To ascertain the effect of main microclimatic and human factors on the aerosol characteristics the size segregated indoor and outdoor particle concentrations were subjected together with temperature, humidity, wind velocity and human activity variables to principal component analysis (PCA). Indoor PM2.5 exceeded the WHO recommended 24-hour limit in 50% and the outdoor concentrations exceeded this limit in 57% of the days measured. During working days the correlation coefficient (cc) between corresponding outdoor and indoor PCIS stages increased with decreasing aerodynamic diameter of collected particles (cc 0.23 -0.82) showing high outdoor-to-indoor penetration of fine particles. Indoor coarse fraction PM2.5-10 (considered to bear allergenic properties) was closely associated with the number of person-hours in the gym during the day (cc 0.77). PCA revealed four factors explaining almost 80% of the dataset variability. Two factors showed good association between outdoor and indoor fine particles, the third involved resuspension of coarse ambient aerosol on dry and windy days, and the fourth one confirmed the importance of human presence for increased indoor coarse aerosol concentrations. Considering high pulmonary ventilation rate of exercising children, and taking into account the fact that on average the mass of indoor PM2.5 contained 44% (+/- 14%) of particles with aerodynamic diameter below 0.25 micro-meters (regarded most toxic), this case study demonstrates that usual coarse and fine aerosol concentrations such as those recorded in the gym may represent a potential health risk to sensitive individuals during indoor physical education.

**11C.03**

Integrated and Real-time PM2.5 Concentrations in Kitchens, Bedrooms, and Outdoors in Highland Guatemala Using both Gravimetric and UCB Particle Monitor. ZOHIR CHOWDHURY (1), John McCracken (2), Eduardo Castro (3), Rufus Edwards (4), Tracy Allen (5), Kirk R. Smith (2), 1 Graduate School of Public Health, San Diego State University 2 School of Public Health, University of California, Berkeley 3 MERTU, Universidad del Valle de Guatemala 4 College of Health Sciences, University of California, Irvine 5 EME Systems, Berkeley

Though indoor air pollution from solid fuel use is responsible for 2.6% of the total global burden of disease (DALYs) and causes between 1.5-2 million deaths each year, the exposure-response curve for particulate matter at high levels has yet to be characterized within a single population. The Randomized Exposure Study of Pollution Indoors and Respiratory Effects (RESPIRE)--with a study population of 534 households from rural Highland Guatemala--provides a unique opportunity to study the long-term effects of high exposure to biomass smoke. We report in here fine particle results in three household microenvironments (kitchens, bedrooms, and outdoors) taken during our RESPIRE study spanning over a period of two years. These households were part of a randomized trial in which half of the households had been given improved woodstoves with chimneys and the other half continued to use open woodfires for cooking. Kitchen PM2.5 concentrations were 1093 +/- 906 microgram/m$^3$ (N = 87) in the open fire homes and 81 +/- 181 microgram/m$^3$ (N = 57) in the improved stove homes constituting a 93% reduction of particles in the improved stove homes (p = 8.53X10$^{-23}$, 95% CI); bedroom concentrations were 73 +/- 350 microgram/m$^3$ (N = 54) in the open fire homes and 26 +/- 48 microgram/m$^3$ (N = 45) in the improved stove homes constituting a 64% reduction of particles in the improved stove homes (p = 0.296, 95% CI); and outdoor concentrations were 44 +/- 31 microgram/m$^3$ (N = 4) in the open fire homes and 14 +/- 3 microgram/m$^3$ (N = 2) in the improved stove homes constituting a 69% reduction of particles in the improved stove homes (p = 0.147, CI=95%). The results demonstrate the potential reduction of particles by installing improved stoves in rural areas where solid fuel is being used for cooking.
11C.04  
Correlations Among Personal, Indoor, and Ambient Pollutant Concentrations: Implications for Studying Exposure to Size Fractionated PM. MOHAMMAD ARHAMI (1), Andrea Polidori (1), Thomas Tjoa (2), Ralph J. Delfino (2) and Constantinos Sioutas (1), (1) University of Southern California, (2) School of Medicine, University of California

Personal PM exposure was studied for 67 elderly subjects at four different retirement communities in southern California between 2005 and 2007. Three of these sites were in the San Gabriel valley, in an area mainly affected by fresh PM emissions, while the fourth site was in Riverside, further east from downtown Los Angeles and downwind of major pollution sources. Two six-week sampling campaigns (phases) were conducted at each community, and integrated (24-hr) personal, indoor and outdoor size segregated PM mass samples (coarse, accumulation and quasi-ultrafine modes) collected at these sites. In addition, hourly indoor and outdoor PM2.5 mass, particle number (PN), elemental carbon (EC), organic carbon (OC), ozone (O3), carbon monoxide (CO) and nitrogen oxides (NO + NO2 = NOx) concentrations were measured at all locations. Four different mixed models and Spearman's correlation coefficients (R) were used to study outdoor-outdoor, indoor-indoor, outdoor-personal and indoor-personal associations between pollutants concentrations and size segregated PM levels. Indoor and outdoor CO, NO2 and NOx were found to be good surrogates for personal particles exposure especially for accumulation of particles. However, at times personal PM was well associated with outdoor and indoor levels, especially for accumulation of mode particles. However, at times personal PM was considerably different from both indoor and outdoor concentrations, mostly because of the presence of substantial indoor PM sources and because both the chemical and physical characteristics of outdoor particles were modified when they penetrated indoor through the building envelope. This study was conducted within the Cardiovascular Health and Air Pollution Study (CHAPS). With almost two years of integrated and continuous data, this study provides one of the richest and most comprehensive data sets of its kind. The outcomes presented here have been used by CHAPS investigators to determine the relationships between cardiovascular outcomes and retirement community exposures by each resident to PM2.5 of indoor and outdoor origin.

11C.05  
Particle Re-suspension and Deposition near Foot during a Simulated Walking. Jung-II Choi (1), Jack R. Edwards (1), Alfred Eisner (2), Jacky A. Rosati (3), (1) North Carolina State University, Raleigh, NC (2) Alion Technologies, RTP, NC (3) US Environmental Protection Agency, RTP, NC

Re-suspension of micron-sized particulate matter (PM) under human activity has been found to have a significant impact on PM concentrations in a building. A precise assessment of short-term re-suspension and deposition of PM is needed for evaluating human exposure. An immersed boundary method for particulate flow in an Eulerian framework is utilized to examine the effects of a simulated walking event on short-term responses of the particle transport near a moving foot. To consider the particle re-suspension and deposition at the foot surfaces, we introduce surface cells which act as reservoirs for mass deposited onto the surfaces. Based on the surface cells, we develop Eulerian / Lagrangian techniques for tracking the surface mass transfer due to the foot motion. We have performed simulations of particulate flow under influences of foot motion neglecting interactions between particulate phase and flow dynamics; i.e., the only deposition from the floor (substrate) to the foot surface is considered for the particle transport when the foot contacts to the floor. We observe the generation and evolution of vortical structures beneath the foot when the foot separates from the floor. The footprints based on the remaining of the particulate mass on the floor are clearly captured and the amount of material on the foot surface is also accurately tracked by the present method during a heel-to-toe walking event. We will extend this work to model the deposition mass flux as a combination of gravitational settling, Brownian diffusion and convective impaction normal to the surface. We will also model re-suspension from the surfaces using the quasi-static rock and roll model of Reeks and Hall (2001). The results will be compared with the recent experiments which provided PIV imaging of particulate capture and re-entrainment during steps of a walking cycle. The effects of particle size, floor conditions and other factors on particle deposition and re-suspension will be discussed.

This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.
Effect of Airflow Characteristics on Indoor Particle Resuspension.

Catherine Mukai, Jeffrey A. Siegel, ATILA NOVOSELAC, University of Texas at Austin

Particles deposited onto surfaces, such as floors and heating, ventilation, and air Conditioning (HVAC) ducts, can be resuspended into the air and affect indoor air quality. In HVAC ducts in particular, on-off cycling of fan operation and turbulent air flow can resuspend previously deposited particles such as pollen, allergens, and combustion byproducts and circulate them into inhabited rooms. Therefore, HVAC systems can act to disperse pollutants rather than removing them from circulation. In addition, human activities, such as walking or closing doors, can cause increased velocities at floor surfaces, which can also resuspend deposited particles. In this investigation, we examine the impacts of bulk velocity, flow acceleration, and turbulence intensity of the passing air stream, as well as relative humidity in the space, on particle resuspension. Studies were conducted in a wind tunnel using hot-wire anemometry to control and measure the impacts of the flow properties of an air stream passing over a substrate seeded with polydisperse KCl particles. We evaluated resuspension from surfaces representative of common ducting and building materials, including galvanized sheet metal, flexible duct and linoleum flooring. The tested particles were in the range of 0.5 to 20 microns, with higher resuspension rates seen for larger particles. The results suggest that bulk velocity and particle size are insufficient to predict resuspension from real surfaces, and that knowledge of acceleration and turbulence are required for accurate assessment of Resuspension critical velocities. The results can be applied to real buildings to determine the magnitude of resuspension and its contribution to indoor particle concentrations.

Distribution of Aeroallergens Measured in Homes.

Suresh Raja, Ying Xu, Andrea R. Ferro, Peter A. Jaques, Philip K. Hopke, Clarkson University, Center for Air Resources Engineering and Science, Potsdam, NY

Asthma prevalence has increased worldwide over the past 20 to 30 years. Over 300 million people worldwide are affected by asthma, which in turn has a high impact on the quality of human life, productivity and health costs worldwide. One hypothesis is that allergens found in homes are strongly associated with the prevalence, incidence, and severity of asthma. Although there are several reports on indoor endotoxin and allergen concentrations in settled dust, there is a dearth of data on airborne allergen and endotoxin concentration and its associated effects on asthma symptoms. The relationship between the settled dust composition and resuspended allergens and endotoxin and its effect on the exposure to asthmatics are not well understood. In this study, settled and airborne dust samples were collected from the homes and school classrooms of asthmatic children from ages 9 to 16 and analyzed for endotoxin and allergens such as dust mite and cockroach allergen and , dog, and cat dander (Der p 1, Der f 1, Bla g 1, Can F 1, and Fel d 1, respectively). Mass-weighted average (MWA) concentrations of endotoxin in airborne samples from schools, living and bed rooms at homes and personal exposure monitors reveal that personal exposure to airborne endotoxin is roughly half the MWA airborne endotoxin concentration measured in living rooms. MWA concentrations of endotoxin and indoor allergens were higher at homes than those measured at schools. Within homes, higher concentrations of airborne allergens and endotoxin were observed in living rooms than in bedrooms.
Isolating Factors that Govern Bioaerosol Inactivation in Weak Electric Fields. Edward Lachendro (1), Peter McKinney (2), MARK HERNANDEZ (1), (1) University of Colorado at Boulder, (2) Strion Air Inc., Louisville Colorado

Weak electric fields have been shown to significantly enhance the capture efficiency of airborne particulate matter through HVAC filters, without the pressure demands of HEPA filters. Electrical enhancements to retrofit conventional HVAC filtration have thus been gaining increased attention as cost-effective control against airborne infectious diseases; however, the rates and mechanism(s) of microbial inactivation in these systems have not been elucidated. A range of weak electric field configurations were investigated for their potential to inactivate common bacterial bioaerosols retained on commercial filter media. Timed series experiments were performed by immobilizing known quantities of bacterial cultures commonly used to model the behavior of pathogenic bioaerosols. The filters hosting these microbes were exposed to different polarities, field strengths and current densities, and the levels of total and culturable bacterial cells immobilized on virgin filters were concurrently measured by direct microscopy and standard plate count techniques before and after electric field exposure.

During these observations, ozone exposure was carefully isolated as a process variable, and was at or below background levels. Electric field exposure(s) caused a significant drop in the recovery of culturable bacteria from filter media as judged by logarithmic declines in plate counts in a range of current density exposures between c.a. 500 microAmp/sq.meter and 100 nanoAmp/sq. meter through a constant potential of c.a. 400 kV/m. In full scale filtration systems maintained at 20°C and constant RH (15% < RH < 55%), electric/ionization field exposure resulted in the following inactivation responses with respect to otherwise identical controls: bacillus subtilis 99% (< 4hrs); pseudomonas aurigenosa 99.9 % (< 6 hr). Results suggest that weak electric fields used to enhance the efficiency of coarse low-pressure drop filters may be an effective engineering technology for rapidly inactivating and/or destroying pathogenic agents in and on polymeric filter media.

The Effect of Coagulation on Size Distributions of Ultrafine Particles Created by Gas and Electric Stoves. Lance A. Wallace (1) Fang Wang (2) Cynthia Howard Reed (1), (1) National Institute of Standards and Technology, Gaithersburg, MD USA (2) Harbin Institute of Technology, Harbin, CHINA

Coagulation is the dominant removal process (compared to deposition and air change) for a sufficiently high concentration of nanoparticles. Characterizing the coagulation impact on particle concentration is essential for estimating the generation rate of UFP by common indoor appliances and activities. The effects of coagulation on ultrafine particle (UFP) size distributions in the range of 2 nm to 64 nm have been studied in a test house at the National Institute of Standards and Technology (NIST). A gas stove and an electric stove were used to generate UFP. UFP were measured with a Scanning Mobility Particle Sizer (SMPS) equipped with a nano-differential mobility analyzer (nano-DMA). Peak concentrations from the stovetop burners/coils occurred at particle sizes of approximately 5 nm to 7 nm. Total number concentrations were high enough to result in high coagulation rates. Several existing algorithms for calculating particle collision probabilities were compared to observed particle concentrations during the decay periods following particle-generating events. These models included corrections for van der Waals and viscosity effects as well as for possible fractal shapes of the aggregated particles. The van der Waals force depends on particle composition, parameterized by the Hamaker constant. Since the particles from the gas stove have different compositions than those from the electric stove, two choices of the Hamaker constant (20 kT and 200 kT) were tested. Although no single correction factor provided a good fit to observations in all cases, the van der Waals/viscosity plus fractal correction using 200 kT for the Hamaker constant was often the best fit for the size distributions produced by the electric stovetop. For the gas stove, the van der Waals/viscosity correction of 20 kT without a fractal correction often provided the best fit.
12C.04
Inhalation Intake of Secondary Organic Aerosol from Ozone-initiated Indoor Chemistry. CHARLES J WESCHLER (1), William W Nazaroff (2), (1) Environmental & Occupational Health Sciences Institute, UMDNJ & Rutgers, (2) University of California, Berkeley

The average indoor concentration of secondary organic aerosol (SOA) derived from ozone-initiated indoor chemistry, $[\text{SOA}]_{\text{avg}}$, is approximated as the ratio of the rate of indoor SOA production to the rate of its removal, with the latter dominated by ventilation and deposition to indoor surfaces. To estimate the rate of SOA production, we consider limonene as a representative indoor chemical that reacts with ozone to form condensed-phase products. We estimate $[\text{SOA}]_{\text{avg}} \approx 4 \micro g \text{ m}^{-3}$, based on an outdoor average ozone level of 50 ppb, an air-exchange rate of 0.5 h$^{-1}$, a surface ozone loss rate of 3 h$^{-1}$, an indoor average level of 10 ppb for the sum of ozone-reactive organic compounds, a second order reaction rate constant of $5 \times 10^{-6} \text{ ppb}^{-1} \text{s}^{-1}$, based on the ozone-limonene reaction, an SOA yield of 0.2, and a mean SOA molecular mass of 180 g/mol.

The inhalation intake is the mass of pollutants inhaled by an exposed population over a specified period. We estimate the annual US inhalation intake of SOA derived from ozone-initiated indoor chemistry as the product of three terms: $I \approx [\text{SOA}]_{\text{avg}} \times P \times B$, where $P$ is the exposed population, and $B$ is the indoor air volume breathed per person per year. With $[\text{SOA}]_{\text{avg}} \approx 4 \micro g \text{ m}^{-3}$, $P \sim 300$ million and $B \sim 4000 \text{ m}^3 \text{ y}^{-1}$ per person, we estimate $I \sim 5 \text{ t/y}$. Reviews of the literature suggest that the average exposure concentration for outdoor fine particles (PM2.5) is $\sim 10 \micro g / \text{m}^3$, which would correspond to a population intake of $\sim 14 \text{ t/y}$. Hence, the US population intake of SOA derived from ozone-initiated indoor chemistry is of similar magnitude as the intake attributable to all outdoor PM2.5. Absent evidence to support an argument that indoor-generated SOA is less harmful than ambient PM2.5, this analysis suggests that the morbidity and mortality associated with ambient ozone may be at least partly attributable to inhalation indoors of the particulate-phase byproducts of ozone-initiated chemistry.

12C.05

Many household products are a source of particulate matter (PM) in indoor environment due to reactions of volatile organic compounds (VOCs). One of the important contributors to indoor PM is the ozonolysis reaction products of essential oils, which act as fragrance and as cleaning agents. The ultimate goal of this work is to measure the contribution of essential oil components towards PM formation and relate the composition of PM from this source to adverse health effects of indoor PM. Herein, effort is made to understand speciation studies during PM formation starting with realistic essential oil mixtures and extending the work to commercially-available air fresheners. PM is generated in a 5.5 m$^3$ Teflon environmental smog chamber by the ozonolysis of monoterpene-containing essential oil standards and/or commercially-available essential oil mixtures. PM concentration is measured using a scanning mobility particle sizer (SMPS). The reaction is simultaneously monitored for changes in temperature and ozone concentration. Speciation studies are carried out by collecting the PM onto quartz filters at various time points during each experiment. The PM from filter samples is solvent extracted from the filters and concentrated by evaporation. The extract, which contains monoterpene-derived carboxylic acids, ketones, and alcohols, is derivatized by silylation and analyzed by a Varian gas chromatography-mass spectrometry (GC/MS). The GC/MS is equipped with an ion trap analyzer, which enables detection and characterization using: electron impact ionization (EI) and chemical ionization (CI); equipped with MS/MS capability. The results of this research provide the composition of a portion of indoor PM derived from VOC/ozonolysis reactions.
Secondary organic aerosol from alpha-pinene ozonolysis in a dynamic chamber system: density and particle bound reactive oxygen species (ROS) measurements. XI CHEN and Philip K. Hopke, Clarson University

The formation of secondary organic aerosol (SOA) produced from alpha-pinene ozonolysis were examined using a dynamic chamber system that allowed simulation of ventilated indoor environments. Particle-bound reactive species (ROS) including peroxides, peroxy radicals and ions may be associated with adverse health effect observed upon exposure to SOA. Particle-bound ROS could penetrate deeper into the lungs and deliver oxidative stress to the tissue causing damage. This process has been suggested to occur in indoor environments where people stay most of the times. Quantitative particle-bound reactive oxygen species (ROS) measurements were conducted to determine ROS concentrations for filters collected from our chamber system. The determination of ROS was performed by using a fluorogenic probe, dichlorofluorescin (DCFH). Fluorescent intensities were converted to equivalent H2O2 concentrations. Recent studies have found that changes in composition of the SOA depend on the precursor VOC concentrations and these compositional changes are reflected in changes in density. Density is an important parameter needed to convert from volume to mass concentration using particle size distribution data. In this study, SOA densities were estimated from scanning mobility particle sizer (SMPS) measurements and mass collected onto filters for volume and mass concentration, respectively.
5A.01
Generation of E. coli Bacteria Bioaerosols using Multiplexed Grooved Nozzles Electrospray. KYOUNGTAE KIM (1), Byung Uk Lee (2), Sangsoo Kim (1), (1) Korea Advanced Institute of Science and Technology, Republic of Korea (2) Konkuk University, Republic of Korea

The grooved nozzle was developed for the high flow rate electrospraying. In this experiment, the generation of the bacteria bioaerosols using the specially designed multiplexed grooved nozzles was tested. The multiplexed grooved nozzles consist of five grooved nozzles and a new type of an extractor. The grooved nozzles were installed in the air-tight box, which was filled with carbon dioxide gas to stabilize the electrospray of the bacteria suspension. E. coli bacteria suspension was used as a spraying liquid to generate the bioaerosols. The flow rates were 0.5 and 1.0 ml/h per jet and the sampling time were 30 and 60 sec. The bacteria suspension was sprayed in a multiplexed grooved mode and the generated bacteria were sampled on an agar plate inside of the Anderson Impactor to check the biological viability. We then incubated the sampled bioaerosols on the agar plate of the impactor for 1 to 2 days before enumerating the colonies. For all experimental conditions, almost all the sampled E. coli bioaerosols beneath the nozzles of the impactor formed the colonies. The number of observed colonies on the agar plates of all conditions was around 400 and this number corresponds to the number of nozzles of the Anderson impactor. The experimental results showed that the multiplexed grooved nozzles were suitable for the generation of the bacteria bioaerosols at the high flow rates and the generated bacteria maintain their viability under highly electrically charged conditions.

5A.02
Production of PLGA Particles for Drug Delivery Systems using Multiplexed Nonconducting Grooved Nozzles Electrospray. KYOUNGTAE KIM, Sangsoo Kim, Korea Advanced Institute of Science and Technology, Republic of Korea

Biodegradable polymeric particles have high-value-added applications including drug delivery systems. Especially PLGA (poly-lactic-co-glycolic acid) is widely used for the drug delivery because it is well known to have the unique ability of high biocompatibility, innocuousness, physical properties, and stability. The nonconducting grooved nozzle is pertinent to produce very small droplets at the high flow rates. The multiplexed nonconducting groove nozzles were employed to produce the PLGA fine particles using the spray evaporation method. The multiplexing system consisted of five nonconducting grooved nozzles and a new type of an extractor. The multiplexing compactness was 12 jets per centimeter square. The operating parameters were flow rates and PLGA concentrations. The sampling time was 30 sec and the 2,2,2-trifluoroethanol (TFE) was used for a solvent. The PLGA solution was sprayed in a multiplexed grooved mode and the generated droplets were sampled on an aluminum mount to measure the particle size using the scanning electron microscope (SEM). The produced PLGA particles have size ranges of around from 300 nm to 700 nm with the monodispersity as changing the flow rates and concentrations. The experimental results showed that the multiplexed nonconducting grooved nozzles were suitable for the production of monodisperse PLGA fine particles in a few seconds and could increase the producing rate dramatically.
Decoration of Carbon Nanotubes with Electrosprayed Nanocrystals via Electrostatic Force Directed Assembly.

SHUN MAO, Ganhua Lu, Junhong Chen, University of Wisconsin-Milwaukee

Hybrid nanomaterials consisting of nanocrystals distributed on the surfaces of carbon nanotubes (CNTs) represent a new class of materials. These materials could potentially display not only the unique properties of nanocrystals and those of CNTs, but also additional novel properties due to the interaction (e.g., electronic or optical) between the nanocrystal and the CNT. Such hybrid nanocrystal-CNT structures have been shown to be promising for various applications, including chemical sensors, biosensors, nanoelectronics, photovoltaic cells, fuel cells, Li-ion batteries, and hydrogen storage. An efficient and simple technique that combines electrospray and directed assembly for decorating carbon nanotubes with nanocrystals is presented. Colloidal CdSe and Au nanocrystals have been successfully electrosprayed and assembled onto random CNTs and CNT arrays in a controlled manner. The high charging level on the electrosprayed aerosol is responsible for the successful assembly. Semiconducting CdSe nanocrystals (quantum dots or QDs) are highly emissive and attractive for photonics applications, such as in solar cells and light emitting devices. Metallic Au nanocrystals are useful for catalysis and biosensing applications. Attaching conducting substrates, e.g., CNTs, to CdSe QDs and Au nanocrystals can promote direct and efficient charge transfer and hence significantly increase the device/process efficiency. This technique can be used to assemble various compositions of nanomaterials onto different substrates and enables a versatile route to produce novel hybrid nanostructures.

Generation of nanoparticles for drug delivery using the electrospray.

BEGONA ALMERIA, Alessandro Gomez, Yale University

The use of the electrospray for the generation of nanoparticles for drug delivery applications is presented. The particles, consisting of a matrix of biodegradable polymer (PLGA) encapsulating an active agent, are usually made by emulsion methods, which involve multiple steps, have a low throughput and typically fail to produce particles of narrow size distribution at the nanometric scale. The electrospray can overcome these limitations and generate monodisperse nanoparticles with relative ease. Multiplexing of the source by microfabrication, that has been successfully demonstrated in our laboratory, can dramatically increase the throughput.

After increasing the conductivity of an organic solvent dimethyl sulfoxide (DMSO) by adding ~0.2% by weight of salt, we operated a stable electrospray of the PLGA-DMSO-salt solution in the cone-jet mode at flow rates of ~5uL/h, which corresponds to an estimated droplet size of ~200nm. PLGA particle relics were generated by subsequent spray drying with diameters between 50-80nm, as measured by SEM. To improve the monodispersity of the nanoparticles and suppress Coulomb fissions during the evaporation process, a corona discharge was introduced to prevent the precursor droplets from reaching the Rayleigh limit.

Work is under way to stabilize a twin-fluid co-axial electrospray with the unique capability of adding surface modification to the nanoparticles by either coating them with ligands to enable targeted drug delivery or by PEGlation for controlled release.
5A.05  
Charge Injection into Dielectric Liquids from Electrosprays of Highly Conducting Liquids. CARLOS LARRIBA, Yale University

Electrosprays of conducting liquids into dielectrics has been pursued for over 15 years, being Professor Pierre Atten the first one who stabilized a liquid metal Taylor cone in an oil bath. Here, we take over his technique to electrospray a highly conducting ionic liquid (IL) inside a hydrocarbon such as heptane. The IL Taylor cone injects charges into the heptane and once the heptane is sufficiently charged, it forms a subsequent cone which vaporizes the heptane liquid into fine drops. Both liquids have been studied. On one side, the current produced by the IL Taylor cone is of several tens of nanoamps in contrast to the atmospheric electrospray which produces several microamps. This was expected as mobilities in liquids become much smaller than in air therefore limiting the current. The charge over mass ratio reveals the possible presence of ions being evaporated from the IL cone at 3.5kV. On the other side, at this voltage, very stable cones of heptane can be observed leaving a cloud of drops of a few microns. At the smallest flow rates, drops of 3 microns of mean diameter size have been measured with the use of a Phase Doppler Particle Analyzer (PDPA). The heptane remains practically pure as barely 60 parts per billion of IL are needed, making this tandem electrospray unique for combustion purposes. Many questions remain to be discussed as to which liquid is most appropriate to inject the charges or whether ion emission can be reached or not inside the insulating liquid.

5A.06  
Production of Clusters from Electrosprays of Ionic Liquids. JUAN FERNANDEZ GARCIA, Yale University

Evidence of the feasibility of generating singly-charged, highly massive molecule-ion clusters, via electrospray atomization of ionic liquids in a vacuum, is presented. As of today, ionic liquids based on the cation 1-alkyl, 3-methyl imidazolium have been tested. In particular, electrospraying of the liquid 1-ethyl, 3-methyl imidazolium - dicyanamide, EMI-[N(CN)2], leads to the emission of clusters that span from a single cation to a ten-molecule + cation group, with the corresponding masses covering a range from 111.2 to 1883.2 Dalton.

The characterization of the masses of these clusters has been accomplished by means of an experimental device consisting of a single-gate Time of Flight setup installed into a vacuum chamber. The liquid was injected into the chamber through a silica capillary, from whose tip it was electrosprayed, by application of a high voltage to the reservoir containing the liquid, with respect to a hollow extractor plate. The received cluster current was measured using a two-stage, fast-response electrometer.

Although all the experiments carried out to date have been performed in vacuo, there is no apparent reason why the same results would not be achieved at atmospheric pressure. This leads to a functionally simple source of highly massive, non-volatile particles which, after being discriminated using a proper focusing method, can be of application in fields such as biological secondary ion mass spectrometry.
5A.07  
**Jet Formation and Continuation Time in the Pulsed Cone-Jet Mode of Electrohydrodynamic Atomization.**
JOONGHYUK KIM, Hyuncheol Oh, Sangsoo Kim, KAIST

We reported simulations and experimental data about the jet formation and continuation time in the pulsed cone-jet mode of electrohydrodynamic atomization. Electrohydrodynamic atomization process is caused by the balance between the electric force and the surface tension of liquid. The one of important parameters in the electrohydrodynamic patterning is the width of drop. It is given by the product of the time for liquid emission and liquid flowrate. The time for liquid emission in the pulsed cone-jet mode means the time for the meniscus and jet formation and continuation in one pulse.

The experiments for the electrohydrodynamic atomization were performed by the electric system connected to a stainless steel capillary nozzle and a stainless steel plate. An arbitrary pulse generator and a high-voltage amplifier were used to apply the pulsed electric field to the nozzle and plate. The time for the meniscus and jet formation and continuation was monitored by a high-speed CMOS camera equipped with a long-distance microscope the microscope. The meniscus and jet formation and continuation process is also simulated using a computational fluid dynamics computation based on the Taylor-Melcher leaky-dielectric fluid model and the volume of fluid model to predict the time for jet generation and continuation. The simulated flowrate-time, electric field-time and liquid properties-time were in good agreement with experimental results.

These results are helpful to understand the transient electrohydrodynamic atomization and produce on-demand patterns with accurate size.

5H.01  
**Assessing the FRM-Likeness of Continuous PM2.5 Measurements in EPA's AQS Database.** ADAM REFF, Tim Hanley, Lewis Weinstock, U.S. EPA, Office of Air Quality Planning and Standards

Instruments that collect hourly mass measurements of ambient fine particulate matter (PM2.5) were deployed into the EPA-required state and local monitoring networks at the beginning of this decade. Data from most of these monitors were being used to calculate the air quality index (AQI) by October 2003, when EPA launched year-round reporting of the PM2.5 component of the AQI as part of AIRNOW (www.airnow.gov). In October 2006, EPA finalized new performance criteria for approval of PM2.5 continuous methods based on a data quality objective process as described in the code of federal regulations (CFR, Title 40, Part 53). Although continuous PM2.5 instruments have a number of potential advantages over the integrated filter-based methods currently designated as federal reference methods (FRM), it is only in recent months that the first continuous PM2.5 method has received approval as a federal equivalent method (FEM).

This work examines the FRM-likeness of continuous PM2.5 data currently archived in EPA's Air Quality System (AQS) database. Data collected by 647 collocated pairs of continuous and FRM PM2.5 samplers during the 2004-2006 time period was analyzed. The major objective of this work is to ensure that the continuous data is classified into newly created AQS parameter codes which indicate that the data either does (code #88502) or does not (88501) meet the FRM performance criteria described in the CFR. Nationwide spatial and temporal trends of FRM-likeness exhibited by the different continuous instrumental methods will also be examined. The goal is to more specifically characterize the quality of the continuous PM2.5 data in AQS, which will benefit processes such as future considerations of FEM status, AQI reporting, and evaluation of air quality models.
5H.02  
Test Results for the Thermo Scientific TEOM Monitors (1405-DF and 8500C), FH62C14, and SHARP Monitors for a US-EPA FEM PM2.5 Method Campaign. JEFFREY AMBS  
Kevin Goohs, Thermo Scientific

The Thermo Scientific PM$_{2.5}$ FEM test campaign is described. Four different instrument models were subjected to a year-long test campaign at five different test locations in order to complete the testing as required by the US-EPA FEM requirements. The four monitors tested were the TEOM Series 1405-DF, the Filter Dynamics Measurement System (FDMS) Model 8500C, the FH62C14, and the Model 5030 SHARP Monitor. The 1405-DF and 8500C TEOM monitors both utilize the FDMS are both based on the proven TEOM technology, while the 1405-DF also includes a dichotomous splitter to provide simultaneous PM$_{2.5}$ and PM$_{10-2.5}$ results. The FH62C14 and the SHARP monitors are both based on beta attenuation and include an intelligent moisture reduction system. In addition, the SHARP adds light scattering photometry in order to provide near a faster time resolution sample result.

The instruments were tested in four regional locations as indicated by the US-EPA FEM test requirements. These test locations were designed to challenge the candidate methods by sampling in different geographical regions and at different times of the year. The instruments were tested in Bakersfield, CA, Denver, CO, East St. Louis, IL, Queens, NY, and New Haven, CT., starting in February 2007 with testing completed in January 2008. The results of the test campaigns are presented.

5H.03  
On the Development of Beta Attenuation and Hybrid Aerosol Monitoring Methods. KEVIN GOOHS, Thermo Fisher Scientific

The use of beta attenuation as a surrogate for aerosol mass concentration measurement has long been accepted in many air quality monitoring networks and studies. Further advances in the art have been made by using hybrid techniques to enhance precision and create highly time resolved data sets for urban airshed modelers. In an effort to increase the tools available to both field technicians and air pollution researchers, a discussion of hybrid aerosol monitoring techniques are discussed.
5I.01
The Continuation of the Personal Data RAM. KEVIN GOOHS, Pedro Lilienfeld, Wayne Harmon, Thermo Fisher Scientific, Franklin, MA

The science of personal aerosol monitoring is continuously evolving. One method that continues to prove useful is the Mie-scattering of incident light in the presence of aerosol. Further emphasis related to particle size discrimination enhances the ability to accurately gauge risk assessment versus dosimetry, while recognizing the importance for gravimetric references. For these very reasons the need for accurate volumetric flow control is paramount to a successful measurement of aerosol exposure. It is further emphasized that the real-time measurement of aerosol by scattered light, in the presence of humidity, can positively bias highly time resolved data sets. Through the combination of legacy MIE pDR optics, volumetric flow control, ACGIH-traceable cyclones, RH correction function and NIOSH methodology a useful personal aerosol monitor and sampler are described.

5I.02

The Clean Air Status and Trends Network (CASTNET) is a national monitoring network aimed at quantifying dry acidic deposition (namely sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid), ozone, and other atmospheric pollutants. Since denuder sampling of gaseous species is usually expensive and time consuming, CASTNET currently uses a multiple-filter canister for sampling all target species. Unfortunately, particulate nitrate often volatilizes from the initial filter and is collected on a secondary nylon gas phase collection filter; thus, nitric acid is overestimated and particulate nitrate is underestimated. Since these species have very different deposition velocities, this bias interferes with the accurate determination of nitrogen deposition. Ammonia, which is an important yet poorly quantified contributor to nitrogen deposition and fine particle formation, is measured only in the particulate phase and is also subject to loss via volatilization. To rectify these shortcomings, a compact, extractable denuder has been designed to fit into the Speciation Air Sampling System (SASS) instrument, to provide a series of denuders and filters for a more complete picture of species concentrations and partitioning. The work presented will focus on denuder development and testing for the efficiency and applicability of the new denuders for ammonia, nitric acid, and sulfur dioxide sampling in CASTNET or other monitoring networks. Phase one of the study consists of efficiency testing and performance comparison to commercial URG denuders using lab-generated gaseous species. Phase two will involve sampling ambient air (containing particulate and gaseous species) alongside industry-standard instrumentation for overall performance comparison. During both phases, attention will be paid to documenting blanks and developing protocols to maximize ease of handling and minimize error.
Efficiencies of Portable BioStage and RCS High Flow in Measuring Culturable Bacteria and Fungi in Shanghai, China.

Shiqi Zhen (1,3), Huili Zhang(3), Lihong Yin (1), Maosheng Yao (2), Minghao Zhou(3), and Xiaodong Chen (3), (1) Shoutheast University, Nanjing, China, (2) Peking University, Beijing, China , (3) Jiangsu Center for Disease Prevention and Control

BioStage traditionally restricted to indoor sampling can now be used to sample at remote sites through use of QuickTake 30 pump. However, its efficiencies have not been adequately validated against available portable samplers such as RCS High Flow.

In this study, we have compared the biological efficiencies of BioStage and RCS High Flow when measuring culturable bacteria and fungi concentrations in train station, subway, hotel, airport and beach side in Shanghai, China. During the experiments, BioStage and RCS High Flow operated at flow rates of 28.3 and 100 L/min, respectively, were placed in the same environments for 5 min. Bacteria and fungi samplings were alternated. The samplings for bacteria and fungi in these locations were conducted three times independently, and for each repeat three bacterial and three fungal air samples were obtained for each sampler in each of the locations.

The average temperature and humidity in this study were observed around 20-24 degrees C and 40-50%, respectively. Results indicated that BioStage consistently reported higher (statistically significant) fungal concentrations than RCS High Flow, as much as two times in some cases, in all locations. The same was observed for bacterial concentration except that no statistically significant difference was found between two samplers for airport and beach side. The total microbial load was observed highest for the train station with fungal concentration about 550 CFU/m3 and bacterial concentration about 469 CFU/m3. Airport was shown to have lowest microbial concentrations, about 60 CFU/m3 for both bacteria and fungi.

When sampling larger fungal species, BioStage outperformed RCS High Flow as observed in this study, and for bacterial species with lower concentrations the performances of these two samplers seemed identical. The observed differences were likely due to the samplers' cut off size and the sampling velocity. BioStage might still remain a robust bioaerosol sampler in many situations.

Characterization of a Slit-jet Nebulizer for use in Bacterial Inhalation Studies.

JOHN TROMBLEY, Jeremy Boydston, Melissa Bridgers, Zara Llewellyn, Mary Minyard, Larry Bowen, Southern Research, Birmingham, AL

Vegetative bacteria are susceptible to oxidative stress, desiccation, and sheer force stress when aerosolized with commercially available nebulizers which may result in decreased viability. We designed and developed a Slit-jet nebulizer, based on the Babington principle(1), to operate at low pressure and deliver large liquid droplets to protect bacterial cells during aerosolization. We determined the volumetric flow rate, aerosol output, liquid use rate, and liquid droplet diameter of the Slit-jet nebulizer using distilled water and Synfluid PAO 2cSt (Chevron Phillips, The Woodlands, TX). Volumetric flow rate, aerosol output, and liquid use rate were similar to published data for the Collison nebulizer(2) (BGI, Incorporated, Waltham, MA). However, the droplet diameter of the Slit-jet nebulizer was significantly larger than the droplet diameter of the Collison nebulizer. Droplets produced by the Slit-jet nebulizer, 58% were greater than or equal to nine microns and 51% were greater than or equal to 14 microns; whereas, 68% of the droplets generated by the Collison nebulizer are less than or equal to 2.5 microns (2). We determined the viability, concentration, and particle size distribution of aerosolized Yesinia pestis KIM 6+ and KIM 10+ (YpK6 and YpK10) with the Slit-jet and Collison nebulizers operated a nine and 30 psig, respectively. In comparison, there was no difference in viability for YpK10 between nebulizers. Conversely, we observed a 36% decrease in YpK6 viability for the Collison nebulizer. Despite having a lower flow rate, Slit-jet YpK6 and YpK10 aerosol concentrations were 33% and 35% higher than respective Collison concentrations in our test system. The particle size distribution (MMAD, GSD) of YpK6 and YpK10 aerosols was 1.4 microns, 1.5 and 1.3 microns, 1.5, respectively, for the Slit-jet nebulizer and 1.0 microns, 1.6 and 1.0 microns, 1.5 for the Collison nebulizer. In conclusion, the Slit-Jet nebulizer is an option for use in bioaerosol studies.
5I.05

In order to better understand the adverse effects of atmospheric aerosol particles on human health and the environment, a real-time technique for particle concentration and composition determination is necessary. While it is not yet commonly used for environmental analysis, the ionic nature of many aerosol components make microchip capillary electrophoresis (micro-CE) an appropriate technique for rapid aerosol composition determination and quantification. The small size and robustness of the microchips make this technique attractive for long-term field use, and fast separation times allow for semi-continuous particle analysis. Reduced sample requirement is another benefit; however, small volumes of solution within the microfluidic channels make interfacing the micro-CE system to external flows challenging. Here we present the development of a micro-CE system that includes an interface between a larger flow sample channel meant to mimic the output from a traditional aerosol sampler such as the PILS, and 10 micrometer channels that serve to inject sample into the microfluidic device. Mathematical modeling of flow resistance, and observation by fluorescence microscopy are used to determine optimal dimensions, voltages, and injection times for the device. Studies are currently underway to observe how detection sensitivity and separation efficiency are affected by the velocity and type of flow (e.g. gravity, hydrodynamic, or electrokinetic) in the continuous flow sample channel. The electrochemical detection used in the microchips will allow for trace analysis of organic acids, inorganic acids, and tetrols, all of which are major components of aerosol particles. The optimized device, interfaced with an aerosol collector, will be used to analyze standard samples, and results will be compared to conventional systems such as ion chromatography and LC-MS. Ultimately, this system will be field-tested in order to validate its use in real world applications of aerosol analysis.

5I.06
Development of an Injection System for Large Particles in an Aerosol Wind Tunnel. ANDREW MAY (1), Sang-Rin Lee (2), Suresh Dhaniyala (1), Thomas M. Holsen (1), (1) Clarkson University (2) University of Iowa

A method for both uniformly injecting and successfully sampling particles larger than 30 micron in an aerosol wind tunnel has been developed and optimized. The final injection and sampling system designs were obtained after several design iterations. Initially, a large particle aerosol generator was located inside the tunnel to avoid seeding difficulties associated with gravitational deposition of these particles in the wind tunnel settling section. The particle concentrations in the tunnel were initially measured using active, open-face, polycarbonate filters. However, several problems arose from this setup. The blunt body nature of the particle generator created a large wake region downstream, thus affecting the spatial distribution of particles at the test section. Additionally, there were mass measurement issues with the polycarbonate filters, and challenges of maintaining isokinetic sampling condition for the active samplers.

To overcome these challenges, several configurations of aerosol injection and wind-tunnel aerosol sampling systems were developed and tested. For particle seeding, the successful technique was the moving injection system while for particle sampling, an array of passive impactors was most effective. A parametric study of the 2D traversing system was conducted to determine optimal speed and step size for uniform aerosol seeding. Measurements with the passive impactors suggested that uniform injection indeed was possible over an area of 10 x 20. The developed wind-tunnel injection and sampling systems are appropriate for inlet testing under a range of ambient conditions.
Design and Development of a Novel Instrument for Large Particle (PM >10) Size Separation: Curved Channel Size Separator (CCSS). Krishanu Banerjee, Thomas Holsen, Suresh Dhaniyala, Clarkson University

Particles larger than 10 um (PM >10) are major constituents of dry deposition and very important in cloud studies. However because of their inertia it is very difficult to measure their ambient concentration using traditional sampling approaches. The objective of this research is to develop a technique to separate large particles by size so that their size distribution can be determined. For effective analysis of particle composition, it is critical to avoid artifacts due to the inadvertent gas-particle conversion during sampling and collection.

In the proposed instrument a curved pipe (90 degree bend) geometry is used. Sampled aerosol flow and clean air passes thorough the pipe and particles are collected in different channels by size. Larger particles, due to their higher settling velocity, are captured in earlier channels. Computational fluid dynamics (CFD) modeling was used to evaluate two types of cross sectional geometries: circular and rectangular. In the circular geometry, particles are not well separated by size due to the formation of two counter rotating vortexes in the pipe cross section. This effect is not as prominent in the rectangular cross sectional geometry so this configuration can separate particles with reasonable resolution. In addition for the rectangular design the particle residence time in the pipe is increased which helps in size separation. CFD studies indicate that the resolution of this sampler depends on : clean flow to aerosol flow ratio, curvature ratio of pipe, aspect ratio (length: width), settling velocity and sampling ratio. A three channel size separator has been built and the performance of the instrument investigated. Modeling and experimental results will be presented.

A Rotary Sampling Disc for Unbiased Measurements of Large Particle Aerosols in a Wind Tunnel. Kirsten A. Koehler (1), John Volckens (1), Renee Anthony (2) and Michael VanDyke (3), (1) Colorado State University, Fort Collins, (2) University of Arizona, Tucson, (3) National Jewish Medical and Research Center, Denver, CO

We have designed and built a bluff-body Rotary Sampling Disc (RSD) to acquire unbiased samples of supermicron aerosols in a wind tunnel setting. The dispersion of large (i.e., inhalable) aerosols typically yields spatial and temporal inhomogeneities within wind tunnel cross-sections owing to the high settling velocities of particles with aerodynamic diameter greater than 10 micro-meters. Such inhomogeneities complicate intercomparison tests when it is desired to array multiple samplers in the tunnel cross-section. The RSD is a 40 cm diameter aluminum disk mounting eight samplers at equal angle increments along its outer edge. Rotation of the RSD allows for acquisition of an unbiased sample, as each sampler traces an identical, circular path in time. Flow though each sampling port is regulated by a critical orifice mounted on a ten-port aluminum manifold at the back of the disc. The manifold connects to an aluminum tube (2.5 cm diameter x 45 cm length) that serves simultaneously as the axis of rotation and the source of air flow. In this way, the flows through all eight samplers can be accommodated with a single pump. At the rear of the aluminum tube is a swivel fitting, allowing the tube and disc assembly to rotate without twisting the air lines to the pump. A bicycle chain and sprocket assembly connects the RSD to a gear motor, which is controlled with an adjustable speed controller. The gear motor and air pump are located below the wind tunnel, such that their exhaust will not impact testing inside the wind tunnel. We present results from wind tunnel evaluations of the RSD, showing improved agreement between samplers exposed to inhalable aerosols for rotating vs. non-rotating conditions.
5J.01
Pattricia Fritz (1), Brian P. Frank (2), Daniel Hershey (2), Lupita Montoya (1), (1) Rensselaer Polytechnic Institute, NY, (2) New York State Department of Environmental Conservation, Albany

Microparticles can be readily visualized and their gross surface characteristics assessed using the Scanning Electron Microscope (SEM). To quantify characteristics such as surface roughness, however, another method was used for comparison purposes. Atomic Force Microscopy (AFM) can, with proper sample preparation, provide a method to obtain such quantification for microparticles less than a few microns in geometric size. While SEM can be used to readily image particles larger than a few nanometers, limitations are reached with particles whose largest dimension is less than 10 nanometers. For particles in the smaller size range, AFM can be used to confirm nanoparticle geometric size and to determine if significant size alteration or agglomeration occurs in nanoparticle suspensions over time. A sample preparation protocol was developed that is amenable for AFM evaluation of polymeric microparticles and inorganic nanoparticles in aqueous solutions. A parallel protocol was developed for SEM sample preparation. SEM and AFM images were compared for particle samples prepared using the parallel protocols to identify and address any potential instrument artifact or operator bias in quantifying geometric particle size of micro- and nanoparticles.

5J.02
Retrieval of aerosol extinction in the lower troposphere based on MAX-DOAS measurement and its application for improved retrieval of trace gas profiles.
Hanlim Lee(1), H. Irie(2), YOUNG J. KIM(1), Jinsang Jung(1), Chulkyu Lee(3), (1) Advanced Environmental Monitoring Research Center (ADEMRC), Gwangju Institute of Science and Technology (GIST), Gwangju, Korea (2) Frontier Research Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Japan (3) Department of Physics and Atmospheric Science, Dalhousie University, Canada

The capability of Multi-Axis Differential Optical Absorption spectroscopy (MAX-DOAS) of retrieving information on atmospheric aerosol extinction based on O4 measurement has been recently demonstrated (Wagner et al., 2004, Sinreich et al., 2005, and Frieb et al., 2006). For determination of O4 Slant Column Density (SCD), its absorption bands in UV (343nm, 360 nm, and 380nm) or visible (477 nm, 532 nm, 577 nm and 630 nm) regions are utilized. This study presents the aerosol retrieval results based on O4 data measured by MAX-DOAS instrument at UV absorption bands (338 nm and 367 nm) at urban sites in northeast Asia; Beijing (16 August ~ 10 September 2006), Seoul (April 15 ~ June 15 2007), and Gwangju (22 February ~ 26 April 2008). UV MAX-DOAS based aerosol extinction coefficient and aerosol optical depth (AOD) obtained for the lower surface layers were compared with those obtained by lidar and sunphotometer measurements. The advantages and shortcomings of UV MAX-DOAS measurement for aerosol extinction retrieval are also discussed in detail. This study also presents the feasibility of improvement in retrieval of NO2 and HCHO profiles from MAX-DOAS data by utilizing the retrieved aerosol extinction profiles in the radiative transfer model (RTM) calculations. Surface NO2 mixing ratio values measured by an in-situ (chemiluminescence) analyzer were used to validate those retrieved by MAX-DOAS measurement.

(Acknowledgement)
This work was supported in part by the Korean Ministry of Environment as part of The Eco-Technopia 21 Project.

(References)
7A.01 Use of Electrospray for Aerosolizing Viruses in Filter Testing. SERGEY A. GRINSHPUN (1), Robert M. Eninger (1), Christopher H. Hogan, Jr. (2), Pratim Biswas (2), Atin Adhikari (1), Tiina Reponen (1), (1) University of Cincinnati, Cincinnati, OH; (2) Washington University, St. Louis, MO

Nebulization has been conventionally used for aerosolizing biological particles (including viruses) as a part of filter testing, in which the aerosol concentration is measured up- and downstream of the filter. Due to presence of contaminants, solutes, and viral aggregates created in the nebulization process, the challenge aerosol is often poorly defined which cause uncertainties in relating the particle filtration findings to the virion characteristics. In this study, a charge-reduced electrospray was examined as an alternative for aerosolizing MS2 bacteriophage viruses and biologically-inert monodisperse dextrose particles to test the performance of three filter swatch samples - the inner layers of commercially available surgical mask and two filtering-facepiece respirators (N95 and N100). Electrospray produced a relatively contaminant-free aerosol with a sharp peak at the mobility diameter corresponding to the single MS2 virion (approx. 25 nm). With appropriate settings, a similar size distribution was observed for dextrose particles aerosolized using electrospray. For MS2 virions, the electrospray-generated particles were nearly monodisperse unlike those generated by the Collison nebulizer. We observed that the filtration behavior of the electrosprayed and nebulized MS2 particles did not differ. However, the filter penetration of the electrosprayed dextrose particles exceeded that of the MS2 particles for both the surgical mask and N95 filter samples. This finding was attributed in part to the difference in electrical properties and shapes of MS2 viruses and dextrose particles (with dielectric constants of 55 and approx. 3, respectively). We concluded that although nebulization produces a polydisperse aerosol, the generation method does not significantly influence the filtration behavior of the MS2 aerosol. We also concluded that the differences in filter penetration between MS2 virions and their dextrose simulants were rather consistent with (a) theory based upon differences in the dielectric constant of MS2 and dextrose (b) recently published data about the effect of shape of nanoparticles on filtration.

7A.02 Using Electrospray to Form Plasmid DNA/Polyethylenimine (PEI) Polyplexes for Nonviral Gene Delivery. YUN WU (1, 2), Zhengzheng Fei (1, 2), L. James Lee (1, 2), Barbara Wyslouzil(1, 2), (1) Department of Chemical and Biomolecular Engineering, The Ohio State University (2) NanoScience and Engineering Center, The Ohio State University

Nonviral vectors for gene delivery are currently receiving considerable research attention because they exhibit several important advantages over viral vectors, including lower immunogenicity and toxicity, low cost, good stability, and ease of manipulation. DNA/polyethylenimine (PEI) polyplexes are one class of promising nonviral vectors. Although the conventional preparation method, bulk mixing, is simple and easy, the formation of the pDNA/PEI polyplexes is not well controlled. In particular, the N/P ratio and the order of adding reagents greatly affect the resulting polyplex size, structure and delivery efficiency.

As an alternative to bulk mixing, we are using electrospray to produce pDNA/PEI polyplexes. Unlike nebulization, electrospray is a gentle process that does not degrade the DNA, and we have confirmed this observation for the pGFP and pSEAP plasmid DNA used in our work. To prepare monodisperse polyplexes of pGFP/PEI and pSEAP/PEI we used a concentric needle electrospray setup and examined the effects of the operating conditions, including N/P ratios, liquid flowrates and applied voltages, on the delivery efficiencies of pGFP/PEI and pSEAP/PEI polyplexes using NIH 3T3 fibroblast cells. A qualitative study showed that NIH 3T3 fibroblasts transfected with pGFP/PEI polyplexes produced by electrospray at an N/P ratio of 6.7, flowrate of 6ml/hr and voltage of 5.3KV exhibited similar GFP expression as cells transfected using Lipofectamine 2000 (Invitrogen). In both cases transfection was much higher than the polyplexes produced by bulk mixing at the same N/P ratio. Quantitative results using pSEAP/PEI polyplexes produced by electrospray under similar conditions showed that transfected cells achieved 2.6 times higher SEAP expression than cells transfected by polyplexes made using bulk mixing. Cells transfected with Lipofectamine 2000 gave the highest SEAP expression (3.3 times higher than bulk mixing), but cell viability was lower than electrospray due to the toxicity of this material.
**7A.03**
Rapid Analysis of Organic Acids in Aerosols by Desorption Electrospray Ionization Mass Spectrometry (DESI-MS).
Mei Li, Hong Chen, XIN YANG, Jianmin Chen, Department of Environmental Science and Engineering, Fudan University, Shanghai, China

Organic acid is an important class of organic compounds in atmospheric aerosol particles. Among the commonly observed organic acids, oxalic acid has been detected as the major fraction of water-soluble organic compounds in urban, rural and even remote background air; while oleic acid is an indicator of recent biogenesis and cooking emissions. The traditional methods for analysis of oxalic acid and oleic acid in aerosol samples are usually ion chromatography (IC) and gas chromatography mass spectrometry (GC-MS) respectively. These methods usually involve several steps like extraction, concentration and pre-separation which are labor intensive and time consuming. Meanwhile, part of target species could be lost in these procedures due to the volatility or limited extraction efficiency. In this study, a new soft ionization technique under ambient conditions DESI-MS was applied to the organic acids analysis in atmospheric aerosols. DESI experiments were carried out by the homemade DESI ion source coupled with a commercial Thermo Finnigan LCQ Advantage ion trap mass spectrometer. Experimental parameters for DESI-MS were optimized to enhance the signal intensity by using their standard solutions. The DESI-MS demonstrated excellent linear responses to oxalic acid and oleic acid standards in a dynamic range of 5 orders of magnitude. The detection limits for oxalic acid and oleic acid are about 1 pg with 5 s sampling time. The two organic acids in both lab-made biomass burning aerosols and ambient aerosols were selectively and rapidly analyzed without any extraction or concentration. The DESI-MS values agreed well with the results analyzed by IC (oxalic acid) and GC-MS (oleic acid). Our experiments showed that DESI-MS was a simple and rapid method for the analysis of organic acids in atmospheric aerosols.

**7A.04**
D-H. Tsai (1), L. F. Pease III (2), R. Zangmeister (2), M.J. Tarlov( 2), M.R. Zachariah(1,2), (1) University of Maryland (2) National Institute of Standards and Technology

We describe the use of Electrospray (ES)-DMA to determine the nature of surface coatings, and their colloidal stability. We present examples through a systematic examination of alkylthiol SAM-and DNA functionalized Au-NP’s. Formation of self-assembled monolayers (SAMs) was detected from a change in particle mobility, which could be modeled to extract the surface packing density. Using ES-DMA we employed a gas-phase temperature-programmed desorption (TPD) kinetic study of SAMs on the Au-NP to extract the SAM desorption kinetics, and binding energy, and therefore the nature of the SAM interaction with a NP. Since the ES-DMA system directly samples from a solution, this approach enables one to monitor temporal changes occurring in solution. In a second set of experiments we demonstrate electrospray gas phase ion-mobility analysis as a new method to investigate colloidal aggregation, and the parameters that govern it. Nanoparticle suspensions characterized by ES-DMA were able to monitor the aggregate distribution as a function of time. By sampling at various times, we determine the degree of flocculation and the flocculation rate, which we find to be inversely proportional to the ionic strength and proportional to the residence time.

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7A.05  
Highly Efficient Integrated Circuit Cooling by Multiplexed Electrosprays. WEIWEI DENG, Alessandro Gomez, Yale University

We report a novel and efficient CPU cooling system based on a microfabricated multiplexed electrospray device. As the power density of the most advanced integrated chips (ICs) quickly exceeds 1 MW/m², the effective removal of the high heat flux becomes a critical and challenging issue. Compared to the conventional fan cooling methods, the spray cooling is advantageous for multiple reasons: first, direct liquid cooling eliminates the relatively high thermal resistance at the solid-solid interface between thermal spreaders and the IC chips; second, the impingement generates large velocity gradients at the stagnation zone that enhance the heat transfer dramatically; and third, the possible phase change in the cooling process allows for the exploitation of the liquid latent heat, which offers high capacity of heat removal at reduced mass flow rate. The electrospray offers additional improvements as compared to regular spray cooling because of the thinner liquid films, more uniform temperature field, more compact volume and lower pressure drop. With a cooling system based on the microfabricated multiplexed electrospray chip, we successfully removed heat flux up to 0.96 MW/m² on a simulation chip. We also discovered that the charge on the droplets reduces the droplet splash and rebound because of the Coulombic attraction force. As a result, the cooling efficiency reaches up to 97%. Because of the compact dimension and small amount of liquid needed, the microfabricated electrospray cooler is very promising in cooling ICs in portable electronics devices.

7A.06  
Hygroscopic Growth of Nanoparticles Containing Surface Active Molecules Prepared by an Electrospray Aerosol Source. SERGEY A. NIZKORODOV, Chris W. Harmon, Ahmad Alshawa, Joelle S. Underwood, Douglas J. Tobias, University of California, Irvine

Nanoparticles containing variable amounts of NaCl and surfactants AOT and SDS are generated by an electrospray aerosol particle source. Particles are size selected into monodisperse populations with geometric standard deviations of roughly 1.05 about a specified diameter using a tandem differential mobility analyzer setup. Upon exposure to increasing relative humidity, NaCl nanoparticles coated with a monolayer of surfactants deliquesce at a reduced relative humidity and show reduced growth compared to pure NaCl particles of the same size. The hygroscopic growth curves are found to depend in a complicated way on the particle size (5-20 nm) as well as the mixing ratio between NaCl and surfactant. For examples, appearance of two distinct phase transitions can be detected in some growth curves. To help interpret experimental observations, molecular dynamics simulations of gas-phase water molecules colliding with NaCl surfaces coated with varying amounts of surfactants are conducted. The simulations predict strong dependence of sticking probability on the density of surfactant layer. To verify whether the nanoparticles are enriched in the amount of surfactant relative to the electrosprayed solution, the composition of the particles is characterized by XPS and by single molecule fluorescence spectroscopy.
Water-soluble iron in the atmosphere influences public health and atmospheric chemistry as catalysts to reactions that produce reactive oxygen species (ROS) as well as ocean biogeochemistry as micronutrients. Quantifying water-soluble iron in aerosols will provide insight into atmospheric processing and sourcing. Currently, offline measurements with extended integration times are predominately used to quantify water-soluble iron in aerosols. Alternatively, online and semi-continuous measurements have unique advantages, including minimizing potential sample alteration prior to analysis, providing unique insights into sources, and assessing acute exposures.

We have developed a method for online measurements of water-soluble Fe(II) in atmospheric particulates using a particle-into-liquid sampler (PILS) to continuously collect particles into purified water and a spectrophotometer coupled to a 1-m liquid waveguide capillary cell to detect water-soluble Fe(II) by the Ferrozine technique. The coupled system (PILS-LWCC) quantifies water-soluble Fe(II) in 12 minute integrals with high precision (<3%) and a detection limit of approximately 3.3 ng/m³. This online method was deployed in field studies in Dearborn, MI and Atlanta, GA to investigate possible sources of water-soluble Fe(II) in an urban environment. Results show temporal variability within the dataset, suggesting that sources within an urban environment are important contributors to atmospheric soluble Fe(II).
7D.03
Development of Aerosol Laser Induced Breakdown Spectroscopy (Aerosol-LIBS) for determination of metals in ultrafine/fine/coarse particles in real time. Ji-hyun Kwak, Gangnam Cho, Kihong Park, Gwangju Institute of Science and Technology (GIST)

Exceeding concentration and/or long exposure of metals could cause toxic effects on human health (Berggren et al. 1999; De Vries and Bakker. 1996; Antonio et al. 2001), although they constitute a small fraction of PM mass. In this study, we developed the aerosol laser induced breakdown spectroscopy (Aerosol-LIBS) to determine metal concentrations of ultrafine/fine/coarse particles in real time. The Aerosol-LIBS uses a powerful laser pulse and generates a microplasma to excite particles, resulting in specific emission lights depending on elemental composition of the constituents when the excited state goes back to ground state. Two aerosol focusing systems (sheath aerosol focusing system and aerodynamic lens focusing system) were employed to increase the hitting efficiency of particles by the laser. By using various metal aerosols generated by an Atomizer and powder disperse system, the performance of Aerosol-LIBS was evaluated. Data showed that metals (Ca, Na, Al, K, Mg, Cu, Cd, Zn, Cr, and Ni) and flyash in the size range between 86 nm and 2.6 um were successfully detected with a sheath aerosol focusing system. However, those metals were difficult to be detected as the number concentration decreased below 10^3 #/cm3. For the case of particles with low number concentrations, we employed the aerodynamic lens focusing system with a collection substrate and successfully determined elemental composition of 91 nm Cu monodisperse aerosols having a number concentration of 300-400 #/cm3 with a collection time of 30 sec. The intensity of emitted emission line was found to be proportional to the collection time, enabling us to quantify metal concentration. Determination of diverse (pure and mixed) metals with varying size and concentration are being conducted to be applied for atmospheric aerosols.

7D.04
Development of an IT-TOF Aerosol Mass Spectrometer.
Julie A. Lloyd, Murray V. Johnston, University of Delaware

A combination of offline mass spectrometry methods such as soft ionization (ESI and MALDI), accurate mass measurements, and tandem mass spectrometry have been previously used to characterize oligomers up to 1000 amu in secondary organic aerosol (SOA). While the offline methods are important, online techniques are needed to study the process of SOA formation, reactivity, and short term variations of the aerosol. Recently, the Photoionization Aerosol Mass Spectrometer (PIAMS) has been used to characterize the formation of SOA by reaction of ozone with monoterpenes online (Heaton et al., 2007). Here, the oligomers were detected but fragmentation was extensive. Therefore, a new method is needed to better characterize high molecular mass species.

In this work, a new aerosol mass spectrometer was developed by replacing the traditional source region of a time-of-flight mass analyzer with a quadrupole ion trap. Incorporation of the ion trap provides increased resolution and sensitivity while keeping the ability to analyze ions over a broad m/z range. Laboratory-generated particles enter a flow limiting orifice and are focused by an aerodynamic lens system. A stainless steel collection probe is inserted through a hole in the ring electrode of the ion trap. The focused particles enter through a hole opposite of the probe and are deposited. At this point, a variety of desorption and ionization techniques such as UV-LDI, UV-LD-EI/CI, IRLD-EI/CI, or MALDI can be employed. Finally, the ions are extracted into the reflectron time-of-flight mass analyzer for detection.

Initial results show the advantage of this hybrid configuration compared to a TOF mass analyzer alone. The soft modes of ionization (CI/MALDI) show detection of the molecular ions of organic aerosol while the hard modes of ionization (EI/LDI) are used for comparison to current techniques. This laboratory instrument is the basis for the construction of a field-deployable IT-TOF aerosol mass spectrometer.
7D.05
Fast and Synchronous Measurements of Inorganic and Organic Components in Atmospheric Aqueous Samples.
YELE SUN(1), Qi Zhang(1), Olga Hogrefe(1), Brian P. Frank (2), Min-Suk Bae(1), James J. Schwab(1), Kenneth L. Demerjian(1), Douglas A. Orisini(1), Kevin P. Rhoads(3), Paul, Fusco(4), (1)Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, New York 122203, USA, (2)Division of Air Resources, New York State Department of Environmental Conservation, 625 Broadway, Albany, NY 12233, USA, (3)Siena College, 515 Loudon Road, Loudonville, New York 12211, USA,(4) GE Analytical Instruments, 6060 Spine Road, Boulder, Colorado 80301, USA

Knowing the composition of atmospheric fog and cloud waters is critical to understanding the roles that they play in atmospheric chemistry and aerosol microphysical processes. We recently developed a method to characterize and quantify inorganic and organic components in fog and cloud waters using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). In this study, we performed extensive evaluation and validation of this method by analyzing a suite of aqueous samples with several on-line aerosol measurement techniques simultaneously. Aerosol particles are generated using a constant output atomizer into the ASRC slow-flow reaction chamber after passing through a neutralizer and diffusion drier. Measurements of particles are performed with a HR-ToF-AMS, a Particle-Into-Liquid System (PILS) coupled with Ion Chromatography (PILS-IC) and a Sievers Total Organic Carbon Analyzer (PILS-TOC), a Sunset Labs OC/EC analyzer, a Tapered Element Oscillating Microbalance (TEOM), and a TSI Scanning Mobility Particle Sizer (SMPS). A series of reference compounds including NH4NO3, (NH4)2SO4, oxalic acid and sucrose are tested and compared for NH4+, NO3-, and SO42- quantifications between HR-ToF-AMS and PILS-IC and for total aerosol mass between HR-ToF-AMS, TEOM, and SMPS. We also compare the total organic carbon (OC) concentrations determined from the elemental analysis of high resolution mass spectra from HR-ToF-AMS with those measured by the PILS-TOC and the Sunset OC/EC analyzer. These comparisons show generally good agreements between different techniques. However, our results show a little lower TOC contents in the aerosolized fog/cloud samples compared to those in the corresponding aqueous solution, suggesting the losses of relatively volatile organic compounds, likely small acids, during aerosol generation.

7D.06

The volatility of atmospheric organic aerosol affects its mass concentration and composition directly through gas-particle partitioning, and can also have a significant impact on aerosol chemistry. Volatility measurements of ambient aerosol are necessary in order to include realistic volatility behavior in models. We describe the characterization of a system consisting of a thermodenuder coupled to a particle beam mass spectrometer, which provides a method for on-line measurement of aerosol volatility and volatility-dependent mass spectra. The thermodenuder is well suited to use with the Aerodyne Aerosol Mass Spectrometer (AMS) and other quantitative aerosol mass spectrometers, making its use in ambient studies practical. The system has been characterized using several model compounds, and the effects of varying aerosol particle size and mass concentration have been investigated through experiments and simulations. A simple method for converting data from this system to vapor pressure distributions using an empirical relationship between vapor pressure and vaporization temperature is demonstrated. Volatility distributions of the type used by Donahue et al. [Environ. Sci. Technol., 40, 2635 (2006)], using a volatility basis set representation based on saturation concentration and including (measured) particle-phase and (inferred) gas-phase concentrations, can easily be calculated from the vaporization profiles measured with this system.

Volatility profiles and volatility-dependent mass spectra of laboratory-generated SOA measured using this technique are quite similar to those measured using the off-line technique of temperature programmed thermal desorption. A database of volatility profiles and mass spectra that we have measured using these two techniques, including various classes of laboratory-generated SOA, is now available online to assist in the interpretation of volatility-mass spectral data measured using this technique.

Thermal Desorption Aerosol GC-MS is a method for automated collection with online GC-MS analysis of organic particulate matter (Williams et al, AS&T, 2006; JGR, 2007). TAG has two modes of operation: sampling with concurrent GC-MS analysis of the collected sample, and thermal desorption of the collected sample onto the GC column. TAG allows for hourly measurements of organic aerosol molecular composition.

We discuss the use of a liquid standard to calibrate TAG response for a wide range of organic compounds. During field campaigns, this standard is injected daily to measure decay in MS sensitivity over time. Ambient samples are also spiked with a liquid standard of deuterated analytes, and analyte responses are compared to offline calibrations to ascertain the presence/absence of matrix effects in ambient samples.

While liquid standards allow for explicit calibration of MS response and thermal desorption efficiency, they do not constrain collection efficiency. This is a concern if collection efficiency changes significantly between gas phase and condensed phase analytes, since many of the compounds of interest partition appreciably between both phases. To examine collection efficiency, we conduct experiments in the CMU air quality lab smog chamber with aerosols formed from compounds that span a wide range of volatility. Mixtures of semivolatile organic compounds are sampled from the chamber with TAG, and compared with concurrent Q-AMS (Aerodyne) and SMPS (TSI) measurements. In one set of experiments, quartz filter samples are collected and analyzed for intercomparison using solvent extraction GC-MS.

To date, TAG has been used exclusively in field campaigns; here, we also present measurements of heterogeneous oxidation kinetics of complex organic aerosol mixtures. With hourly measurements, TAG allows for nearly real-time feedback of experimental conditions and chemical analysis of complex organic aerosol mixtures, making it a complimentary instrument to other methods currently used in smog chamber experiments.

8D.02 Continuous Monitoring of Water-Soluble Aerosol Composition with Microfluidic Devices. SCOTT D. NOBLITT (1), Susanne V. Hering (2), Jeffrey L. Collett, Jr. (1), Charles S. Henry (1), (1) Colorado State University, (2) Aerosol Dynamics Inc.

Routine, continuous monitoring of aerosol composition is desired since aerosols have been shown to negatively impact both the environment and health. Methods such as the particle-into-liquid-sampler coupled to ion chromatography (PILS-IC) and aerosol mass spectrometry (AMS) provide automated, time-resolved concentrations of various aerosol species. However, a less-expensive, faster, and more portable analysis system is desired for widespread deployment. Here, we present the coupling of microchip capillary electrophoresis (MCE) to a water-based condensation particle counter (WCPC) for rapid and continuous monitoring of aerosol chemical composition. To achieve a working system, several obstacles were overcome. An interface between the electrophoresis microchip and the WCPC sampler was developed to minimize unwanted hydrodynamic flow in the microfluidic network arising from the sampling-induced pressure gradient. The electrophoresis separation chemistry was optimized for the small chip size, to be free from potential interfering compounds, and to operate continuously for several hours. The integrated MCE-WCPC system has been tested with ambient aerosols and results verified using established methods. Analyses can be performed with time resolution of approximately one minute and aerosol detection limits below 0.1 micrograms per cubic meter. Portability is improved and cost reduced relative to current methods. Coupling microfluidic devices to aerosol sampling technology proves successful for inorganic ion analyses and shows potential for faster and more sensitive measurements as well as monitoring of other water-soluble aerosol components such as organic acids and carbohydrates. The reduced cost and size relative to current technology indicate that greater deployment of monitoring stations or the advent of portable analyzers may be feasible.
Minimization of Artifacts in Sulfuric Acid Mist Measurement Using NIOSH Method 7903. YU-MEI HSU(1), Chang-Yu Wu(1), Dale A. Lundgren(1), Brian K. Birky(2), (1) University of Florida (2) Florida Institute of Phosphate Research

NIOSH Method 7903 is an approved method that is used for measuring acid concentration in workplace. The sampler of this method is a silica gel tube that consists of section of glass fiber filter and silica gel. However, our prior study found SO₂ can be adsorbed by the glass fiber filter and silica gel. Furthermore, the sample preparation of this method aids the oxidation of S(IV) to S(VI), causing the positive artifact of sulfate. The objective of this study is to minimize the artifact.

Two methods, a honeycomb denuder system (HDS) and a modified deactivation model, were studied. Field sampling was conducted at 7 phosphate fertilizer plants. Three sets of samplers were employed to measure sulfuric acid mist concentration which are: (1) the honeycomb denuder system; (2) the silica gel tube for total sulfuric acid mist concentration which also includes artifact sulfate; (3) a cascade impactor that collects solely sulfuric acid mist. The modified deactivation model was applied to calculate the artifact sulfate concentration based on the silica gel tube measurement.

The HDS was demonstrated to be able to effectively remove SO₂ and reduce the artifact when SO₂ concentration was high and H₂SO₄ concentration was low. When H₂SO₄ mist concentration was high (> 400 micro-gram/m³), however, the system also collected the mist which caused an underestimate of H₂SO₄ mist concentration. Meanwhile, the corrected H₂SO₄ concentration using the deactivation model was closer to the acid mist concentration measured by the cascade impactor than that determined by the honeycomb denuder system at high H₂SO₄ concentration. The honeycomb denuder system and the deactivation model were shown to reduce the artifact sulfate concentration. However, they were still higher than the sulfate aerosol concentration measured by a cascade impactor. One possible reason is the residual sulfate in the glass fiber filter and the silica gel.

The Aerodyne aerosol mass spectrometer (AMS) is a powerful tool for the study of ambient aerosol particles. The AMS measures the non-refractory inorganic and organic mass, composition, and size of ambient submicron aerosol particles. Chemical composition is measured via flash vaporization on a heated surface followed by mass spectrometric detection of the vaporized material. The overall mass-based collection efficiency for ambient particles has averaged approximately 50% in numerous field campaigns. Laboratory and field studies suggest that the mass-based collection efficiency is less than 100% due to ‘bouncing’ of particles from the vaporizing surface, instead of vaporization and subsequent detection, particularly for solid particles. We are developing a conditioning inlet for the AMS that will coat particles with a liquid layer. Laboratory results show that a liquid layer can reduce or eliminate particle bounce, depending upon the layer thickness. Sampling procedures that alternate sampling through the conditioning inlet and through a by-pass will enable a direct measurement of the mass-based collection efficiency due to particle bounce. Careful choice of coating material will introduce mass spectral peaks that do not interfere with the detection of organic components of ambient aerosol particles. Potential sampling artifacts caused by temperature and relative humidity changes inside the conditioning inlet will be explored. Application of the conditioning inlet to measurements of ambient particles will be discussed.
Controlling emissions from mobile sources are critical for continued reduction in health impacts of air pollution, and for addressing regional and global climate impacts. Several modern emission control strategies for diesel engines employ metal catalysts to reduce tailpipe emissions of regulated species. The use of platinum in fuel-based catalysts and Pt-catalyzed diesel particulate filters, and the use of vanadium in selective-catalytic reduction reactors are key examples. However, the use of these metals raises concerns about potential environmental contamination and the health implications of widespread trace metal dissemination.

There is increasing recognition that the toxicological responses of many metals (e.g. Cr, Cu, Mn, Ni, Pt, and V) are determined by the specific chemical/physical speciation in the emissions. For platinum, the primary focus is on soluble (and likely halogenated) species, where the threshold exposure limits are 500 times lower than metallic species. For vanadium, the pentoxide species is considerably more toxic than the lower oxidation state species. Unfortunately extant methodologies provide little relevant speciation information, and most analytical tools that are speciation capable lack the required sensitivity, particularly in the context of the lower emissions from vehicles operated with modern control devices.

We have been developing novel tools for the chemical speciation of these trace metals in mobile source PM emissions, employing a strategy of parallel development of species selective wet-chemical approaches and direct solids speciation using synchrotron x-ray techniques. The wet-chemical extraction approaches for platinum and vanadium address the regulatory construct of solubility, and further advance our understanding by providing information on specific chemical species (e.g. soluble halogenated Pt and soluble V+5 species). The synchrotron tools complement the wet-chemistry techniques in that they can provide information on the total pool of a specific species directly from the PM solids. The paper will detail the analytical protocols that we have developed for platinum and vanadium speciation, and provide concrete examples where they have been applied.
9G.01
Temperature and humidity controlled resuspension chamber as a tool for measuring size distribution of fugitive dust. MARTIN CIVIS, Devraj Thimmaiah, Jan Hovorka, Charles University in Prague, Czech Republic

High aerosol concentrations, its spatial distribution and frequent contravention of the limiting values are one of the largest air quality problems in the Czech Republic at nowadays. Studies made at the West coast of the USA in the nineties of the last century show, that resuspended aerosol fraction is contributing to the total of PM$_{10}$ budget by more than 80 %. No similar study has been made in the Czech Republic up to now. Therefore, we have recently manufactured a 0.4 m$^3$ cylindrical chamber for resuspension of street dust, local top-soils and standard reference materials in the volume of the chamber. The samples are pneumatically dispersed by filtered dry air and kept resuspended for desired period by two fans with regulated speed. The chamber has an inbuilt system of temperature and humidity regulation. Process of dispersion is continually viewed by an Aerodynamic Particle Sizer. Required size fraction of aerosol formed are then sampled by Harvard Impactor (TSP, PM$_{10}$, PM$_{2.5}$ and PM$_{1}$), Sioutas Cascade Impactor (>2.5, 1.0-2.5, 0.50-1.0, 0.25-1.0 and <1.0 micro-meters). Results of test runs and first resuspensions of street dust, field soils from Prague and the North West brown coal basin in the Czech Republic is presented.

Supported by the Grant Agency of the Charles University in Prague No. 40307/2007

9G.02
Particle Neutralization using a Carbon Fiber Charger for Fine and Ultra-fine Aerosol Particles. BANGWOO HAN (1,2), ZHI NING (1), NEELAKSHI HUDDA (1), CONSTANTINOS SIOUTAS (1), HAK-JOON KIM (2), YONG-JIN KIM (2), (1) Department of Civil and Environmental Engineering, University of Southern California (2) Environmental System Research Division, Korea Institute of Machinery and Materials

Particle neutralization has been of interest in aerosol processes such as aerosol generation, transport, measurements and so on. Radioactive sources are commonly used to electrically neutralize the aerosol particles. However, radioactive chargers such as Kr-85 and Po-210 are limited to use owing to its life-time and radioactive regulation. In this study, a novel bipolar charger using carbon fiber ionizers has been developed to neutralize fine and ultra-fine aerosol particles. Two carbon fiber ionizers for generating positive and negative ions were placed in front of a charging chamber. Carbon fiber ionizers consisted of a bundle of carbon fibers and clean air carrier gases were introduced into the ionizers to transport the generated ions into the charging chamber. Positive and negative D.C. voltage of +3.0~+4.0 kV and -2.0~-3.0 kV were applied and the carrier gases of 4.0 and 6.0 l/min were used to the ionizers, respectively. Charge currents generated by ions were monitored by an electrometer. Sodium chloride, ammonium sulfate, ammonium nitrate and glutaric acid particles were used as test aerosols. Charge probabilities of the carbon fiber charger were investigated at different particle sizes from 20 to 100 nm and compared with those of a Kr-85 neutralizer. Size distributions of various particles were obtained from the carbon fiber charger and they were also compared with those obtained from the Kr-85 neutralizer. The charge probabilities and size distributions of the carbon fiber charger were in good agreement with those of Kr-85 neutralizer. Therefore, it can be concluded that the carbon fiber charger can neutralize aerosol particles as effectively as the existing radioactive neutralizers.
**9G.03**

**Application of Inlet and Transport Diffusion Loss Correction to SMPS Data: Effects on Reported Size Distributions at Urban and Rural Locations in New York.**

MIN-SUK BAE (1), James J. Schwab (1), Brian Frank (2), Olga Hogrefe (1), G. Garland Lala (1), Kenneth L. Demerjian (1), (1) Atmospheric Sciences Research Center, University at Albany, State University of New York, (2) Air Resource Division, Bureau of Mobile Sources, New York State Department of Environmental Conservation, Albany, New York

As aerosol particles diffuse to the walls of tubes and other flow path elements making up the inlet and transport path of an SMPS, there are diffusion losses and the measured size distribution will be underrepresented for small particles. Since the Scanning Mobility Particle Sizer (SMPS) spectrometer, with the appropriate DMA tube, flow rates and CPC, is capable of measuring particles near and below 10 nm in size, diffusion losses are unavoidable.

A Nano Differential Mobility Analyzer and an SMPS with a long-tube Differential Mobility Analyzer in concert with a Condensation Particle Counter (CPC) were operated at the sites of Pinnacle State Park (PSP) and Whiteface Mountain (WFM) in rural areas of New York State and at the urban site of Queens College (QC) in New York City in summer 2001 and winter 2004. We have retrospectively applied the diffusion loss correction supplied by TSI to these data sets. For both the QC 01 and QC 04 campaigns, the corrected average number size distribution has an additional clear mode at approximately 13 nm. For ambient aerosols at rural sites (WFM and PSP), the diffusion loss correction affects the absolute values of the size concentrations but not the overall structure of the size distribution. Thus, diffusion loss correction may not be necessary for the examination of relative trends in the rural locations. For ambient aerosols at urban sites (QC 01 & 04), the diffusion loss correction affects both the absolute values of the size distribution and the overall modal structure. Our results indicate that the diffusion loss correction is always necessary for SMPS data gathered from an urban location. These findings may be useful for deciding whether reprocessing extremely large data sets (that is, retrospectively applying the TSI diffusion correction) from rural or urban ambient monitoring sites will yield useful information.

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**9G.04**

**Effect of Particle Properties on Determination of Mean Particle Size Using the Electrical Aerosol Detector.**

BRIAN P. FRANK (1), Olga Hogrefe (2), (1) NY State Dept of Environmental Conservation, Albany, (2) Atmospheric Sciences Research Center, SUNY-Albany

Determining the particle size distribution for ultrafine particle sources with transiently varying behavior presents a technical challenge due to the rapidly changing particle behavior of the source, often in the range of 1 Hz. An instrument which has the potential to perform such measurements is the electrical aerosol detector (EAD), which employs diffusion charging of aerosol particles and their subsequent detection by sensitive electrometer. EAD measurements of total aerosol length (millimeters/cubic centimeter) can be combined with measurements of total particle number concentration from the Condensation Particle Counter (CPC) to yield mean particle size for an aerosol, which can also be determined by utilizing the Scanning Mobility Particle Sizer (SMPS). Previous experiments employing a combustion aerosol source determined that poor agreement was found between EAD/CPC and SMPS data when mean particle size was used as a basis for comparison, but good agreement was found between EAD and SMPS data when total aerosol length was used as a basis for comparison. The largest contribution to the poor correlation between the two methods was the difference in concentration measured by the SMPS and the CPC. The contributions of both diffusion losses and nanoparticle aggregate mobility were also evaluated, but neither phenomenon completely explains the discrepancy between the two methods. This poster examines three additional particle properties - charging, composition, and morphology - and their relative effects on the correlation between the EAD/CPC and SMPS methods for determining mean particle size.
9G.05
Size Distributions of Lead-containing Particles From Aerosol Sampler Filter and Wall Deposits as Determined by Scanning Electron Microscopy. TAEKHEE LEE (1), William P. Chisholm (1), James E. Slaven (2), Martin Harper (1), (1) Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, Morgantown, West Virginia, (2) Biostatistics and Epidemiology Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, Morgantown, West Virginia

The objective of this laboratory study is to compare the size distributions between filter catches and wall deposits collected by closed faced cassette (CFC) and Institute of Occupational Medicine (IOM) samplers. The number and mass-weighted particle size distribution of aerosols of three different sizes of standard microspheres and two different lead-containing compounds (lead oxide and lead sulfide) were determined by an Aerodynamic Particle Sizer (APS) and computer controlled scanning electron microscopy (CCSEM) with energy dispersive x-ray analysis (EDX). The aerodynamic diameter of individual particles was calculated from the SEM projected area measurement and estimated densities and shape factors. The number and mass-weighted size distributions of the standard microspheres as calculated from SEM images agreed with the measurement of the APS. Furthermore, the shape of the mass-weighted size distributions calculated from the APS data agreed with that measured by Marple personal cascade impactors. The size distributions measured by the APS and calculated from the SEM images of lead containing particles with spherical particle assumptions agree within a factor of 2. A Mann-Whitney U-test revealed that for both the number and mass-weighted distributions differences between filter and wall deposits were not significant over the size range (0.5-20 micro-meter aerodynamic equivalent diameter) included in this study. By comparing direct measurements of APS to SEM images and known particle densities, the empirical shape factors for lead oxide and lead sulfide were determined to be approximately 2.8 and 1.2 respectively. In subsequent work these shape factors and SEM-EDX analyses of field samples will be applied to the calculation of size distributions of lead-containing sub-populations of aerosol dust samples taken in occupational environments.

9G.06
Design Modifications to TSI 3071 Differential Mobility Analyzer (DMA) for High Sheath Flow Operation. Meilu He, and Suresh Dhaniyala, Clarkson University

Differential mobility analyzers (DMAs) have been central to classification and analysis of ultrafine particles since their commercialization by TSI in 1976. A particularly popular DMA is the TSI long cylindrical DMA model (TSI 3071). This DMA has an annular flow channel with a long classification length and four flows, as originally conceived by Knutson and Whitby (1975). The sizing resolution of this DMA (as well as others) is limited by ratio of aerosol to sheath flow in the DMA. For typical operation of the commercial 3071 DMA, the maximum sheath flow is ~ 10-15 LPM. This upper limit is largely because of the pressure drop through the base of the DMA and the turbulence generated by the sheath flow screen at the upstream end. To overcome these limitations, a new, low pressure DMA base was designed and tested. In designing the base, care was maintained to ensure that the flow quality in the vicinity of the sample port was not affected. In the new base design, pressure drop is achieved over an annular slit rather than through small holes in the base, as currently manufactured. A fine fiber screen, which is selected based on the critical Reynolds number in Karman vortex system, is used to laminarize the high flowrate sheath air. The classification performance of the high-flow, low-pressure-drop DMA was compared against that of the commercial 3071 DMA. The DMA base design modifications and experimental testing results will be presented.
9G.07
Influence of Aerosol Generation Methods on Size Distribution Parameters of Standard Particles. KEIJI TAKAHATA, Kensei Ehara, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan

The standard particles are produced by atomizing a suspension of polystyrene latex (PSL) particles in water. However, the size reliability of PSL aerosols may be impaired by the formation of particle aggregates and the effect arising from the impurities. The non-volatile impurities in PSL suspension result in formation of residue particles and of residue shell on the PSL particles. In the present study, the size distribution parameters of standard PSL particles generated by two methods were evaluated. The performance of an electrospray type aerosol generator (TSI 3480) and a pneumatic nebulizer type aerosol generator (JSR AEROMASTER V) were investigated based on parameters of PSL particles in the size range from 30 nm to 300 nm at varied solution concentrations. The size distributions of generated PSL particles were measured with a differential mobility analyzer (DMA), and the size distribution parameters were determined with the DMA-moment method. For all PSL particles generated by an electrospray, the background overlapping the PSL particle peak in the DMA spectrum was practically absent. For the PSL particles at sufficiently diluted solution, the parameters such as the number average diameter and the standard deviation obtained by an electrospray were in good agreement with the parameters obtained by a pneumatic nebulizer.

9G.08
Aerosol Sample Collection with the In-Tox Products Cascade Impactor. LARRY BOWEN (1), Larry Bowen, Sr. (2), (1) Southern Research Institute, Birmingham, (2) In-Tox Products, Albuquerque

In-Tox Products cascade impactors are inertial sampling devices used to determine size distributions of aerosols based on their aerodynamic properties. Their design and theoretical behavior has been well described. However, practical issues such as instrument preparation, sampling techniques and data reduction are often left to the user. We will describe the steps necessary to properly clean, calibrate, load, and collect aerosol samples with the In-Tox impactor. Additionally, procedures to reduce cascade impactor data using the lognormal distribution and cumulative mass of particles collected will be discussed.
9G.09
Performance of Aerosol Measurement Devices under Extreme Environmental Conditions. JASON QUIZON, Shanna Ratnesar, Christopher Bare, Neal Baker, Jerome Gilberry and Joshua L. Santarpia, Johns Hopkins University Applied Physics Laboratory

There is a need for the ability to characterize aerosol particles in a wide range of environmental conditions. It is often desirable to measure both fine and coarse mode aerosol in both ambient sampling and in laboratory tests, which typically requires multiple measurement technologies. In this study two common aerosol measurement instruments, the TSI Scanning Mobility Particle Sizer (TM) (SMPS (TM)) Spectrometer Model 3936L75 (TSI, Inc., Shoreview, MN) and the Grimm Technologies, Inc. Model 1.01 Portable Aerosol Spectrometer (PAS) are evaluated for the ability to measure aerosol size distributions under extreme environmental conditions. The SMPS and the Grimm have overlapping size bins between 0.2 and 0.6 microns, allowing measurement comparison. These experiments will look at the effects of temperature, humidity and pressure conditions, beyond the limits specified by the manufacturer, to examine effects on thier measurement accuracy and operability under these conditions. Extreme temperature (-25 degrees C to 65 degrees C), and humidity conditions (0 to 95% RH) will be created using the JHU/APL Environmental Chamber and high altitude, low pressure experiments (282 Torr) will be conducted in at the JHU/APL Space Systems altitude simulation chamber. Aerosolized PSL spheres of known size will be used to determine the measurement accuracy of the instruments during the experiments, and instrument operational variables will be continuously monitored to determine functionality. Results relating functionality of the instrument and required modifications to the instrument hardware will be discussed.

9G.10
Characterization of a High Flow Rate Water-Based Condensation Particle Counter for Clean-Room Monitoring. Jinhong Ahn(1), Kitai Kang(1), Jinuk Yoon(1), Youngtaek Kwon(1), KiSoo Jeon (2), Kangho Ahn(2), (1) HCT CO.,LTD. (2) Hanyang University

As the semiconductor manufacturing process is developed the critical dimension is continuously shrunk down to below 100 nm. However, the air-born particle measurement technique using laser in clean environment reached its limit, i.e., ca. 60 nm. To breakthrough this limitation, a new approached is applied using particle condensation technique. When a particle is place in a super-saturated vapor, the super saturated vapor molecules will start condense onto the particle. So the particle with condensed vapor will continuously grow and become a large droplet. During this process each particle forms an individual droplet. So this large size droplet can easily be detected by optical means. In this process initial particle size information is lost. It only gives particle number concentration. This particle condensation technique has been used more than 30 years in aerosol research field. However, this technique usually used alcohols as a working fluid, which may be an organic contamination source in semiconductor manufacturing clean rooms. Another limitation of this condensation technique was that the small sampling air flow rate - usually less than 1 lpm, which is not sufficient to give good statistical particle data in clean environment.

To overcome these problems, new water based high sampling flow real time nano-particle counter is developed and its performance is evaluated. Contamination free, water operated 2.83 lpm flow rate condensation particle counter (CPC) is successfully tested in clean environment at nanoparticle size range. The particle detection characteristic of water based CPC in clean environment showed good linearity with respect to aerosol electrometer.
9G.11
Water-based CPCs Models 3781, 3785 and 3786 Design Enhancements. KATHLEEN A. ERICKSON (1), Derek R. Oberreit (2), Fredrick R. Quant (2), Brian L. Osmondson (1), (1) TSI Inc., Shoreview, MN, USA (2) Quant Technologies, LLC, Blaine, MN, USA

Design improvements have been implemented in the 3781, 3785 & 3786 WCPCs which include flow system modifications, firmware enhancements, the addition of a water trap sensor, the addition of optional analog output of concentration, and several changes specific to the 3786.

In order to improve the time between servicing of the water-based CPCs the flow system of the 3781, 3785 & 3786 was reviewed and enhanced. Flow control orifices were modified and several additional filters were added upstream of flow orifices to prevent orifice clogging. Accelerated load testing has shown over a 100% improvement in intervals between clogging. Additionally, firmware modifications have been implemented to indicate a clog on the display of the 3785 & 3786 CPC if the pump voltage value is out of range.

Water-based CPCs feature a water recovery system utilizing a water trap to reduce water consumption and eliminate water vapor in the flow control and exhaust sections of the instrument. The trap works well in operation but can be problematic if there is not sufficient water in the trap. A trap sensor has been added to the models 3785 and 3786 WCPC to verify that the amount of water in the reservoir is sufficient for operation. The sensor is also used to monitor the amount of water available for recycling.

Analog output of concentration via the BNC connection as been added as an optional feature to the 3785 & 3786 WCPC. Also several modifications have been made exclusively to the 3786 WCPC. These include the addition of a vent in the inlet of the 3786 to prevent potential air locks, the modification of the fan to improve cooling in warm environments and a firmware change to modify the 'over-range' condition.

9G.12
Direct-Reading Nanoaerosol Instrument Comparison.
TERRI PEARCE, Christopher Coffey, National Institute for Occupational Safety and Health, Division of Respiratory Disease Studies, Laboratory Research Branch

Difficulty in using conventional weight-based methods for assessing worker exposure to engineered nanoaerosols has increased the use of real-time monitors for assessing workplaces. This laboratory study compared results from several monitors measuring dioctyl phthalate nanoaerosols to reference concentrations measured by a feedback-controlled aerosol generation and detection system. Nanoaerosols across seven discrete particle sizes from 25 to 700 nm were sampled by the reference and combinations of two condensation particle counters (CPCs), two laser spectrometers, an aerosol time-of-flight analyzer, or a hybrid instrument combining a scanning mobility particle sizer (differential mobility analyzer and CPC) with a laser spectrometer. Compared to the reference concentrations, the CPC measuring the smallest particle size provided the best comparability overall but reported concentrations generally greater than the plus or minus 20 percent accuracy ascribed by the manufacturer. Both laser spectrometers reported much less than 100 percent of the reference at sizes up to and including 300nm, with concentrations ranging from 100-150 percent of the reference at the larger sizes. The time-of-flight instrument provided concentrations approximately 50 percent of the reference with the hybrid instrument reporting 125-150 percent for particles 100 nm and smaller and the data for the larger sizes disregarded due to data output issues. Possibilities for differences in performance include variations in aspiration, transmission, and counting efficiency between the individual instruments and the reference. Differences in detectors meant that the laser spectrometers were unable to count the particles smaller than 300 nm with comparability not truly established until the 400 nm size. Future research should seek to define the attributes of an optimal reference standard. An established reference will allow researchers to compare multiple instruments of the same or different models. Those evaluations should include using aerosols with different sizes or constituents to determine instrument performance and comparability across nanoaerosol types.
High Speed Particle Size Distributions Measurements of Diesel Exhaust using a Standard SMPS. Laura A. Kranendonk, John M. Storey, Teresa L. Barone, Oak Ridge National Laboratory - Fuels, Engines, and Emissions Research Center

Commercial scanning mobility particle sizers (SMPS) make particle size distribution measurements useful for diesel particulate research; however these measurements are typically much slower than combustion events. Standard SMPS models generally take ~1 minute to generate a single particle size distribution measurement. Specialized and more expensive high-speed differential mobility devices can get down to 0.1 s at the expense of size range and resolution. Even with the fastest scan rate, only 1 measurement per engine revolution is achievable at 600 RPM, a relatively slow engine speed. To study variations in individual engine cylinders, these measurement rates are too slow.

We report on an alternative method of data collection and processing using a standard SMPS (TSI 3936). We record diameter (signal A), particle counts (signal B), and crank angle (signal C) using a multifunction data acquisition system. Assuming no correlation between the engine speed and classifier rate and steady-state engine operation, a size distribution at any engine position can be reconstructed from the 3 signals (A, B, and C).

The exhaust must be diluted and passed through the SMPS in a very controlled fashion to retain cycle-resolved particle size distribution. Details concerning the experimental setup, data collection, and processing will be described. We verify the methodology by measuring known aerosol samples. Finally, size distribution measurements integrated over 90 crank angle degrees (CAD) will be presented (~12.5 ms reconstructed distributions at 1200 RPM), corresponding to two reconstructed distributions per cylinder per cycle (720 CAD). This type of particle size analysis is widely applicable to a number of fast, repeatable processes. By using a standard commercial instrument, fairly simple changes to the data collection and post processing can greatly expand the capabilities to high speed measurements.

Determination of dissolved and suspended nanoparticles in water using an aerosolization method combined with membrane filtration technique. JIYEON PARK, Kihong Park, Gwangju Institute of Science and Technology

We propose an aerosolization method combined with membrane filtration technique to determine size and number of nanoparticles dissolved and suspended in water in real time. The dissolved nanoparticles are defined here as those that are originally not in particle phase in water but that are able to crystallize in the form of particle phase in the air. Particles suspended and dissolved in water before and after treatment by a nanofiltration (NF) membrane were in-situ aerosolized and dried, and their size and number were determined by a Scanning Mobility Particle Sizer (SMPS) in real time. After treatment of NF membrane, the remaining particles represent dissolved particles survived through the NF membrane with a pore size of 0.9 nm. This enables us to separate dissolved and suspended nanoparticles in water, leading to determine their relative contribution in the water. To determine the relationship between particle concentration in water and in air, we conducted measurements using NaCl, CaCl2, KCl, and MgCl2 particles (dissolved) and humic acid, CaCO3, and MgCO3 particles (suspended) having known mass concentrations in water. A linear relationship between number concentration of particles in the air measured with the current aerosolization method and the solute concentration (ppm) was found for those particles. For example, as the solute concentration of CaCl2 increased from 200 ppm to 3500 ppm, the total number concentration in the size range of 20-600 nm in the air increased linearly from 2.3*105 particles/cm3 to 2.1*106 particles/cm3. Various slopes and maximum solute concentrations of the linear relationship were observed for different materials. Also, we found that for dissolved particles such as NaCl, CaCl2, KCl, and MgCl2, the geometric mean diameter (GMD) of particles formed in the air depends on their conductivity and ionic radius.
9G.15
New Approach for Engineered Nanoparticle Sizing Studies.
SHERRIE ELZEY, VICKI GRASSIAN, University of Iowa, Iowa City, IA

Engineered nanomaterials are being used in commercial products and developed for medical applications such as targeted drug delivery. Increased use of engineered nanomaterials raises questions concerning environmental and human health effects of such materials. Particle size can directly influence how nanomaterials interact with their surroundings. A new method is being developed to determine particle size using an electrospray and a Scanning Mobility Particle Sizer (SMPS) coupled with microscopy techniques to measure the particle size distribution of aerosols generated from engineered nanomaterials. This method has been successfully used to measure primary particle size, particle aggregates, and surface coatings and solvent coatings not detected by common characterization methods. Results offer insight into the effect of particle interactions, particle-solvent interactions, and surface coatings on particle size. This work provides a better understanding of the effects of engineered nanomaterials to recognize potential hazards and optimize benefits.

9H.01
High Flow Rate Aerodynamic Lens System. GUAN ZHAO (1), Parsa Zamankhan (2), Philip K. Hopke (1), and Suresh Dhaniyala (1), (1) Clarkson University, Potsdam NY, (2) City College of New York

Aerodynamic lens systems are commonly used to get collimated particle beams to facilitate analysis with spectrometers. Current aerodynamic lens are limited by the low mass flow rate through the lens system. Here, we investigate a new analytical model to optimize the design of a high flow rate lens system. The results suggest that the lens operating under compressible flow conditions will have orifices of increasing diameters along the flow direction, contrary to the existing lenses designed for incompressible flow conditions. Numerical predictions of particle trajectories are complicated by the difficulty of accurately predicting flow-turbulence under compressible flow conditions. An experimental setup was designed and developed to find the effect of Reynolds number (and hence flow rate) on the focusing characteristics of particle beams generated by the compressible-flow lens systems. The experimental results suggest that focused particle beams are possible at higher Reynolds number than previously thought possible. The theoretical and experimental results of high flow aerodynamics lens systems will be presented.
**9H.02**

**Aerosol Focusing in the Size Ranges of 30~300nm and 5~50nm in Air Using the Two Types of Aerodynamic Lenses.**

KWANG-SEUNG LEE, Songkil Kim, Yongsuk Oh, Donggen Lee, Pusan National University, South Korea

This study describes a design and a development of aerodynamic lens as an inlet of the single particle mass spectrometry. Several key designing parameters and systematic factors are investigated through the CFD. Firstly, the simulation demonstrates the ability of aerodynamic lens to focus 30-300nm NaCl unit density particles. We find in this design that particle behavior is well characterized mainly by two dimensionless parameters such as particle Stokes number and flow Reynolds number. We verify that 30-300 nm aerosol particles are tightly focused with near 100% transmission efficiency. We attempts to experimentally demonstrate the focusing capability of the aerodynamic lens inlet, as assembled into the single particle mass spectrometry. The formation of sub-millimeter beams of 30-300 nm NaCl aerosols is verified by microprobe observation of deposited aerosol beams. The measured sizes of aerosol beams are agreed reasonably with those from the simulations as a function of particle size. Secondly, we develop a new type of aerodynamic lens, say converging-diverging configuration, to focus 5-50nm ultrafine nanoparticles in air. An orifice type of aerodynamic lens is generally used to focus nanoparticles. However, it is impossible to focus particles of below 10nm in air as a carrier gas because of instability of fluid in a lens. In this case, we use a converging-diverging lens instead of an orifice type to focus particles of 5~50nm in air. Finally, it is confirmed that such ultrafine aerosols are focused into a narrow beam with ~1mm in diameter and a good particle transmission efficiency over 90%. We add another important designing parameter to the designing parameters, a shape factor describing the geometry of the converging-diverging orifice.

**9H.03**

**Separation of Optically Different Particles in a Microchannel Using Radiation Force.** Eunjung Jung, Sang Bok Kim, Sang Soo Kim, Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology

Separation of micro spheres according to their optical mobility was first accomplished using the cross-type optical particle separation (COPS). The COPS system can sort micro particles continuously using loosely focused laser beam propagating in perpendicular to the direction of a flow in a micro channel. When micro spheres suspended in a flow meet the laser beam, they are pushed by a scattering force in the direction of the laser beam propagation. While passing the laser beam zone, the position of the particle changes; after the zone, the particle is delivered by the flow in analysis districts, remaining its position. The pushed distance is defined as retention distance and we can classify micro particles by the difference of retention distance. In contrast to the previous studies which separate micro spheres according to only a physical property, radius or the index of refractive of micro beads, we first separated the particles applying to the concept of optical mobility. The optical mobility is the ratio of the terminal velocity of a particle to the external force, radiation force. With our study, we demonstrated that the micro beads of the same optical mobility have the same retention distance and the beads of different optical mobilities can be sorted. In real world, we frequently encounter the case to sort particles or cells having different physical properties, different size and the index of refractive. Thus, our demonstration, the particle separation according to the optical mobility, can broaden the applicable range of optical particle separations and make it more reliable.
9I.01
Development and Characterization of an Ice Nucleation Chamber. ANDREW GLEN, Sarah Brooks, Auromeet Saha, Brandon Dooley, Texas A&M University, Texas

A Continuous Flow Diffusion Chamber (CFDC) has been developed by Texas A&M University for the measurement of Ice Nuclei (IN) concentrations as a function of ice saturation and aerosol temperature. The chamber design is based on the Colorado State University CFDC. The CFDC is composed of a 1 m long annular chamber with refrigerated walls of different temperatures. The aerosol sample flows vertically from top to the bottom of the chamber in laminar flow, separated from the iced chamber walls by a re-circulating sheath flow. Within the chamber, the aerosol is exposed to controlled conditions of ice saturation and temperature. Ice crystals which nucleate and grow on sample aerosol are counted at the base of the chamber by a Climet Optical Particle Counter (OPC). To successfully study ice nucleation in multiple cloud types including mixed phase clouds, an instrument with precision control of temperature and ice saturation is required. The instrument must also be able to distinguish between ice and liquid water droplets. We have characterized our instruments' ability to accomplish these tasks through a series of laboratory experiments. In addition, we have successfully conducted measurements of IN concentrations in polar mixed phase clouds near Barrow, Alaska, during the Indirect Semi-Direct Aerosol Campaign (ISDAC).

9I.02
Design and Development of an Energy-Dispersive X-ray Spectrometer: A tool for Environmental Research in Kenya. Michael J. Gatari Gichuru (1), Johan Boman (2), (1) University of Nairobi, Kenya, (2) Goteborg University, Sweden

Contribution of scientific research to local and international journals from Africa and indeed Kenya is weak in comparison to other regions (Gibbs, 19995). One of the main problems is the non-availability of reliable and affordable analytical instrumentation. Energy-Dispersive X-ray Fluorescence (EDXRF) analysis is a special analytical technique for trace elements in that it is economical and easy to use. Its analytical capacity has the advantage of having multi-elemental characteristics and satisfactory speed (Markowicz, et. al., 1996). Conventional EDXRF analysis is used in identifying toxic trace elements in the general environment, trace elements in airborne particles for source apportionment, investigation of micronutrients in different ecosystems and agriculture practices among other areas of scientific investigations.

A new EDXRF Spectrometer has been built and installed at the Institute of Nuclear Science and Technology, College of Architecture and Engineering, University of Nairobi. It is a new research tool that has improved local analytical detection limits of heavy metals in environmental and air pollution samples. A Siemens type D x-ray tube-stand was modified to facilitate x-ray irradiation of a Mo-secondary target. The target is a glued disk that was cut from a 1 mm thick Mo plate of 99.99 % purity. The fluoresced secondary x-rays propagate through three Ag collimators giving a near monochromatic Mo characteristic x-rays for sample excitation. The disk holder was designed to be easily removable, from the Al-measuring head, thus allowing the flexibility of carrying out experiments using different secondary targets. This has improved the detection limits of trace elements in samples by a factor of 10. It has also provided a facility for direct analysis of air samples without having to use Myra foils to hold the cellulose filters hence minimizing sample contamination. Regional research scientists have now an extra research spectrometer to boost studies of aerosol particles.

Acknowledgement

The International Programme in the Physical Sciences, Uppsala University, Sweden, funded the project.
Computer modeling of an axial vapor-gas flow for the various scientific and technical applications is realized. A laminar vapor-gas flow is used for the vapor nucleation rate measurements in so called Flow Diffusion Chambers [M.P. Anisimov and A.G. Cherevko (1985) Gas-flow diffusion chamber for vapor nucleation studies. Relations between nucleation rate, critical nucleus size and entropy of transition from a metastable into a stable state. J.Aerosol Sci., V. 16, No. 2, P. 97-107]. That kind of flow is characterized by wide spectrum of parameters which govern the flow regimes and the various physical transformations in it. These parameters impose the strict requirements on used mathematical models and computational methods. In the present research an accurate mathematical model of a vapor-gas flow is developed for high pressure flow diffusion chamber application. Model is based on using a full set of Navier Stokes Equations where an equation for a vapor partial vapor pressure is involved. A realistic for broad interval of temperatures and densities coefficients of viscosity, thermal conductivity, and nonideal equation of state are used to close a set of Navier-Stokes equations. A valid numeric algorithm based on a predicator-corrector method is developed. Algorithm makes it possible to reduce a differential equation solution to a routine scalar sweeps for the various dimensionality problems. Algorithm was tested on a problem of a viscous gas flow in channel. An approximate numerical algorithm efficiency and accuracy is evaluated by comparison of accurate and rough solutions. A glycerin-carbon dioxide flow is calculated for case of a variable wall temperature on example of a high-pressure flow diffusion chamber. Results are compared with regular algorithm data which is applied for high pressures.

Research is supported by RFBR grants No 07-08-13529-ofi and 07-03-00587-a.

Performance of individual protective equipment (IPE) designed to protect an individual from harmful airborne substances has been characterized when the individual is exposed to high wind conditions, but only for the rigid body case. A simple, ideal IPE component model is designed considering a cylindrical component (representing, say, an arm or leg) with an outer cylindrical protective layer (IPE fabric) separated from the component by a constant spacing. Based on permeability, ambient wind directed towards the component causes air flow through the IPE fabric, making aerosol filtration efficiency an important design characteristic. Aerosol filtration efficiency in elevated wind conditions (above 10 mph) was studied for the case of the rigid IPE fabric layer. Filtration performance was measured using both benchtop filter-holder as well as wind tunnel tests. Benchtop tests consisted of measuring particle concentration upstream and downstream of the fabric placed in a filter holder. Tests were run at varying face velocities ranging from 0.06m/s to 0.4m/s. Wind tunnel tests were performed at constant fabric face velocity, with varying wind speeds ranging from 10mi/hr to 80mi/hr. A particle injection technique was developed for seeding the wind-tunnel at these ranges of velocities with uniform concentrations. Particles of several different densities and sizes ranging from 60nm to 2 mm were used in the tunnel and filter test setups. Initial test results show that particle penetrations increase with increasing wind speed for a constant face velocity. Also, the wind effect on particle penetration is seen to be most visible for particles of higher density. A theoretical model correlating filtration efficiency and design variables such as fiber diameter was created using data from penetration tests and electron microscope analysis of the IPE fabric. Characteristics of particle deposition on the component are obtained from wind tunnel experiments for a range of operating conditions. For these tests Fluorescein-tagged test particles with aluminum foil patches on the component are used to determine the mass-fraction of deposited particles. The wind-tunnel test procedure and penetration results for varying test conditions will be presented as well as deposition measurements. The development stages for determining techniques to capture the flapping phenomena of a sleeve will also be presented. This will include wind tunnel preparation and apparatus as well as CFD modeling and predications.
9L.01
Modeling and Monitoring of Particulate Matter in a Semi-arid/Arid Area in Support of Health Assessment Study. R. Dimitrova, H. J. S. Fernando, B.C. Hedquist, P. Hyde, J. Anderson, Arizona State University, Tempe

Three approaches of analysis -- atmospheric modeling, interpolation techniques for measured concentrations, and statistical methods -- were applied to determine the relationship between concentrations of elevated particulate matter 10 microns and smaller (PM10) and asthma incidences in metropolitan Phoenix. The results of the first two approaches are considered in this paper. The main goal of this study was to develop, evaluate and demonstrate the advantages and limitations of different methods of generating the spatial concentration fields of PM10 that can be linked with the public health data.

The MM5/SMOKE/CMAQ modeling system was employed to simulate the concentration distribution at three nested domains focused on metropolitan Phoenix and surrounding mountains. This sophisticated platform is widely used and is accepted as a regulatory tool. For the central city area, the emphasis was on the measured PM10 concentrations from the permanent network of continuous monitors operated by governmental agencies, augmented by an additional three months of temporary continuous PM10 monitoring stations. Both Ordinary Kriging and Inverse Distance Weighting interpolation techniques were used to provide spatial distributions of PM10 based on the permanent/temporary monitoring network.

The results of regional air quality modeling and interpolation of measured PM10 concentrations were used to produce a set of concentration maps, with the resolution of census tracts in the central city and of 4x4 km for the whole domain. The advantages and limitations of the different methods and estimation of the models’ performance were evaluated. The mapped distributions, expressed as 24-hour averages, provide the basis for the application of statistical methods to explore the relationship between PM10 concentrations and asthma incidences.

9L.02
Vehicular Fine Particles Transport and Formation in the Urban Atmosphere of Sao Paulo. BEATRIZ SAYURI OYAMA Maria de Fatima Andrade, Atmospheric Sciences Department, University of Sao Paulo, Sao Paulo, Brazil

This work is part of a comprehensive project conducted by Atmospheric Sciences Department and Medical School from the University of Sao Paulo that aims to evaluate the health and economic impact of PM2.5 in six Brazilian cities (Sao Paulo, Rio de Janeiro, Belo Horizonte, Recife, Curitiba e Porto Alegre). The contribution of this work is related to the evaluation of the emission sources participation to the concentration of fine particles and mainly the role of vehicular emission, inasmuch the PM2.5 is unwholesome to the health. During a year, starting in August 2007, samples were collected in a daily base in the cities above, allowing a better identification of the sources and an evaluation of the health's impact using epidemiological analysis. The particles are characterized by its mass concentration, elemental speciation by means of X-Ray fluorescence analysis, ionic composition and Black Carbon mass concentration. Receptor modeling was applied as a methodology for the identification of sources and eulerian air quality modeling for the formation and dispersion of pollutants. This work focus on the samples collected in the city of Sao Paulo and the major conclusions regarding the contribution of identified sources for the air quality will be compared with the previously results obtained mainly by means of receptor modeling studies.

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**9L.03**

Synthesis of hydrogenated silicon nanoparticle and its application to secondary battery. Kwangsu Kim(1), Jin-Hwan Park(2), Seok-Gwang Doo(2) and T Kim(1,3), (1) SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University (2) Energy & Environment Lab, Samsung Advanced Institute of Technology (3) School of Mechanical Engineering, Sungkyunkwan University

Secondary batteries have long been considered as the most promising back-up power source for portable equipment. However, capacity of current anode materials, graphitic carbon, is quite low (372 mAh/g). To increase the capacity, silicon (4200 mAh/g) is regarded as one of the most promising candidates. However, the cycling performance of silicon is poor, owing to severe volume expansion and shrinkage. To solve this problem, nano sized Si nanoparticles should be used. Here we generated hydrogenated silicon nanoparticles in plasma using pulsed hydrogen gas and applied them to anode of Li ion battery as mixture with graphitic carbon.

An inductively coupled RF plasma was used to synthesize nanoparticles. Experiments were performed for 0.1, 0.3, 0.6, 0.7 and 0.9 sec hydrogen gas on time with 1 sec period. The generated nanoparticles are immediately put into THF bottle to prevent oxidation. Then, THF solution was mixed with 20wt% (to hydrogenated Si nanoparticles) pitch and dried with nitrogen. The composition of anode is Si-C (from pitch):SFG6: PVDF=25:60:15. After 1 hour heat treatment, we assembled coin half cell and measured its capacity.

As hydrogen on time is increasing, a residence time of primary particle is decreased but collision number and time is increased due to turbulence by hydrogen gas. Therefore, agglomeration would be main mechanism during hydrogen pulse on time so that uniformity is increased. Here, cases for 0.1 and 0.3 sec hydrogen on time which uniformities are below 0.2 are monodisperse.

Using case with 0.9 sec hydrogen pulse time, we manufactured mass hydrogenated Si nanoparticles and made coin half cell. The measured capacity is over 500 mAh/g, which is lower than expected value (1000 mAh/g). That means nanoparticles cannot react efficiently with Li ion because of oxidation during assembly of coin cell but the reaction rate is increased as times goes.

**9L.04**

Monitoring of Transient Ultrafine Particle Size Distribution at a Roadside Using SMPS and TR-DMPS. Dawkwang Woo (1), Seungbok Lee(2), Gwinam Bae(2) and Taesung Kim(1,3), (1) School of Mechanical Engineering, Sungkyunkwan University (2) Environmental Technology Research Center, Korea Institute of Science and Technology (3) SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University

Traffic related air pollution has been studied to understand correlation between air pollution and health effects of air pollutants in urban area. Many studies have been carried out to measure aerosol characteristics at roadside using SMPS (Scanning Mobility Particle Sizer). However, SMPS has some limitation to measure urban aerosols which vary frequently. In this paper, to understand the effect of vehicle exhaust on transient roadside air pollution, the number size distribution of ultrafine particles was measured at the Cheongyangni roadside in Seoul, Korea from March 22 to 23, 2007. SMPS and TR-DMPS (Transient Differential Mobility Particle Spectrometer) were utilized to characterize transient roadside aerosols. Number size distributions was measured with an SMPS (TSI model 3936) which consist of a DMA (TSI model 3081), CPC (TSI model 3025A). To investigate the size distribution of ultrafine particles in an environment not affected directly by emissions, SMPS was installed in a mobile cabinet. As a result, the concentration of ultrafine particles at a roadside was highly fluctuated because of variation of traffic flow. And the SMPS did not follow rapid change of particle number concentration at a roadside. The TR-DMPS quickly responded to a rapid change of particle number concentration due to abrupt traffic flow.
Rain-Aerosol Coupling In the Tropical Atmosphere of Southeast Asia.

Jun He, RAJASEKHAR BALASUBRAMANIAN, Division of Environmental Science & Engineering, National University of Singapore

The occurrence of inorganic ions in both aerosol particles and rainwater was studied at a coastal site in Southeast Asia over a period of nine months (January-September 2006). The ionic composition of aerosols was dominated by SO$_4^{2-}$, Na$^+$, and NO$_3^-$ with concentrations 2.81, 1.77 and 0.73 ug m$^{-3}$, respectively; the most important species found in the precipitation are SO$_4^{2-}$, Cl$^-$, NO$_3^-$ and Na$^+$, with 4.71, 1.09, 0.97 and 0.72 mg L$^{-1}$, respectively. The molar Cl$^-$/Na$^+$ ratio in aerosol was only 0.3, while the value in precipitation was 1.51, much higher than that of aerosol particles. In addition, the equivalent acid-base balance showed that the aerosols collected in this study had alkaline characteristics, but the volume-weighted mean concentration of H$^+$ of precipitation was 19.05 micro-eq L$^{-1}$ (pH = 4.72). Real-time physical characterization of aerosol particles during rain events showed changes in particle number distributions which were used to assess particle removal processes associated with precipitation or scavenging. The average scavenging coefficients for particles in the range 10 -500 nm and 500-10 um were 6.95 x 10-5 +/- 2.76 x 10-5 s$^{-1}$ and 1.85 x 10-4 +/- 1.63 x 10-5, respectively. A critical analysis of the scavenging coefficients obtained from this study suggested that the wet removal of aerosol particles was greatly influenced by rain intensity and was particle size-dependent as well. The scavenging ratios, another parameter used to characterize particle removal processes by precipitation, for NH$_4^+$, Cl$^-$, SO$_4^{2-}$, and NO$_3^-$ were found to be higher than those of Na$^+$, K$^+$, and Ca$^{2+}$ from oceanic and crustal origins. This enrichment implied that gaseous species NH$_3$, HCl, and HNO$_3$ could also be washed out readily and these additional sources of ions in precipitation counter-balanced the dilution effect caused by high total precipitation volume in the marine and tropical area.

Direct Comparative Measurements of Aerosol Hygroscopicity.

KATE L. HANFORD, Laura Mitchem, Nana-Owusua A. Kwamena and Jonathan P. Reid, University of Bristol, UK

Hygroscopic properties govern the partitioning of water between the gas and condensed phases in atmospheric aerosol and are therefore important for understanding the activation of cloud condensation nuclei. Laboratory studies can provide a rigorous test of thermodynamic models that predict the hygroscopic properties of mixed component aerosol.

Optical tweezers can be used to trap single aerosol particles of diameter 2-20 micro-metres for an indefinite period of time. When coupled with cavity enhanced Raman spectroscopy, CERS, the size of the trapped particle can be determined with nano-metre accuracy. A dual optical trap enables comparative measurements of the evolving size, composition and phase of two droplets of differing composition within the same gas phase to be made. A droplet such as a sodium chloride droplet has well characterised hygroscopic properties and can provide highly accurate measurements of relative humidity, RH, with a 1 second time resolution and an accuracy of +/- 0.09 % even up to saturation.

The influence of water soluble, insoluble and immiscible organic components on aerosol hygroscopicity was investigated. The influence of water-soluble organics on hygroscopicity was investigated by trapping a glutaric acid/inorganic/aqueous droplet and measuring its evolving size and composition. An inorganic/aqueous droplet was simultaneously trapped and employed as a probe for the accurate determination of RH. Thus, the Kohler curve of the glutaric acid/inorganic/aqueous droplet, which characterises the variation in equilibrium droplet size with relative humidity, was determined directly. The experimental data were compared with theoretical treatments from ADDEM, AIM and a growth factor parametrisation from the literature. Typical deviations of the experimental measurements from theoretical predictions are shown to be around 1 % in equilibrium size. In a preliminary study into the aging of organic aerosols, evolving hygrosopicity following oxidation of an aqueous/inorganic/oleic acid droplet was also investigated.
9L.07
Physical Characteristics of Ultrafine Particles Generated from Cooking Ranges.

David Cha-Chen Fung, William C. Hinds, Nola Kennedy, Nancy Jennerjohn, University of California, Los Angeles

Cooking activities are a significant source of indoor ultrafine particles (UFP) both in home and occupational settings. Exposure to these UFP can potentially cause serious health effects such as cancer. The aerosol plume from a cooking activity is a mixture of particles from the cooked ingredients and the heat source. Physical processes, such as coagulation and condensation occur when the vapors and particles from the cooking ingredients and the heat source interact. This will change the physical and chemical characteristics of the particles. Since adverse health effects are due to such characteristics, studying the particles from the ingredients and the heat source both before and after their interaction will provide important information for evaluating health risks due to exposure to UFP generated from cooking.

In this study the focus is on the analysis of particle size distribution from 3 to 300 nm and the morphology of the UFP generated from cooking ranges. Cooking ranges provide heat by either fuel combustion or electrical power. Five types of ranges were studied in this project, one natural gas range and four electric ranges. Two of the four electric ranges provide heat from electrical resistance through metallic alloys. One electric range uses infrared radiation through quartz heating elements. The last electric range generates a magnetic field and generates heat from electrical resistance through the cookware. Size distribution data were obtained with a SMPS with a nano-DMA and a SMPS with a long-DMA. Particle morphologies were distinguished from TEM samples obtained with a Hering low pressure cascade impactor and imaged with a JEOL JEM1200EX operated at 80 kilovolts. Average particle number concentrations over 20 minute periods were $1.5 \times 10^5$ /cm$^3$ for the gas stove, $10^4$ /cm$^3$ for the electrical resistance stoves, and $1.25 \times 10^4$ /cm$^3$ for the infrared radiation stove. TEM images revealed particle morphologies of chain aggregates, oily droplets, and crystalline shapes.

9L.08
Radiological Dispersal Device Outdoor Simulation Test: Cesium Chloride Particle Characteristics.


Particles were generated from simulated radiological dispersal devices (RDD) using non-radioactive CsCl. The physical and chemical properties of the resulting Cs particles were characterized. Two RDD simulation tests were conducted at Lawrence Livermore National Laboratory to investigate the impact of soil entrainment on the properties of the Cs particles generated by an explosive device. Particles were collected 150 m from the origin of RDD device with filters, and particle mass concentrations were monitored with real time particle samplers. Particles collected on filters were analyzed via scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM/EDX) to determine their size distribution, morphology, and chemical constituents. This analysis showed that Cs particles can be associated with other materials (e.g. soil) in close proximity to the device and that the morphology and chemical makeup of the particles change depending on the interaction of the device with the surrounding materials.
9L.09 
**Size-specific Real-time Measurements of Roadside PM1/UFP Concentration and Charge.** MATTHEW D. WRIGHT, Alison J. Buckley, Denis L. Henshaw, *Department of Physics, University of Bristol, UK*

Characterization of roadside aerosol is important from a human health perspective as it is a potentially important exposure route for submicron and ultrafine particles. Mobility Particle Sizers (MPS) with poor time resolution can produce artifacts in size distributions due to temporal variation in concentration on faster timescales than the measurement period. This can occur at roadsides where individual vehicles pass close by the measurement site. Real-time measurements are required to obtain accurate information in environments where aerosol concentrations change rapidly.

In the present work, two MPS devices (Grimm Aerosol Technik) are used at fixed voltage to determine the concentration of fixed particle sizes, between 20 - 200 nm, at 1 s resolution at several roadside sites in the city of Bristol, UK, during weekday afternoons. Additionally, using one of the MPS systems without a charge-neutralizer (241-Am), mobility rather than size measurement is obtained. This allows for qualitative assessment of the charge state of the aerosol, through comparison of the two concentrations which differ because of the charge of the aerosol relative to equilibrium. Size- and mobility-distributions are obtained over the size range 11 - 1000 nm illustrating the 'artifact' problem. Traffic volume (vehicles per hour) was also counted and camera footage used to identify individual vehicles corresponding to points during the measurement period.

Time-series data are presented illustrating the effect of so-called 'super-polluting' vehicles, usually heavy duty diesel engines, which produce significant peaks in concentration. The longevity of these peaks is highly dependent on localised topography and weather conditions, and the particular characteristics of the vehicle. The contribution of these peaks to overall concentration over the measurement period is examined. Observations of highly charged aerosols in these peaks are presented. The implications for human exposure are discussed.

9L.10 
**From NANO Particles to large Aerosols - Ultrafast Measurement Methods for Size and Concentration.** JUERGEN SPIELVOGEL (1), Dr. Lothar Keck (2), Dr. Hans Grimm (3),

A major challenge in aerosol technology is the fast measurement of number size distributions with good accuracy and size resolution. The dedicated instruments are frequently based on particle charging and electric detection. Established fast systems, however, still feature a number of shortcomings.

We have developed a new instrument that constitutes of a high flow Differential Mobility Analyser (high flow DMA) and a high sensitivity Faraday Cup Electrometer (FCE). The system enables variable flow rates of up to 150 lpm, and the scan time for size distribution can be shortened considerably due to the short residence time of the particles in the DMA. Three different electrodes can be employed in order to cover a large size range.

First test results demonstrate that the scan time can be reduced to less than 1 s for small particles, and that the results from the fast scans feature no significant difference to the results from established slow method. The field of application for the new instrument comprises the precise monitoring of fast processes with nanoparticles, including monitoring of engine exhaust in automotive research.
10D.01

This paper describes a novel instrument that simultaneously measures size segregated aerosol mass concentrations, i.e., PM10, PM4 (respirable), PM2.5 and PM1 over a wide concentration range in real time.

This new instrument combines aerosol cloud photometric measurement with single particle optical particle counting (OPC) in one optical system. A collimated laser beam intersects the particle beam in the detection chamber. Scattered light over a wide solid angle is collected by a spherical mirror and projected onto a photodiode detector. The electrical signal from the photodiode detector is processed into the OPC signal and the photometric signal. The OPC signal records the height of each electrical pulse generated by light scattering from a single particle. The pulse height is factory calibrated to represent the aerodynamic size of Arizona Road Dust, from which the particle mass is calculated. To reduce coincidence error, only particles greater than 1 micro-meter are used in mass calculation. The photometric signal is an integrated DC voltage generated by light scattering from the particle cloud in the sensing volume, which is correlated to PM2.5 mass concentration by calibration. The size segregated mass concentration is calculated from the OPC and photometric signals.

This measurement technique is superior to OPC based mass measurement, being able to measure high concentration aerosols. It only counts and sizes larger particles which has less coincidence errors, and measures indistinguishable small particle masses with the photometric signal. It is also better than photometer based mass measurement, because it offers additional information about particle sizes. Furthermore, it is also more accurate in measuring large particle mass, which is significantly underestimated by photometers. Data comparing this new instrument with other mass measurement techniques will be reported in this paper.

10D.02
Quantification of Mass Dependent Response Factors in a Novel Chemical Ionization Mass Spectrometer for Detecting Neutral Molecular Clusters. Mari Titcombe (1), Jun Zhao (2), Peter McMurry (1), Fred Eisele (2), Jeff Roberts (1), (1) University of Minnesota (2) National Center for Atmospheric Research, Boulder, CO

New particle formation is believed to be a significant global source of cloud condensation nuclei. According to the Intergovernmental Panel on Climate Change, the indirect radiative forcing effects of aerosols contribute the greatest scientific uncertainty in our understanding of climate forcing. Reducing this uncertainty will require improved models for nucleation and growth rates of particles in the atmosphere. To this end, we are using a novel chemical ionization mass spectrometer to measure the concentrations and masses of neutral molecular clusters formed by nucleation in the atmosphere. We refer to this instrument as the Cluster CIMS. These measurements are providing us with information about the species that participate in nucleation as well as the mass-dependent concentrations of clusters. We are using this information to make inferences about the types and rates of reactions that are responsible for nucleation. This paper describes work that we have done to quantify the relationship between cluster concentration and response of the Cluster CIMS when sampling ions of known mass and concentration. Calibration ions are produced using techniques developed by Fernandez de la Mora and coworkers. The gas phase ions are produced by electrospray and are separated by mobility using the high resolution Hermann DMA designed by Ude and Fernandez de la Mora. Results indicate a strong mass-frequency correlation for ion transmission. These results, applied as calibration factors to the CIMS system, will allow for a more accurate description of atmospheric cluster formation and growth.
10D.03
Scanning Flow CCN Analysis for Fast Measurements of CCN Spectra. RICHARD H. MOORE (1), Greg Kok (2), Athanasios Nenes (1,3), (1) School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, (2) Droplet Measurement Technologies, Boulder, (3) School of Earth and Atmospheric Sciences, Georgia Institute of Technology

The Droplet Measurement Technologies Continuous Flow Streamwise Thermal-Gradient CCN Chamber (DMT-CFSTGC) is rapidly becoming the instrument of choice for laboratory and field measurements of cloud condensation nuclei (CCN). Currently, the instrument is operated at a constant flow rate (ranging between 0.2 and 2 L min\(^{-1}\)) and its supersaturation is adjusted by changing the column temperature gradient in the streamwise direction. Although a well established and robust approach, it is relatively slow, requiring 20-40 seconds for column temperatures to stabilize (and occasionally longer periods for the temperature in the optical particle counter used for droplet detection to stabilize) during a supersaturation change. Data collected during transient periods are often discarded, which is a problem if CCN measurements are done in rapidly changing environments (such as those encountered in aircraft studies). We present a new mode of operation, in which the flow rate is changed over time in the flow chamber, while maintaining a constant temperature gradient; this allows supersaturation to continuously change, allowing the measurement of a supersaturation spectrum much more quickly over the timescale of a flow scan.

The new mode of operation, termed 'Scanning Flow CCN Analysis' (SFCA) was first studied numerically using a comprehensive model of the CFSTGC, in which the transient profiles of temperature, water vapor concentration, supersaturation and CCN activation were determined by numerically solving the Navier-Stokes equations using a finite volume method. The model was used to optimize the characteristics of the flow scan, which is key for interpreting the detected signals and inverting them back to CCN activity and droplet growth kinetics. The method is demonstrated using laboratory-generated inorganic salt particles, as well as ambient aerosol sampled from the Georgia Tech rooftop measurement platform in Atlanta, GA.

10D.04
Recent Progress in the Detection and Sizing of 1 to 3 Nano-meter Particles. Chongai Kuang (1), Kenjiro Iida (2), Peter H. McMurry (2), (1) University of Minnesota, Department of Chemical Engineering & Materials Science, (2) University of Minnesota, Department of Mechanical Engineering

Methods for measuring sizes and concentrations of aerosol particles larger than 3 nano-meter are now well established. Measurements of nanoparticles and molecular clusters smaller than this are needed to better understand rates and mechanisms of particle nucleation from the gas phase. Two new aerosol instruments for "bridging the gap" in measurements from neutral molecular clusters to nanoparticles have been developed and deployed in measurement campaigns. The first instrument is a proto-type Nano-SMPS that uses a newly developed diethylene glycol CPC followed by a conventional CPC "booster" for detecting aerosols with mobility diameters as small as 1.2 nano-meter. This proto-type Nano-SMPS has been continuously deployed at Boulder, CO for the detection of atmospheric nucleation events. The second instrument utilizes the controlled condensation of oleic acid to grow sampled nanoparticles before passing them to a conventional SMPS. This pre-growth step enables a higher charging efficiency for sampled particles and mitigates the effect of particle production within the SMPS aerosol charger. Experiments were performed to obtain size and material dependent activation efficiencies, as well as to characterize the growth response of sampled nanoparticles of various composition to oleic acid condensation.
10D.05
Dynamic Characteristics of an Aerosol Size Spectrometer.
Jason Olfert Jian Wang, Brookhaven National Laboratory

Rapid measurements of aerosol size distributions are required in a number of applications in aerosol science. The fast integrated mobility spectrometer (FIMS) is capable of measuring sub-micrometer aerosol size distributions with excellent time resolution, size resolution, and counting statistics. In fast-response aerosol size spectrometers, the time-response of the instrument is limited by time delays and mixing of the aerosol in the inlet/sampling line and by possible time delays in the classification of the aerosol, which causes the measured aerosol concentration to be 'smeared' over several time bins, leading to error in the inverted size distribution.

The purpose of this work is to determine the dynamic characteristics of the FIMS in order to understand the limitations and errors associated with very fast measurements and to show that the smearing effects of the FIMS inlet can be corrected with a 'de-smearing' data inversion technique.

The time constant of the FIMS was determined by analyzing the step-response and frequency-response of the instrument. The time constant was used in a model of the system to correct for the smearing of the aerosol in the inlet. This de-smearing inversion effectively eliminates the attenuation of the measured aerosol concentration. However, this technique amplifies the random noise in the measurement and should only be used when the aerosol is changing rapidly.

Although this work was carried out with the FIMS, the techniques used here are applicable for testing the dynamic characteristics and for correcting 'smeared' data of other fast-response aerosol spectrometers.

11D.01
Development and Evaluation of the IOSH-NCTU Personal Nanoparticle Sampler.
CHUEN-JINN TSAI (1), Cheng-Han Wu (1), Sheng-Chieh Chen (1), Shi-Nan Uang (2), Tung-Shung Shih (2,3), (1) National Chiao Tung University, Taiwan (2) Institute of Occupational Safety and Health, Taiwan (3) China Medical University and Hospital, Taiwan

There is a critical need to develop personalsamplers for the exposure assessment of nanoparticles in the workplaces. In this study, a personal nanoparticle sampler was developed in which the IOSH cyclone is used as the first stage for respirable particle classification. The second stage is a PCTE (Polycarbonate Track Etch, 10mm in effective filtration diameter) membrane filter with an acceleration nozzle at its inlet to achieve a localized high filtration velocity for nanoparticle classification. The final stage is an after filter which collects nanoparticles. When the PCTE pore size is 20 micrometer and the air flow rate is 5.3 L/min (nozzle velocity: 112.47 m/sec), the cut-size of the sampler for monodisperse NaCl particles is 101.1 nm and the collection efficiency curve is sharp. The corresponding pressure drop is 110 +/- 10 cm H2O. The pressure drop will be lower when the flow rate is lower. Then a personal sampling pump such as SKC XR5000 can be used for this personal sampler. The particle loading tests indicated when nanoparticle loaded mass was less than 11 micro-grams, the cut-size of the sampler was kept nearly the same at 100 nm and the pressure drop increased to about 130 +/- 10 cm H2O. More study and tests will be conducted and the results will be reported.
11D.02
Evaluation of IOM Personal Samplers at High Flow Rate.
YUE ZHOU, Jun Wu, and Yung-Sung Cheng, Lovelace Respiratory Research Institute

Personal aerosol samplers are used to evaluate the exposure to airborne particles of workers in occupational environments. Workers usually mount samplers on their lapel collecting aerosols in the breathing zone. A sampling pump is also worn to draw air in the sampler, usually at 2.0 L/min for the Institute of Occupational Medicine (IOM) sampler. The IOM sampler was designed to have the sampling efficiency following the Inhalable Mass as defined by the ACGIH and ISO. However, workers have to wear the sampler for a relatively long time to collect enough material for further analysis with 2 L/min flow rate. Recently, there is a new sampling pump, Leland Legacy sampling pump with a flow rate up to 15 L/min. Because the IOM sampler was designed at the flow rate of 2.0 L/min, the performance of the sampler at high flow rate must be evaluated. In this study, 8 samplers were mounted on different locations (front, sides, and back) of a mannequin in an aerosol wind tunnel. Monodisperse aerosols of oleic acid tagged with sodium fluorescein in the size range of 2 to 100 micro-meter were used in the test. The sampling flow rates of the IOM samplers are 2.0 and 10.6 L/min (the maximum flow rate through the IOM sampler using a 25 mm cellulose filter). Wind speeds of 0.56 and 2.22 m/s were also used in the aerosol wind tunnel. Results showed that the sampling efficiency of the IOM samplers mounted at front portion of the mannequin was always higher than that at side and back regardless the wind speed and flow rate. On average, for the wind speed of 0.56 m/s, the collection efficiency of the samplers at 2.0 L/min was slightly higher than that of at 10.6 L/min. For the wind speed of 2.22 m/s, the collection efficiencies at both flow rates were the same when particle size smaller than 60 microns. Our results also show that the sampling efficiency of the IOM at two different flow rates follows the Inhalable Mass curve for particles in the size range of 2 to 50 micro-meter. The test results indicate that the IOM sampler can be used at higher flow rate to collect larger quantity of material or to collect similar amounts of material at shorter sampling time as at original designed flow rate of 2 L/min.

11D.03
A Miniature Water Condensation Aerosol Collector.
GREGORY S LEWIS, Nathan Kreisberg, Susanne Hering, Aerosol Dynamics Inc., Berkeley CA

A miniature aerosol collector has been developed using a laminar flow condensation method, analogous to that employed in the water-based condensation particle counters. This collector provide concentrated, low-pressure drop collection of fine and ultrafine particles deposited in to a small spot (~300 microns) or in to a small volume of liquid (~20 µl). The system utilizes a single thermo-electric device as a heat pump to provide a ~25 degrees C temperature difference. The miniature collector weighs ~200g (excluding power source), and provides collection at 0.4 L/min with a lower cut point of 10 nm, a pressure drop of 1 kPa, and a power consumption of 1 Watt.

With the laminar flow water condensation approach, the aerosol flow is first chilled by a cold walled conditioner, and then introduced into a hot wet-walled condenser. Because water vapor diffuses more rapidly then heat, the air vapor is supersaturated resulting in particles large enough to be collected by impaction. The design of the system was guided by numeric modeling of the saturation ratios, particle activation and growth. The model includes the heat release from condensation, and the associated warming of the flow that reduces the supersaturation and particle growth at high particle number concentrations. By controlling the system geometry (either plate separation or tube diameter), we are able to activate at small particle sizes while minimizing concentration effects. Our method of particle collection provides a number of other advantages. Particle bounce off the impaction surface can be eliminated by controlling the temperature of the impaction surface so as to maintain a thin film of water on the surface. Collecting into a small liquid vial eliminates the need for particle extraction from filters or resuspension from surface, it minimizes the total volume of the sample, and it allows for continuous automated collection and analysis.
11D.04 Compact Sampler for Secondhand Tobacco Smoke and Other Airborne Particles. Michael Apte, Michael Spears, Lara Gundel, Lawrence Berkeley National Laboratory

This presentation describes a sampler developed at Lawrence Berkeley National Laboratory to meet the need for compact, inexpensive tools for measuring human exposure to airborne particles, especially secondhand tobacco smoke (SHS) and Diesel exhaust. Better SHS methods can show how closely asthmatic children's cotinine levels track reductions in SHS particulate exposure, for example. Research strongly suggests that relying only on nicotine or its metabolites as surrogates for exposure to SHS can lead to misclassification of exposure status, because particles and many volatile organic compounds in smoke behave much differently than nicotine.

The instrument has three pairs of collectors with controllers that are programmed for sequential sampling by the user. For example, the instrument can collect three one-week integrated SHS samples to represent three distinct daily periods. Particles are deposited by thermophoresis onto quartz rods using a miniature pump, and organic gases diffuse onto sorbent tubes. After sampling, the light absorption (ultraviolet to near-infrared) is measured to assess the contributions of black and ultraviolet absorbing particles. In many indoor environments, concentrations of Diesel exhaust and tobacco smoke can be determined from the infrared and ultraviolet absorbance, respectively. The sorbent tubes are analyzed for the tracers for exposure to SHS can lead to misclassification of exposure status, because particles and many volatile organic compounds in smoke behave much differently than nicotine.

Laboratory validation of the SHS sampler is being conducted with low concentrations of SHS in air that also contains woodsmoke, Diesel exhaust or cooking fumes, at realistic indoor concentrations, to establish sensitivity, stability and selectivity for each constituent. A small field study includes simultaneous monitoring of SHS with the new sampler and conventional sampling methods in residences with smokers; comparing SHS concentration data from each approach, as well establishing the limits of detection, specificity and stability; and assessing potential misclassification of SHS exposure by comparing inferences about exposures from nicotine alone, to inferences from data on SHS particles and gases.

11D.05 Miniature Ultrafine Particulate Sensor (MUPS): Design, Development, and Testing. Manish Ranjan and Suresh Dhaniyala, Department of Mechanical and Aeronautical Engineering, Clarkson University, Potsdam, NY, USA

Ultrafine particles (UFP, Dp<100nm) can penetrate deep into the lung, and due to their large surface area (Oberdorster, 1996, 1998) and high retention time (Donaldson et al., 1998), they can cause respiratory related illnesses (Palmgren et al., 2003). UFP monitoring tools are required to study the effect of these particles on human health and our microenvironment. Effective monitoring requires measurements to be accurate, in-situ, and real-time. The optimal instruments for such measurements will be portable, small, inexpensive, and easy to deploy.

Such tools are largely unavailable for monitoring at this time. The successful operation of the Miniature Electrical Aerosol Spectrometer (MEAS, Ranjan and Dhaniyala, 2007, 2008) has promised similar performance in a wide variety of other electrical mobility based applications. Another similar instrument, called Miniature Ultrafine Particulate Sensor (MUPS), was developed at Clarkson University to measure real-time total ultrafine particle concentration with features of low pressure drop, single flow operation, and compact size.

MUPS works on the principle of particle electrical mobility classification. Various range of particle diameters are captured on a single shaped collection plate connected with an electrometer. The single collection plate in this instrument is shaped such that the size dependence of charging and collection efficiency from the inversion equation is balanced out in the collection plate shape. This means that the electrometer signal is linearly proportional to the total ultrafine particle count, and the bigger particles are collected away from the collection plate due to the low mobility.

Theoretical model for collection characteristics computation which accounts for the non-uniformity in the electric fields within the instrument (Ranjan & Dhaniyala, 2007) has been used for transfer function calculations. An inversion routine based on regularization technique has been used to solve a set of ill-posed system of equation governing the plate shape. The design description, modeling, simulation, and experimental testing towards the instrument performance validation and comparison with existing commercial instrumentation will be presented in the conference.
11D.06  
**Development of a Miniature Particle Size Magnifier with Saturated Water Vapor as the Condensing Fluid.**  
JIN YOUNG CHOI, Sang Young Son, *University of Cincinnati*

Heterogeneous condensation of supersaturated vapor is the most traditional, but still the most powerful method for detecting ultrafine particle which is too small for optical measurement, even though numerous other technical advances have been proposed. Many innovative improvements and modifications to the design of particle counter using condensation have continued over the last century, and now various types of sensors are commercially available. The objective of our current work is to develop a particle size magnifier which is enough small to be applicable to portable device using this condensation principle. The developed condensation chamber has a wick-type inner wall structure to manage liquid flow, and the total volume of the condenser parts except for water feeding system does not exceed 0.5cc. The pure water is used as the condensing fluid, which is desirable for many applications. The performance of the fabricated chamber was investigated by the test aerosol generation system using the collision type nebulizer and optical detection technique with Nd:YAG pulsed laser. The standard PSL particles of 50nm size were used for test. The particle activation efficiency was determined from the ratio of particle number concentration detected by the pulsed laser at the exit of chamber to that measured by a commercial handheld CPC (TSI Model 3007) at the inlet. The experimental results present that the ultrafine particles successfully grew to micron size droplets through the developed chamber and then could be counted with the optical detection system. The counting efficiency estimated by image analysis is more than 85%. The best results for particle growth can be obtained when operating at the particle-laden air flow rate of 0.2 to 0.3lpm, which is equivalent to about 50 milliseconds residence time of particles inside the chamber.

12D.01  
**Characterization of a Large Particle Concentrator.**  
ANDREW MAY (1), Sang-Rin Lee (2), Suresh Dhaniyala (1), Thomas M. Holsen (1), (1) Clarkson University (2) University of Iowa

A novel Large Particle Inlet (LPI) was previously designed and developed by Lee et al. (2008) using computational fluid dynamics (Fluent; Fluent, Inc., NH; Version 6.1.22). From this design, theoretical inlet efficiency curves were generated using particle trajectory simulations (Lee et al., 2008). To validate this design, it was necessary to perform experimental work in a controlled environment. These experiments were performed in the Clarkson University Aerosol Wind Tunnel for a range of test conditions. A successful method of uniformly injecting large particles was developed and utilized during experimentation. A variety of test particles were used in the experiments, with mass median diameters ranging from 34 to 74 micron and geometric standard deviation less than 1.2, as reported by the manufacturer (Washington Mills, North Grafton, MA). The experiments were performed at wind speeds ranging from 3 to 7 m\(^{-1}\). Particle concentrations in the wind tunnel were measured using novel passive large particle impactors (PLPI), and the LPI measurements were compared to those of PLPI upstream values. In most cases, the experimental inlet efficiency was determined to be greater than that predicted by the theoretical correlation developed previously.

Downstream from this novel LPI is a two-stage virtual impactor, designed by CFD to concentrate the large particles. Concentration is performed by converting the sampling flow rate from 1400 Lpm at the inlet to 25 Lpm at the exit of the second VI. Experimentation has been performed within a closed chamber having a known concentration of particles. Measured particle mass concentrations from the concentrator have been compared to the measured concentration in the chamber to validate the design.

References:

12D.02

Design and Development of an Annular Inverted Impactor (AII) for Large Particles (PM>10) Size Separation. Krishanu Banerjee, Thomas Holsen, Suresh Dhaniyala, Clarkson University

Particles larger than 10 um (PM>10) are major constituents of dry deposition and very important in cloud studies. However because of their inertia it is very difficult to measure their ambient concentration using traditional sampling approaches. The objective of this research is to develop a technique to separate large particles by size before they are compositionally characterized. A conventional impactor is not suitable for separating these particles because gravity in combination with inertial effects results in a non-sharp collection curve and loss of particles on the impactor walls. Computational fluid dynamics modeling (CFD) suggests that the adverse effect of gravity can be eliminated by inverting the impactor. To avoid turbulent dispersion which would result in particle loss, the impactor must be operated in a laminar flow regime. Modeling results suggest that with an inverted impactor, particles can be collected with sharp collection characteristics. The upper size range of collection is limited by the operating velocity ratios, i.e., the ratio of impactor nozzle velocity to the terminal settling velocity. For velocity ratios < 20, the effect of gravity results in non-impaction of particles on the collection surface. With this upper limit, annular inverted impactors (AII) are seen to separate particles up to a cut-off diameter of 50 um, while a circular inverted impactor is limited to particles < 30 um cut-off diameter. Modeling results were validated by using a MOUDI impactor operating in various velocity ratios. Large particles were generated by using Vibrating Orifice Aerosol Generator (VOAG) and calibrated by Aerosol Particle Sizer Spectrometer (APS). Modeling and experimental results will be presented.

12D.03

Characterization of Bioaerosol Sampling Devices Using ATP Bioluminescence. SATYANARAYANAN SESHADRI, Taewon Han, Valdis Krumins, Donna E. Fennell, and Gediminas Mainelis, Rutgers University, New Brunswick

A variety of liquid-based samplers have been developed for collecting bioaerosols. While detailed information about samplers’ collection efficiency and losses can be obtained using fluorescent microspheres via mass balance analysis, such information often lacks detail or is difficult and labor-intensive to obtain with actual bioaerosols. In a search for a better and faster technique to provide detailed information about sampler performance with bioaerosols, we explored application of Adenosine Tri-Phosphate (ATP) bioluminescence method. Here, the intensity of luminescence produced by the interaction of firefly luciferin/luciferase enzyme with bacterial ATP is linearly proportional to the ATP content and is quantified using a luminometer.

The feasibility of the method was tested by developing a protocol for characterization of bioaerosol sampling devices using ATP bioluminescence and using it to characterize the performance of a BioSampler (SKC Inc.). Calibration curves were built by plotting the Relative Luminescence Units (RLU) indicative of total ATP content of P. fluorescens and B. subtilis bacteria in liquid samples against total bacterial counts obtained via epifluorescence microscopy. The curves were then applied to characterize the collection efficiency and losses of the BioSampler.

The performance of the BioSampler was evaluated at 8.5, 10.5 and 12.5 L/min flowrate and with P. fluorescens and B. subtilis bacteria. The average collection efficiency of P. fluorescens and B. subtilis over all flow rates was 69% and 54%, respectively. Collection efficiency determined by the ATP method at all flow rates agreed well with the direct counts for both bacteria. The internal losses determined by the ATP method were approximately 5% for both bacteria while the inlet losses were 15% at 8.5 L/min, gradually increasing to 20% at 12.5 L/min. Thus, our experiments indicate that the ATP technique could be used for rapid and detailed analysis of performance characteristics of bioaerosol sampling devices challenged with actual airborne microorganisms.
12D.04
A New Sampler to Collect Infectious Viruses from Exhaled Breath. James McDevitt (1,2), Stephen Ferguson (1), Jack Wolfson (1), Patricia Fabian (1,2), Marco Martins (1), Petros Koutrakis (1), Donald Milton (1,2), (1) Harvard School of Public Health, (2) University of Massachusetts Lowell

Understanding the transmission pathways of influenza and other emerging infectious diseases is essential for assessing risk, providing effective interventions, and minimizing public fear. Very little information is available on the number and size of particles generated by infected persons, in part because limitations of conventional air samplers which do not efficiently capture fine particles or do not maintain microorganism viability. We designed and built a new sampler, called the G-II, which can collect exhaled breath particles that can be used in viral infectivity analyses. A truncated cone shaped inlet collects exhaled breath and allows test subjects to comfortably perform various breathing maneuvers (i.e. tidal breathing, coughing, and talking) and also allows subjects to wear a mask or respirator during testing. A 5.0 um slit impactor collects particles greater than 5 um. Subsequently, condensation of water vapor is used to grow remaining particles, including fine particles, to a size large enough to be efficiently collected by a 1.0 um slit impactor and be deposited into a buffer-containing collector. We evaluated the G-II for fine particle collection efficiency with nebulized ammonium sulfate aerosols. Comparison of up and downstream samples collected on filters and analyzed via ion chromatography showed 96% removal of sulfate aerosols. These results were confirmed using a scanning mobility particle sizer and a condensation particle counter which measured 90-98% fine particle removal efficiencies for sulfate particles from 50 -750 um (AED). These data show that the G-II can efficiently collect submicron sized viruses from the air stream. The new design will enable us to determine exhaled infectious virus generation rate and evaluate simple control strategies such as wearing a surgical type dust mask to prevent the release of viruses from infected persons. We are currently evaluating the G-II with laboratory generated influenza virus aerosols.

12D.05
A Fundamental Study of the Effect of Multiple Round Nozzles on Particle Deposits in Inertial Impactors. Joshua M. Rocklage (1), Virgil A. Marple (2), Bernard A. Olson (2), (1) Solar Turbines, San Diego, CA (2) Particle Calibration Laboratory, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN

When multiple round nozzles are used in a stage of an inertial impactor, particle deposits are often found in locations other than directly under the nozzles. The locations, and the fraction of particles collected at these locations, were the subject of a fundamental study of multiple round nozzle impactors. This was accomplished through a combination of experimental and numerical techniques.

Experimental studies were performed to determine the deposition location and quantity of particles captured in a custom designed impactor. The impactor stage contained nozzle spacing ratios of 2.5 and 4.0, and at Reynolds numbers of 500, 1,000, 1,875 and 3,000. It was found that particle deposits could be categorized into four distinct groups: primary, secondary, halo and nozzle deposits. Several interesting phenomena were observed during the experimental testing that highlighted the effect of multiple nozzles and Reynolds number.

In addition, three-dimensional numerical modeling was used to study the flow fields and particle deposits from pairs of nozzles with spacing ratios of 2.5, 4.0 and 7.0 and Reynolds numbers of 500 and 1,000. It was found that both the secondary and nozzle deposits are due to a combination of impaction and interception resulting from recirculation regions formed by the interaction between jets. The magnitude of these deposits was seen to increase with the Reynolds number, which is consistent with impaction theory. It was determined that the halo deposits are caused by particle sedimentation, and the magnitude of the deposits increased with lower Reynolds numbers and larger particle diameters, which is consistent with particle sedimentation theory.

Finally, several criteria are specified for designing and operating inertial impactors such that non-ideal particle deposition may be minimized. Examples of the primary, secondary, halo and nozzle deposits as a function of nozzle spacing ratios and Reynolds numbers will be shown.
12D.06
Experimental study and modeling of two-phase heat and mass transfer in an air-blast atomized wetted-wall cyclone.
JOSH HUBBARD, John Haglund, Ofodike Ezekoye , Applied Research Laboratories at the University of Texas at Austin

Two-phase flow in a 100 liter per minute wetted-wall cyclone was studied experimentally and a one-dimensional model was developed to predict rates of liquid evaporation. Evaporation rates were measured over a range of inlet air temperatures and relative humidity to determine the functional dependence on ambient conditions and liquid injection rate. An air conditioned chamber was used to produce inlet air conditions ranging from 20 to 50 degrees Celsius, and 20% to 70% relative humidity. The liquid injection rate was varied from 100 to 1000 micro liters per minute for each inlet air condition. The data show that the evaporation rate increases linearly with liquid injection rate. Tests were conducted in which the wetted-wall cyclone was submerged in an ice-water bath to reduce evaporation. Chilling the cyclone in this manner reduced the liquid surface temperature and vapor density, thus limiting the driving force behind evaporation. For the case of the cyclone wall temperature of 0 degrees Celsius, substantial condensation was observed. Condensation rates were on the same order of magnitude as liquid atomization rate, suggesting that liquid input can be minimized or eliminated by cooling of the cyclone body. A steady-state one-dimensional numerical heat and mass transfer model was used to predict the rates of evaporation and condensation. The air temperature, air vapor density, and liquid surface temperature profiles were solved along the length of the cyclone and the resulting net mass transfer rate was calculated. The simple model shows good agreement with data trends when the heat and mass transfer coefficients are fit to the data at one temperature and relative humidity condition.

13D.01
Study of A New Corona-Based Unipolar Aerosol Charger.
LIN LI, Da-Ren Chen, Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis

Particle charging plays an important role in both scientific studies and practical applications of aerosol science and technology. Unipolar charging has recently attracted much attention due to the potential applications of nanoparticles, considered as the building blocks for nanotechnology, and the easy process of nanoparticles using the electrostatic means. In general unipolar charging provides a higher charging efficiency for particles compared with that offered by bipolar charging. Because of the limitation in using the radioactive sources worldwide, corona-based unipolar charging has been the focus in recent studies. However, corona-based unipolar chargers currently available are suffered by several issues, such as electrostatic loss and the generation of particles and ozone. Furthermore, most available unipolar chargers are designed to pursue the higher charging efficiency. However, particles larger than 50nm may get too many charges at the same time, which leads to more particle loss and more difficult control of charged particle.

In this study, a corona-discharge-based unipolar aerosol charger has been constructed, and its performance has been systematically evaluated. The configuration of this prototype unipolar charger is similar to that proposed by Qi and Chen (2007), consisting of corona ionization and charging zones separately. Different from Qi's mini-charger no mesh screen was used in the prototype to partition two zones. The charger performance was optimized by varying different operational parameters, i.e., total and ion flowrates, driving or reverse voltage, and the size of ionization zone. Both intrinsic and extrinsic charging efficiencies of the prototype charger were evaluated at the optimal operational conditions for particles in diameters ranging from 5 to 100 nm. Charge distributions of test monodisperse particles of different sizes were measured by the Tandem-DMA technique. Further, the performance of the prototype under different aerosol carry gases was evaluated in this study. The results of this experiment will be given in this presentation.
13D.02
The effect of initial charging state on NSAM's response.
CHAOLONG QI (1), Christof Asbach (2), Weon Gyu Shin (1), Heinz Fissan (2), David Pui (1),
(1) University of Minnesota, Minneapolis (2) Institute for Energy and Environmental Technology (IUTA), Duisburg, Germany

Nanoparticle Surface Aera Monitor (NSAM) has been used to measure lung-deposited surface area concentration of different aerosols. The design of NSAM is based on unipolar charging of aerosol. Therefore, the initial charging state of the sampled aerosol could produce a deflected response on NSAM. It is especially serious when characterizing highly charged particles, such as the soot particles emitted from Diesel engine. In this study, we firstly evaluated NSAM's response to four types of aerosol with monodisperse particles ranging from 20 nm to 200 nm: uncharged particle, neutralized particle, singly charged (positive) particle, and singly charged (negative) particle. It was found that the response deviation is more than 20% for positively charged particles smaller than 30 nm. By challenging the NSAM using particles carrying different number of charges, we found that the response deviation is always negligible for particles with negative charges while it is increased for particles with increasing positive charges. This result suggested that there might be a noticeable response deviation on NSAM when dealing with particles carrying mutiple initial charges even the sampled particles follow a Boltzmann charge distribution in high temperature, which is the case for Diesel engine exhaust particles. A model based on Fuchs limiting-sphere charging theory and particle penetration measurement in different part of NSAM was also developed to predict the response deviation. The modeling results agree very well with the experimental test data. This model can be easily extened to other aerosol instruments based on unipolar charging to study the effect of initial charging state.

13D.03
Charging of concentration-enriched aerosol particles via water-based condensation growth and ozone-free unipolar charging.
Bangwoo HAN (1,2), Neelakshi HUDDA (1), Zhi NING (1), Constantinos SIOUTAS (1), (1) Department of Civil and Environmental Engineering, University of Southern California (2) Environmental System Research Division, Korea Institute of Machinery and Materials

A novel approach for charging aerosol particles to improve charge number on particles in an ozone-free unipolar charging environment was investigated. This was realized on concentration-enriched aerosols with a versatile aerosol concentration enrichment system (VACES), developed by our group, and a unipolar charger equipped with carbon fiber ionizers. The particles grown to micrometer size through condensation of water vapor were charged using a positive unipolar charger with applied voltages of 2-5 kV. After the aerosols were dried with a diffusion dryer, the original size distributions was restored, while conserving the acquired charges on the particles. Charging performance was investigated for both mono-dispersed PSL particles (99, 130 and 170 nm) and poly-dispersed species (ammonium nitrate, ammonium sulfate, glutaric acid). It was observed that number of charges on particles was highly dependent on particle concentration as well as particle size. The average electrical mobility of the charged particles exceeded 1.4x10^{1} cm^{2}/(Vs), corresponding to more than 250 elementary charges per particle on average for concentrations in the range of 1.4-1.9x10^{5} particles/cm^{3} for ammonium nitrate, ammonium sulfate and glutaric acid. Lower number of charges per particle were observed for PSL particles, probably due to their hydrophobic nature, and number of charges per particle was on average 98, 191 and 349 for PSL particles of 99, 130 and 170 nm respectively, at particle concentrations of 1.1-1.7x10^{5} particles/cm^{3}. Even in the case of PSL, these charges still far exceed those obtained by means of traditional corona chargers.
13D.04
Analysis Of Scanning Dma Transfer Functions. Praney Dubey, Suresh Dhaniyala, Clarkson University, Newyork

To operate the DMA for sizing particles over a wide range of mobilities over a short time, the DMA exponential voltage scanning technique was introduced by Wang and Flagan (1990). For small scan times, relative to the particle residence times in the classifier section, the transfer functions for scanning DMAs was shown by Collins et al. (2004) to be substantially different from the expected triangular transfer function. Their calculation technique, is time consuming and not amenable for real-time transfer function calculation.

A new approach to determine transfer functions of scanning differential mobility analyzers (DMAs) is introduced. An expression for non-diffusive particle trajectories in a cylindrical DMA operating in a scanning voltage mode is obtained analytically. Particle trajectory simulations are then used to determine the scanning DMA transfer functions. The results suggest that the shape of the scanning DMA transfer functions may vary with mobility for scan times smaller than a certain value, which depends on the DMA flowrates, and this provides one criteria limiting the fastest scan possible with the conventional DMAs.

A simple approach to determine upscan scanning DMA transfer functions in near real-time with minimal number of simulations will be presented. Parameterized expression of variation of area under transfer function with scantime is obtained. The parameterized expression of area and solution of four equations corresponding to four critical trajectories are able to provide real time transfer function of very fast scan. Further, CPC smearing effect can be included in arrival time based transfer function (ATF) to obtain the transfer function of the entire scanning mobility particle sizer (SMPS) system. For upscan operation, the choice of the scantime is seen to impose upper and lower limits on the particle mobility range classified by a scanning DMA. The predicted effect of voltage scanning on altering DMA transfer functions is validated with fast scan experiments.

13D.05
Measurement of nanoparticles at low pressure conditions using the GRIMM SMPS+E. Dae-Geun Cho (1), Jihun Mun (1), Young-Jin Kim (1), Sang-Woo Kang (2), Ju-Young Yun (2), Yong-Hyeon Shin (2), Taesung Kim (1), (1) Sungkyunkwan University, Suwon, (2) Korea Research Institute of Standards and Science, Daejeon

In this study, the operation of the differential mobility analyzer (DMA) at low pressure conditions was performed to measure nanoparticle (<100nm) size distribution using a middle type DMA (the length of 88mm) and a faraday cup electrometer (FCE) commercialized by GRIMM Aerosol Technik Co. This system was improved and modified by additional equipments, which consisted of vacuum rotary pump, massflow controller, capacitance manometer and plumbing for low pressure. As sheath and aerosol flow rate were 1–5 slpm and 0.1–0.5 slpm respectively, the modified DMA with FCE was successfully operated under low pressure conditions (20–50 Torr). A tandem DMA method and a least squares sense were used to calibrate the modified system and obtain empirical parameters (height, half-width) of DMA transfer function.

The height and the half-width were varied from 0.1 to 0.25 and 0.15 to 0.25 with a size range from 20nm to 80nm. We also compared the empirical transfer function at low pressure with that at an atmospheric condition.
A New Real-Time Method for Determining Particles Sphericity and Density: Application to Secondary Organic Aerosol Formed by Ozonolysis of a-Pinene. ALLA ZELENYUK (1), Juan Yang (1), Chen Song (1), Rahul A. Zaveri (1), Dan Imre (2), (1) Pacific Northwest National Laboratory, Richland, WA, (2) Imre Consulting, Richland, WA

Particle volumes are most often obtained by measuring particle mobility size distributions and assuming that the particles are spherical. Particle volumes are then converted to mass loads by using particle densities that are commonly, either calculated or estimated from measured mobility and vacuum aerodynamic diameters, assuming again that the particles are spherical. Depending on the system, these assumptions can introduce significant errors. We present in this work a new method that can be applied to any particle system to determine in real-time whether the particles are spherical or not. We use our second generation single particle mass spectrometer (SPLAT II) to measure with extremely high precision the vacuum aerodynamic size distributions of particles that are classified by differential mobility analyzer and demonstrate that the line shape of these vacuum aerodynamic size distributions provide a way to unambiguously distinguish between spherical and aspherical particles. Moreover, the very same experimental system is used to obtain the size, density, composition, morphology, and dynamic shape factors of individual particles. We present an application of this method to secondary organic aerosols that are formed as a result of ozonolysis of alpha-pinene in the presence and absence of an OH scavenger and find these particles to be spherical with densities of 1.198 +/- 0.004 g/cm$^3$ and 1.213 +/- 0.003 g/cm$^3$ respectively.

Real-Time Aerosol Density Determination Utilizing a Modified Scanning Mobility Particle Spectrometer-Aerosol Particle Mass Analyzer (SMPS-APM) System. QUENTIN G. J. MALLOY, Li Qi, Shunsuke Nakao, David R. Cocker III, University of California-Riverside, Bourns College of Engineering, Department of Chemical and Environmental Engineering

Recently much attention has been given to evaluating the density of aerosol generated in smog chambers in hopes of gaining further insight into the processing of Secondary Organic Aerosol (SOA). Here we present data generated from the UC Riverside/CE-CERT Environmental Chamber utilizing a modified Scanning Mobility Particle Spectrometer-Aerosol Particle Mass Analyzer (SMPS-APM) setup. The new configuration allows for automated real-time density data collection over the course of multi-hour experiments. Results obtained for alpha-pinene (rho=1.28 g/cm$^3$) match remarkably well with those previously reported obtained using an Aerosol Mass Spectrometer (AMS) (rho=1.32 g/cm$^3$) (Kostenidou et al 2007). Interestingly, little change in aerosol density is seen during the course of the experiment, further supporting the apparent lack of aging of aerosol. Density data of several different SOA precursors and implications of the apparent lack of aerosol aging are presented and discussed.
14D.03
Online Nanoparticle Mass Measurement by Aerosol Particle Mass Analyzer and Differential Mobility Analyzer: Comparison of Theory and Measurements. ANSHUMAN AMIT LALL, Xiaofei Ma, Suvajyoti Guha, George W. Mulholland and Michael R. Zachariah, University of Maryland, College Park

An aerosol particle mass analyzer (APM) has recently been used in a number of studies for direct measurement of particle mass. The APM classifies particles by balancing the electrostatic and centrifugal forces. The centrifugal force is directly proportional to the particle mass which makes it possible to determine particle mass directly by APM measurements. The method is particularly useful for determining particle mass for non-spherical single or aggregate particles or when the particle density is unknown or varies during a certain process.

A combination of a differential mobility analyzer (DMA) and an APM is often used to measure mass of the mobility classified particles. The particles are classified in a narrow mobility size bin determined by the DMA transfer function. This spread in the particle diameter leads to a larger spread in particle mass. Thus the trend in particle concentration measured as a function of APM voltage is wider than the theoretical APM transfer function.

In our calculations, we account for the narrow spread in near-mono-dispersed particles using a triangular particle size distribution that resembles the DMA transfer function. We made two comparisons: The modal mass measured by the DMA-APM system was compared with the modal mass of the calibration spheres; and the calculated combined DMA-APM response is compared with the theoretical APM transfer function. The measurements were made with 60 nm and 100 nm NIST Standard Reference Materials (PSL spheres) for particle diameter and with 300 nm NIST traceable PSL spheres. The combined uncertainty in the measurements was determined by taking the uncertainty in calibration particle size and repeatability uncertainty into account.


14D.04
Uncertainty in light scattering measurements by nephelometer with absorbing particles: results from laboratory studies and implications for ambient measurements. PAOLA MASSOLI (1,2), Tahllee Baynard (1,2)*, Edward Lovejoy (2), Charles Brock (2), Daniel Lack (1,2), Adam Wollny (1,2)#, Daniel Murphy (2), (1) University of Colorado, Boulder (2) NOAA ESRL CSD, Boulder * Now at Lockheed Martin Inc. # Now at Max Plank Institute, Mainz

We performed a series of laboratory studies to assess uncertainties in aerosol optical property measurements. We used a pulsed cavity ring down aerosol extinction spectrometer (CRD AES) to measure the light extinction coefficient, a photo-acoustic absorption spectrometer (PAS) for light absorption and a commercial integrating nephelometer (TSI, model 3563) for the scattering coefficient. The test aerosols generated for the study consisted of absorbing and non-absorbing particles, delivered to the systems as pure compounds or mixtures. The lowest uncertainty in single scattering albedo ($\omega$) was obtained by combining CRD-AES and PAS data. Determination of single scattering albedos by differencing the extinction and scattering measurements had significantly higher uncertainties. For non-absorbing aerosols we found that the CRD-AES and nephelometer instruments agreed within expected uncertainty. With absorbing aerosols ($\omega<$0.7), the discrepancy was higher than expected. We suggest as a reason that the literature expressions for nephelometer truncation errors are not adequate for absorbing particles. This is consistent with Mie theory predictions of larger nephelometer angular truncations in the case of absorbing aerosols. Based on our instrumental capabilities we revise the current uncertainty for scattering and single scattering albedo values obtained by using nephelometry, but a more comprehensive expression to correct for the effects of angular truncation should be determined. The implications for the overall uncertainty of aerosol optical property measurements are discussed.
14D.05
Kelvin Effect Measurement of the Surface Energy of Nanocrystals. XIAOFEI Ma, George W. Mulholland, Michael R. Zachariah, University of Maryland

A novel method to study the evaporation kinetics of nanocrystals (NC) is developed. Direct in situ measurement of mass change using a Differential Mobility Analyzer (DMA) coupled to an Aerosol Particle Analyzer (APM) is used to determine the size dependent evaporation rate. A simple kinetic model is used to relate the evaporation rate to the temperature dependent surface energy. We report measurements for Zn NC surface energies of 9.0 and 13.6 J/m² at 375 °C and 350 °C, respectively. We also observed using electron microscopy crystal edge effects which leads to an evaporation anisotropy for Zn NCs.
Viral aerosol capture and retention by a novel alumina nanofiber filter. Hsing-Wang Li (1), Chang-Yu Wu (1), Fred Tepper (2), Jin-Hwa Lee (1) and Christiana N. Lee (3), (1) Department of Environmental Engineering Sciences, University of Florida, Gainesville, FL (2) Argonide Corp., Sanford, FL (3) Department of Chemical Engineering, University of Florida, Gainesville, FL

The spread of airborne pathogens and the potential of intentional release of biological agents have raised the public's concerns about bioaerosols and the need for their effective control. Alumina nanofiber filters, a novel concept developed recently, offer a potential solution. This study was aimed to evaluate the capture and retention of a novel commercial alumina nanofiber filter (NanoCeram) for viral aerosols.

The physical collection efficiency of the nanofiber filter was determined by comparing MS2 aerosol size distributions before and after the filter. The viable collection efficiency was determined from the infectivity of virus collected by Biosamplers. For comparison purposes, three HEPA filters (glassfiber, PTFE, Lydall) were also tested.

The physical efficiency for 10-100 nm particles was over 89.7%, and its viable efficiency was slightly lower than the other filters. However, its pressure drop was much lower than the others. Due to the slip on the nanofiber surface, the drag force on the nanofiber is smaller than in a non-slip flow. Consequently, the nanofiber filter had the best filter quality, which was three time higher than the glass fiber filter. The main contribution to this gain in performance is its unique feature of low pressure drop. The average survival fraction on nanofiber filters was $8.64 \times 10^{-2} \pm 7.00 \times 10^{-2}$. It indicates the viruses were effectively retained in the nanofiber filter, which is due to electroadhesive force. In contrast, the survival fractions of the other three filters were all three orders higher.

In summary, the alumina nanofiber filter can provide the similar level of removal efficiency as conventional filters with a lower pressure drop and superior retention.

Acknowledgement: This work was partially supported by US Air Force Research Laboratory (Grant No. FA8650-06-C-5913). H. W. Li acknowledges the financial support of Graduate Students Study Abroad Program by the National Science Council, Taiwan (096-2917-I-006-017).

Figure of Merit of Composite Filters with Micrometer and Nanometer Fibers. JING WANG, Seong Chan Kim, David Y. H. Pui, Particle Technology Laboratory, Department of Mechanical Engineering, University of Minnesota

We investigate the filtration performance of composite filters composed of micrometer and nanometer fibers. The filter quality is evaluated using the figure of merit, also known as the quality factor. We use analytical expressions for the pressure drop and filtration efficiency to compute the figure of merit. The effects on the figure of merit by fiber diameter, solidity and thickness of nanometer and micrometer fibers and face velocity are investigated. Experimental data obtained using conventional filter media and nanofiber composite filters are then used to verify the calculated results. We find that for large particles (approximately 100 nm and above), nanofibers can improve the figure of merit compared to conventional filters. Smaller fiber size, larger solidity and thickness in the nanofiber layer lead to better filtration performance in this size range. For small particles (approximately below 100 nm), nanofibers do not improve the figure of merit compared to conventional filter media. Larger fiber size, smaller solidity and thickness in the nanofiber layer are preferred in this size range. We demonstrate that our procedure using analytical expression is a fast and effective tool for filter media design.
1E.03
Filtration of Carbon Nanotube Aerosols with Mechanical and Electret Filters. Takuma Furukawa, Yuki Takeuchi, Takafumi Seto, Yoshio Otani, Kanazawa University

Since carbon nanotubes (CNT) have unique characteristics that cannot be achieved by the bulk materials in micrometer order, they have great potential applications for developing new devices in various fields, such as electronics, medicine, nanotechnology. However CNT is similar to Asbestos in shape, the health effects of CNT via the inhalation is of great concern. In order not to repeat the same tragedy as in the case of asbestos, we must evaluate the health effects of CNT particles and establish precautionary countermeasures. Air filtration is the simplest means to prevent the workers from the exposure to airborne CNT particles. In the present work, we first investigated the collection performance of fibrous filters for carbon nanotube particles.

Multi-walled carbon nanotube (MW-CNT) aerosols were generated by atomizing the suspension of MW-CNT dispersed in water. The CNT aerosol was generated by an atomizer and then classified by a differential mobility analyzer (DMA). The penetration of MW-CNT particles through both medium performance fibrous filter and electret fibrous filter were measured with a condensation particle counters (CPC) and they were compared with those of spherical ZnCl2 particles. As a result, it was found that both fibrous filters have higher collection efficiency for MW-CNT particles than the spherical ZnCl2 particles at the same electrical mobility. Through the analysis of single fiber collection efficiency, it was shown that the dominant collection mechanism of MW-CNT particles by the medium performance fibrous filter is interception caused by the rotation of CNT around the fibers. Whereas, for electret fibrous filters, it was found that the induced force exerts on CNT particles more effectively than the spherical particles with the same electrical mobility because MW-CNT particles have a high dielectric constant.

1E.04
Nanoparticle Agglomerates Loading on Fibrous Filter. SEONG CHAN KIM, Jing Wang, David Y.H. Pui, University of Minnesota

Most filtration studies have been conducted with spherical or similar shape particles due to the difficulty of evaluating the filtration behavior of irregular particles. However, real particles often have a complicated structure which influences their deposition behavior and pressure drop across filter media, so it is desirable to investigate the filtration of nanoparticle agglomerates. We performed filtration efficiency and loading test with silver nanoparticle agglomerates. An annealing furnace was used to control the agglomerate structures by varying the annealing temperature. Agglomerate loading test has been conducted with three different annealing temperatures (ambient, 200 degrees C, 600 degrees C) in depth filtration region (pre-cake formation). In this region, agglomerate particles show higher pressure drop increase than spherical particles due to their higher air flow resistance and higher particle mass deposition (caused by their lower penetration comparing with spherical particles). Loading test will be extended to cake filtration region (post-cake formation) in the on-going research.
1E.05  
Filtration media in magnetic field. Vadim Tovstoy,  
Filtration media could be designed in magnetic field for filtration of ferromagnetic and (or) diamagnetic particles. To create filtration media necessary at least some portion of ferromagnetic particles that could be artificially inserted in the activate position. Given a sample of filtration media in magnetic field that can be used for separation of particles in industry.

2E.01  
Filter Loading Characteristics of Supermicron Liquid-Coated Particles. Ta-Chih Hsiao and Da-ren Chen, Washington University in St. Louis, St. Louis  
Extensive studies have been conducted to investigate the behavior of filters when loaded with solid and liquid particles. In the real-word applications particles are often liquid-coated particles, so called oily particles or dusty oils. The objective of this study is to investigate the filter loading behavior of supermicron liquid-coated particles. In the experiment the co-solvent method was used to prepare liquid solutions for the generation of test particles by an ultrasonic generator. Dioctyl Sebacate (DEHS) was dissolved in 2-propanol and mixed with the aqueous solution of potassium chloride in the volume ratio of 1:1. The well-mixed solution was then introduced to an ultrasonic particle generator (Sono-tek 8700) to produce supermicron liquid-coated particles. By varying the solute concentrations in co-solvents, liquid-coated particles of fixed sizes with various liquid volume percentages were produced. In this test the overall particle size was kept about 2.5 micrometer and the filter face velocity fixed at 11 cm/s. Generated particles were loaded on two low-performance filter media, made of cellulose and glass fibers, to study the particle loading behaviors. 

The result shows in general the loading behavior of liquid-coated particle transits from that of loading solid-only particle to that of loading liquid-only particle as the percentage of liquid volume in particles increases. However, the transition between two limiting cases (i.e., solid-only and liquid-only cases) is different for the cellulose filter and fiber glass filter due to the difference on fiber surface properties of test filters. It is also found that small percentage of solid mass in liquid-coated particles could dramatically change the loading behavior. The detail of experimental results will be presented in the conference.
2E.02
Effects of Temperature and Relative Humidity Variation on Fungal Growth on Loaded Ventilation Filters. Weihua Tang, Thomas H. Kuehn, Department of Mechanical Engineering, University of Minnesota

The prevalence of airborne microorganisms in indoor and outdoor environments and the amount of organic aerosols that can serve as nutrients make loaded ventilation filters potential sites for microbial growth under appropriate environmental conditions [1]. Temperature and relative humidity (RH) are two important factors that affect microbial growth rates. Previous laboratory research focused on constant temperature and relative humidity, which may not be the case for real applications. The objective of this work is to experimentally study the fungal growth rate on loaded ventilation filters at room temperature (RT)/constant RH (CRH), sinusoidal temperature (SIN T)/CRH, and RT/step change in RH.

A MERV-14 synthetic pleated filter was loaded with sterile malt extract as the artificial nutrient and Cladosporium sphaerospermum conidia in an ASHRAE Standard 52.2-2007 [2] wind tunnel. Small pieces of filter sections 3.8 by 5.1 cm were cut from the loaded filter and placed in sealed incubation flasks, inside which the RH was controlled by saturated salt solutions. The flasks were placed in an air-conditioned lab for RT conditions and in a temperature controlled chamber for the sin T condition (T = 23+10 sin (PI*t/12); t=0, 2, 4, ..., 24, T: degrees C). For the step change in relative humidity, the filter sections were switched between 97% and a lower RH (75%, 43%, 11%) every 12 hours. The filter sections were removed from the incubation flasks for biomass measurement using a) an elution-culture method to obtain total colony forming units (CFUs) and b) an ergosterol assay method to obtain ergosterol amounts per section in day 0, 2, 4, 6, 8, and 10.

The elution-culture results indicated the growth ratio increased with time for both the RT/CRH and SIN T/CRH conditions; the increase in CFU values was delayed for RH=97-75% and RH=97-43%; no growth was found for RH=97-11%. The growth ratio at RT/CRH was significantly higher than all the other conditions (p=0.05) except for two points where the variance was too large, which suggested that variation in temperature and RH could slow down or even prevent growth. Results from the ergosterol assay method did not show a reduction in biomass after incubation. The increase in growth ratio started earlier than the results from the elution-culture method. No growth was found under the 97 -11% RH condition again. Because of the magnitude of variance, the growth ratio at RT was significantly higher (p=0.05) than the other conditions only for the early stages.

REFERENCES

2E.03
Effect of Wind Velocity on Particle Collection Using a Multi-Domain Magnetic Passive Aerosol Sampler. Peter A. Jaques (1), Pengfei Gao (2), (1) EG&G, Pittsburgh. (2) National Personal Protective Technology Laboratory, NIOSH, Pittsburgh

Particles that pass through protective ensembles can make contact with the skin, potentially resulting in skin irritation, dermatitis, or toxic responses. Current testing for particle penetration through protective ensembles is mainly based on active filtration principles, which may overestimate the particle penetration due to additional driving forces. Therefore, a novel prototype personal multi-domain magnetic passive aerosol sampler (MPAS) was developed to more accurately measure particle penetration through protective ensembles. The MPAS consists of 186 one-mm2 square magnets arranged with an alternative N and S pole pattern on a 25 mm disc to collect magnetic aerosol particles onto a Polyvinyl Chloride (PVC) filter. In this study, a novel recirculation aerosol chamber was used to determine the effect of wind velocity on particle collection. At an average wind velocity of 0.45 m/s, a stable bimodal (32 nm and 130 nm) Iron (II, III) Oxide (Fe3O4) aerosol of about 620,000 particles/cm3 was generated using a 6-jet atomizer. At a higher average velocity of 0.9 m/s, the second mode of the delivery aerosol decreased to 115 nm and the total particle number concentration decreased to 270,000 particles/cm3, likely due to turbulent deposition losses within the chamber. MPAS prototypes were co-located and operated passively for 80 minutes along two axes on a single plane, perpendicular to the air-flow direction. At all velocity conditions, a uniform deposition pattern resulted on the MPAS. Deposition steadily increased with increasing velocity up to 0.3 m/s. Consistent collection efficiencies were observed under wind velocities ranging from 0.3 to 0.6 m/s for collocated samples. Additional results on other factors affecting collection efficiency, including particle size, concentration and orientation under various flow conditions, will be presented.
**2E.04**

**Performance of Filters When Loaded with NaCl and KCl Particles in Low Relative Humidity Environment.** Ta-Chih Hsiao and Da-Ren Chen, *Washington University in St. Louis*

Two low efficiency cellulose filters were loaded with sodium chloride (NaCl) and potassium chloride (KCl) particles of supermicron sizes at low relative humidity (RH) environments (i.e., RH < 30%). Because of the similarity of NaCl and KCl particles in crystalline and hydroscopic property it is common brief that no difference would be observed in the filter loading curves (i.e., pressure drop vs. the loaded particle mass/volume per unit filter area) of particles in the same size at such low RH environments. In this study it is shown that at 30% RH the initial penetration and the loading curves of filters loaded with NaCl and KCl particles are nearly the same. As the RH decreased to 15%, the loading curve of NaCl particles however deviated from that of KCl. Compared to KCl curves the curves of NaCl particles moved to the range of higher particle volume per unit filter area. It infers, for the same pressure drop, the filter can be loaded with more volume of NaCl particles than KCl particles. SEM examination of test particles reveals that the morphology of test NaCl and KCl particles is different when RH is varied. It was thus concluded that a possible reason for the dissimilarity of the NaCl particle loading curve at 15% RH is the difference in the particle morphology. The detail of this experimental work will be presented in the conference.

**3G.01**

**Discharge Characteristics of Wet Electrostatic Precipitators.**

DONG KEUN SONG (1), Sang Hyun Jeong (1), Yong Jin Kim (1), Sung Hoon Shim (1), Jongoung Won (2), (1) Korea Institute of Machinery and Materials, Daejeon, Republic of Korea, (2) KC Cottrell Co., Seoul, Republic of Korea

Regulation for air pollution materials emitted from industrial equipments is getting stricter and it needs to develop control technologies for preventing air pollution. Among various facilities for preclusion of air pollution, electrostatic precipitators (EP) are most widely used due to advantages of easy install and low maintenance cost. EPs are classified into dry and wet ones depending on water supply. Generally, dry EP has outstanding performance in removal of particulate matters of wide size ranges; however, it has still some issues, which are degraded removal efficiency for ultrafine particles, corrosion of collection plate by acid particles, and difficulties in rapping deposited particles, and a wet type EP can be a workaround for resolving these problems.

Here, we have developed a wet EP having collection plates covered by irrigating water film, and studied discharge characteristics with changing discharge electrodes of various shapes, and collection plates of various materials, stainless steels, Plexiglas's, woven and nonwoven fabrics.

The V-I curves representing corona discharge characteristics for various configurations of discharge and collection electrodes were obtained and compared. There is no distinct difference in the V-I curves with and without the irrigating water films, which suggest that there is no degradation in the discharge pattern from that of the dry EP. Moreover, non-conducting materials such as Plexiglas's and fabrics can be used as collection plates by provoking water film over.
3G.02
Enhanced removal efficiency of high temperature ESP by using additional ion sources. YONG JIN KIM, Hakjoon Kim, Bangwoo Han, Dong Keun Song, Sang Hyun Jeong, Sung Hoon Shim, Won Seock Hong, Wan Ho Shin, Korea Institute of Machinery and Materials, Daejeon, Republic of Korea

Suppression of spark-over is highly needed for air pollution control process using electrostatic precipitators (ESP) at high temperature condition, since the spark-over occurs at relatively lower voltages as higher the operating temperature.

To overcome the lower spark-over voltage, which results in increase of collection efficiency of high temperature ESP, we evaluate performance of removal submicron particles by introducing a newly designed ion sources and effect of applying pulsed electric power is also investigated.

The experimental setup used in this study consists of a particle generator, electric furnace, ESP, and measurement system for counting particle number concentration. Potassium chloride (KCl) particles generated by a constant output atomizer (Model 3076, TSI) with the air gas of 2 l/min, were introduced with clean air gas into the electric furnace to increase the gas temperature up to about 500 degrees C. The air velocity in the ESP varied from 0.2 to 1.0 m/s, and negative high voltage of 5-11 kV was applied to the ESP, which has a rectangular cross section (55 mm x 160 mm) with a length of 260 mm.

A newly designed ion source, which has four ion emitters consist of carbon fibres around a cylindrical ceramic insulator, was attached to increase ion number concentration. Providing additional ions enhanced the collection efficiency of ESP for submicron particles at high temperature condition.

The applied voltage was modified by coupling an AC power supply with a DC power supply to have pulsed waveform. The collection efficiency of ESP for submicron particles was also increased by applying pulsed voltage coupled with DC and AC.

3G.03
Carbon Fiber Unipolar Charger for Fine and Ultra-fine Aerosol Particles with Negligible Ozone Generation. BANGWOO HAN (1,2), HAK-JOON KIM (1), YONG-JIN KIM (1), CONSTANTINOUS SIOUTAS (2), (1) Environmental System Research Division, Korea Institute of Machinery and Materials (2) Department of Civil and Environmental Engineering, University of Southern California

Particle charging is the most effective way to control the behavior of particles using transport in electric fields. In this study, a simple and novel unipolar charger using carbon fiber ionizer has been developed to charge fine and ultra-fine aerosol particles. Carbon fiber ionizers consisted of a bundle of carbon fibers were vertically placed on the upper and lower side of the inner wall of the cylindrical charging chamber. A positive D.C. voltage of 2.3-4.0 kV was applied to the carbon fiber ionizers to generate stable positive ions. Potassium chloride (KCl) particles were used as a test aerosol. Particle loss and the exit and extrinsic charging efficiencies were investigated for non-charged particles at different applied voltages to the charger. Particle losses in the charger could be decreased by decreasing the applied voltage to the charger from 4.0 kV to 2.3 kV and thus obtained about 12% at 20 nm particles. The exit particle charging efficiency was almost independent of the applied voltage and the extrinsic charging efficiency was higher for the lower applied voltage. About 60% of the extrinsic charging efficiency was acquired at 20 nm particles. Ozone generated from the charger was also measured using an ozone monitor. Ozone concentrations were below the limit of detection (0.6 ppb) of the ozone monitor for the 2.3-4.0 kV voltage range. We found that the carbon fiber unipolar charger can charge fine and ultra-fine particles as effectively as existing corona chargers, with the advantage of generating negligible ozone. This will be a promising method for particle charging, especially in application involving sampling and collection of atmospheric aerosols, often rich in organic compounds, which could be degraded by reactions with ozone produced by corona chargers.
3G.04  
Fabrication of Bag Filter Media for High Temperature Use.  
MYONG-HWA LEE, Byung-Hyun Park, Sang-Bum Kim and Gyung-Soo Kim, Korea Institute of Industrial Technology

Air pollution control devices are usually installed in the order of a combustor, a heat exchanger, a SCR, a bag house and a FGD system. However, the particles in flue gas are deposited on the system and influence on the heat recovery efficiency and the inactivation of SCR catalysts. Therefore, the fabrication of bag filter media available at high temperature region (250–280 °C) plays a key role to solve those problems. Even though a few filter media such as ceramic and metal fiber filter media can be available at the temperature range, they are too expensive to use in a bag house. Recently, we have developed new bag filter media for high temperature use using a foam coating technology. The filtration characteristics of developed bag filter media are discussed in this study.

PTFE emulsion and woven glass filter media were chosen as filter materials in order to obtain the thermal stability. PTFE emulsion was foamed in a foam generator and coated on the glass filter media, followed by a dryer and a winder. The fabricated filter media have evenly distributed microporous structures, which average pore size is 17.8 micro-meter. These inner porous structures have resulted in air permeability of 4.0 cm³/(cm²·sec), which is twice higher than that of PTFE-laminated filter media. Furthermore, the developed filter media had collection efficiency of over 99.9% and were thermally stable for one month exposure at 280 °C.

3G.05  
Wood Pulp Based Filters for High Efficiency Removal of Submicrometer Aerosol Particles. Biljana Grgic (1), Jingliang Mao (2), WARREN H. FINLAY (1), John Kadla (2) and Richard J. Kerekes (2), (1) University of Alberta, Edmonton (2) University of British Columbia, Vancouver

The objective of this work was to develop a wood pulp filter media with high efficiency and low resistance, and which is easily disposed of when used against fine and ultrafine aerosols including airborne viral and bacterial agents. Accomplishment of this objective was achieved by creating large specific surface area by fibrillation of the cellulosic fibre wall surface. The air filters are used in a dry state whereas fibrillation is produced in the wet state. The wet fibrillation was retained into the dry state by partial freeze drying. We made filter pads by two methods: dry forming and wet forming. The resulting filters were tested for pressure drop. In addition, initial filter capture efficiency was measured at a face velocity of 12 cm/s using an Electrical Low Pressure Impactor (ELPI) with sodium chloride aerosol particles having diameters in the range 0.018-1.29 micrometers.

The lowest efficiency for filters occurred in the 0.19 and 0.3 micrometers particle size range and varied from 56 to 98.4%. Pressure drop was between 127 and 417Pa, which is low compared to commercially available high efficiency mechanical filters. For a given resistance to air flow, the wet-formed filters have better capturing ability than dry-formed paper filters due to the higher fibrillation on their cellulosic fibre surfaces.

We have demonstrated that wood pulp filters can be created with efficiency close to commercially available synthetic respirator filters. Such pulp filters may be useful for household air filtration, or protection against airborne submicrometer pathogenic particles. The use of wood pulp filters for high efficiency mechanical filtration is a novelty, and involves a renewable natural resource that permits environmentally friendly disposal.
3G.06
Characteristics of Dust Particle Emission through Bag Filters. HYUN-SEOL PARK, Kyoung Soo Lim, Korea Institute of Energy Research, Korea

Bag house is a high efficient and stably operated dust removal device. A bag house is composed of gas inlet, dust hopper, bag filters, cell plate, filter cleaning unit, ID fan, and gas exhaust stack. Among these components of a bag house, dust collection efficiency directly depends on both the bag filter media and filter cleaning method. In this study, we investigated the effect of filter cleaning method on the dust emission of a bag house. As a filter cleaning method, we adopted a pulse jet cleaning, which is the most popularly used one worldwide. The concentration of dust particles emitted from a bag house was measured and continuously monitored by using an electrical low pressure impactor. The dust particle concentration showed a peak right after filter cleaning and rapidly reduced to a level of ambient air. That is, most of dust particles were emitted only when filters were cleaned. Therefore, if the interval between filter cleanings is increased by some means or other, such as reducing dust loading to bag filters, dust emission from a bag house will be reduced.

3G.07
Comparison of Nanoparticle Filtration Performance of NIOSH-approved and European Certified Filtering Facepiece Respirators. SAMY RENGASAMY (1), Benjamin Eimer (2), Ronald Shaffer (1), (1) NIOSH/NPPTL, Pittsburgh, PA (2) EG@G Technical Services, Inc., Pittsburgh, PA

The National Institute for Occupational Safety and Health (NIOSH) and European certifications of filtering facepiece respirators (FFRs) employ different test protocols. NIOSH requires a minimum of 95% and 99.97% efficiencies for N95 and P100 FFR, respectively, while, European certification requires 94% and 99% efficiencies for FFP2 and FFP3 respirators, respectively. To better understand their filtration performance, initial penetration levels of N95, P100, FFP2 and FFP3 FFRs were measured using three methods: a polydisperse aerosol test (PAT), similar to NIOSH respirator certification, and two monodisperse aerosol tests (MAT). The PAT method (TSI 8130) uses polydisperse NaCl aerosols with a count median diameter of 75 nm and a geometric standard deviation of less than 1.86. In the PAT method, all of the particles penetrating the filter are measured simultaneously using a forward light scattering photometer. One MAT procedure utilized an in-house test system employing 4-30 nm silver nanoparticles, while the other (TSI 3160) used 20-400 nm NaCl particles. Both MAT procedures use a SMPS and a condensation particle counter to measure the number of penetrating particles for each selected size. Two models for each FFR type were selected and five samples from each model were tested against charge neutralized aerosol particles at 85 L/min flow rate. Filtration performance measured using PAT indicated penetrations were less than 1% for N95 and FFP2 models and less than 0.03% for P100 and FFP3 models. The MAT data from the two test systems indicated that the MPPS was in 40-60 nm range for all four types. Average percentage penetrations were 1.95 and 4.18 for N95 and 1.87 and 2.64 for FFP2 models and 0.005 and 0.007 for P100 and 0.11 and 0.29 for FFP3 models at the MPPS. The data obtained in this study suggest that NIOSH and European certified FFRs have similar laboratory filtration characteristics.
Increase of Collection Efficiency in Fibrous Filter Media Through Magnetic Alignment of Elongated Aerosol Particles. CHRISTOPHER LAM W.H. Finlay, University of Alberta, Canada

High aspect ratio aerosol particles, tend to align their major axis parallel to fluid streamlines, making filter capture of such particles more difficult. These fibers, when oriented perpendicular to flow, however, have an increased chance of depositing on surfaces through interception, as shown by single-fiber theory and the literature on fiber deposition. Recently, it has been shown that magnetic composite fibers, entrained in air flow and passing through a uniform magnetic field, experience a magnetic torque capable of aligning their major axis with the direction of the field. This study used these concepts to increase the capturing efficiency of a filter, challenged with such aerosol fibers under the influence of a magnetic field.

A suspension of cromoglycic acid and magnetite nanoparticles was prepared and aerosolized in a nebulizer producing the desired fibers, loaded with magnetic nanoparticles on their surface. The poly-disperse aerosol had a CMD = 0.39 micrometers, CML = 1.81 micrometers, and GSD for length and diameter of 1.63 +/- 0.15 and 1.43 +/- 0.16, respectively. Particles, as large as 15 micrometers and with aspect ratios up to 40, were found. Nylon net filters, with a 20 micrometer pore spacing, were used as the testing filters. The efficiencies of the filters were tested at face velocities of 1.5, 5.1, and 10.2 cm/sec, magnetite compositions (by mass) of 10, 20, and 30%, and magnetic field strengths of 0, 50, and 100 mT. At a face velocity of 1.5 cm/sec, filtration efficiency increased with field strengths for all magnetite compositions tested. At 5.1 cm/sec, there was an observed difference in efficiency at 20 and 30% magnetite loadings with increased field strengths, while all other combinations of parameters yielded no change in efficiency. This data indicates that magnetic alignment of fibrous aerosol particles can be used to increase filtration efficiency in filters.

Performance Evaluation of Virtual Cyclones for Dust Removal. HYUN-SEOL PARK, Kyoung Soo Lim, Korea Institute of Energy Research, Korea

Bag filters have been widely used for dust removal from gas stream of various industrial processes. In order to enhance the performance of bag filters, a hybrid type dust collector is being developed. The hybrid dust collector combines a virtual cyclone and a bag house as a single body, and has the box shape in contrary to existing cylindrical dust collectors. The virtual cyclone has a role of the primary dust collector and it is located below the bag filters corresponding to secondary or final dust collector. Through the virtual cyclone, over 70% of dust particles are removed, and only a little amount of particles remained after passing through the virtual cyclone is collected on bag filters. In this study, we designed and fabricated the virtual cyclones, and tested the pressure drop and collection efficiency of them for different flow rates and design parameters. The virtual cyclone showed almost same dust collection efficiency and about 75% reduction of pressure drop compared to an existing cylindrical cyclone.
3G.10
Analytic solutions of cyclone efficiency for polydispersed aerosol. C. H. JUNG (1), H. S. PARK (2), (1) Kyungin Women's College, Incheon, Korea (2) Korea Institute of Energy Research, Daejeon, Korea

Cyclone collectors are widely used because they are simple, inexpensive to fabricate, economical to operate and adaptable to a wide range of operating conditions. There are lots of theoretical and experimental studies on the efficiency of cyclone collector (Smith et al., 1983, Licht, 1988; Zhao and Pfeffer, 1997). Usually, the total efficiency of cyclone collector for polydispersed aerosol can be calculated by summing the grade efficiency and the weight fraction in each size range. Thus, the accuracy of the total efficiency of cyclone strongly depends on the number of the particle size and width of the individual intervals which may result significant error. In this study, simplified analytic type of solution for the removal efficiency of polydispersed aerosol by cyclone collector is studied theoretically. The radial back mix approach, which is developed by Leith and Licht (1972) was adopted to describe the overall collection efficiency of polydispersed aerosol. The analytic type of solution was obtained using the moment method under the assumption of lognormal aerosol size distribution. Subsequently, this study can consider the continuous change of the particle size distribution along the cyclone and predicts both the overall mass and number collection efficiencies of polydisperse particles without computing the grade efficiency of each different size region.

This study also obtained the simplified type of expression for the generalized Lapple's collection efficiency for polydispersed aerosol under the assumption of lognormal size distribution using the polydispersity correction factor. The correction factor was approximated through the regression of numerical integration for the collection efficiency over the entire particle size ranges. The obtained simple and straightforward results compared with numerical results and showed a good agreement.

The research described in the abstract is funded by Korea Ministry of Environment as "The Eco-technopia 21 project".

3G.11
Particle Removal of Scrubbers with Different Vortex Chambers. KYOUNGSOO LIM, Sihyun Lee, Hyunseol Park, Korea Institute of Energy Research, Daejeon

Three types of vortex scrubbers with opposing nozzles were used to investigate the performance factors affecting its particle removing efficiency by varying operation condition and size parameters. The scrubbers have a tangential inlet for generating the spiral flow and opposing nozzles located in center of the vortex chamber for producing tiny liquid droplets by collision between liquid flows. Two scrubbers have an additional cylinder or cone guide wall in the scrubbers to increase the number of rotations, as a double cyclone does. The diameter of nozzles and length between opposing nozzles were varied to examine the characteristics of particle removing efficiency. The particle removing efficiency was also determined at different gas flow rates and liquid flow rates.

The particle removing efficiency of scrubbers with additional cylinder or cone guide wall was higher than that of scrubber without it at low gas flow rate when nozzles didn't spray. However, there was little difference of particle removing efficiency between scrubber with additional cylinder or cone guide wall and scrubber without it when nozzles sprayed. High gas flow leaded to high gas velocity, resulting in strong impaction and centrifugal force. The particle removing efficiency increased with an increase in impaction and centrifugal force. As the liquid flow rate increased, the particle removing efficiency also increased due to the tiny and many liquid droplets. Small diameter of nozzle and short distance between nozzles lead to strong collision of liquid flows from opposing nozzles producing tiny liquid droplets, which increase the particle collection efficiency.
3G.12


The wide range aerosol particle spectrometer, WAPS (HCT Co., Ltd.), is an instrument combining laser scattering, electrical mobility (DMA) and CPC technologies. It is instrument that measures the particle concentration and particle size distributions from 10 nano-meter to 5 micro-meter. The WAPS is based on the well-known principles of aerosol particle sizing and counting by CPC, DMA and OPC. The WAPS was applied to water based CPC to prevent organic contamination source in semiconductor manufacturing clean-room. The major objective of this instrument is measuring generated particles in burn-wet scrubber of semiconductor fabrication environment. Also, this instrument can be applied the ambient air particle, indoor air particle and inhalation toxicology research of nanoparticles.

Measurement of contaminant nanometer and micrometer aerosol particles in exhaust gases of processing equipment has meaningful micro-contamination implications. Particle measured in burn-wet scrubber can give important and easily obtainable information concerning the operating status and cleanliness of the exhaust duct.

In this study, aerosol particles generated in burn-wet scrubber were measured in the exhaust line downstream. The aerosol particle size distributions in the gas exhaust was measured using WAPS. Experimental results showed different particle size distributions for processing run and without processing. Thus we expect processing work conditions can be better understood by measuring and monitoring the particle size distributions of exhaust gases in burn-wet scrubber during a processing run.

3G.13

The Consistent and Reproducible Generation of Test Aerosols. NEAL BAKER, Christopher Bare, Michael Wagner and Joshua L. Santarpia, Johns Hopkins University Applied Physics Laboratory

In order to accurately challenge biological and chemical detection sensors with realistic background environments it is often necessary to generate a broad range of compositionally diverse aerosols. The ability to vary the concentration of these aerosols in an environmentally relevant, realistic and reproducible manner is essential for effective and consistent test methodologies. Multiple generation technologies are often required to generate the diverse aerosol types necessitated by current testing requirements. The use of an ultrasonic aerosol generator is a flexible way of generating a diverse range of aerosol sizes and concentrations. The size distribution of the output aerosol may be modified by changing the flow rate of the stock solution or by varying the concentration of the stock solution. Decreasing the concentration of the stock solution will lower the output concentration and the mean diameter of the generated aerosol, while increasing the concentration of the stock will increase the output concentration and the mean diameter. However, increasing the concentration of the stock can result in clogging of the liquid feed line. Changing the feed rate of the stock solution to the ultrasonic atomizer allows variation of the number concentration of the aerosol while maintaining a consistent mean particle diameter. The suitability of various configurations of a commercially available aerosol generator has been studied using a variety of aerosol stock materials. Configurations allowing the best control, access and broadest range of generation conditions are discussed. The ability to produce consistent output over many hours of testing is also discussed.
Aerosol spectrometers offer precise particle resolution in diverse applications. Typical applications include aerosol research, HEPA/ULPA filter testing, chemical process monitoring and control, pharmaceutical research and manufacturing, powders and food products research, inhalation toxicology research, combustion and emission source research, nebulization analysis, coalescence and nucleation research, and disk drive development and research.

The industry roadmap forecasts that by 2010, semiconductor manufacturers will break the 45 nanometer feature limit. Smaller line widths require instruments that can detect particles in nanometers -- not microns. Already, quality control requirements are tightening as customers demand more sensitivity and proven statistical methods for future products.

Newly-developed spectrometers from Particle Measuring Systems' employ technology that provides variable sampling rates and particle size ranges from 60 nanometers to several microns. In addition, these spectrometers include one-hundred (100) particle-sizing channels that provide the highest spectrometer resolution in the industry.

The new spectrometers, HSLAS II Spectrometer and the LAS-X II Spectrometer, meet the industries' demand for more sensitive particle detection. These spectrometers provide variable sampling rates from 10-100 sccm, one hundred user-selectable data channels, and an industry-recognized LabView interface operating under the popular Windows XP Operating System.

Since the spectrometers have variable flow rates and user-selectable data channels, each customer can tailor their spectrometer to monitor only those particles that interest them. This will provide significantly better trend analysis, higher yield, and greater product throughput. Plus, higher sensitivity at 60 nanometers allows the user to develop quality-assurance methods that offer higher performance and exceed current testing standards.

The dynamics of mercury condensation on activated carbon in turbulent flows is investigated via direct numerical simulations. Attention is focused on particle dispersion and gas-particle mass transfer in unsteady, turbulent flows. A mixed Eulerian/Lagrangian formulation is used for the fluid and particle field, respectively. The fluid and particle fields are coupled through gas-particle mass transfer of condensible vapor and the effects of the Thiele number, Stokes number, convective time-scale, and particle surface concentration are considered. Results show an alignment of particles with vortical structures, a decrease in dispersion with increasing Stokes number, and gas-particle slip velocities are found to increase overall mass transfer rates (as compared to a stagnant fluid environment). Additionally, Simulations utilizing the "perfect sink" assumption are compared with simulations in which the non-zero, steady-state surface concentration is calculated taking into account the sorption properties of porous particles.
4E.02
Effect of Selective Catalytic Reduction Unit on Emissions from Marine Auxiliary Engine. Varalakshmi Jayaram (1,2), Abhilash Nigam (1,2,3), William A. Welch (2), J. Wayne Miller (1,2), David R Cocker III (1,2), (1) University of California, Riverside, (2) CE-CERT, Riverside (3) Currently at Johnson Matthey, Philadelphia

The contribution of the Ocean Going Vessels (OGVs) to the global emissions inventory is increasing significantly due to the increasing international trade and the lack of stringent emission standards. Auxiliary engines typically operate at ports for transit, maneuvering, hotelling and cargo refrigeration. Hence, auxiliary engines have a significant effect on regional air quality in populated areas near ports. Selective Catalytic Reduction (SCR) is the most efficient technology available for the reduction of NOx emissions from the diesel engines. Currently there is very little in-use emissions data available on SCRs installed in the exhausts of marine auxiliary engines.

The goal of this research was to measure the in-use emissions upstream and downstream of an SCR installed on the exhaust of a marine auxiliary engine. Measurements were made based on ISO 8178-1 protocol following the loads specified in the ISO 8178-D2 cycle. Emissions of carbon dioxide, nitrogen oxides, carbon monoxide and particulate matter (PM) will be reported for the engine operating on three different fuels HFO, MDO and ULSD. Additional speciation of PM (Elemental Carbon, Organic Carbon and hydrated Sulfate) will also be presented. The SCR reduced the NOx emissions by 80-90% while the PM emissions increased across the SCR for engines operating on HFO and MDO fuels due to the increase in the sulfate fraction of the PM mass. A comparison of the behavior of the SCR across the fuel types will be discussed.

4E.03
Development of a Mini-Cyclone for Miniaturized Particle Devices. Ta-Chih Hsiao (1), Da-Ren Chen (1) and Sang Young Son (2), (1) Washington University in St. Louis, St. Louis, (2) University of Cincinnati, Cincinnati

Much of particles in larger diameters are present at ambient environment. Light scattering and electrical mobility techniques are often used to measure or monitor particles in submicron size range. The same techniques have recently applied to miniaturized sizers or photometers for personal-level or distributed measurements. The presence of large particles often introduces the measurement interference for the devices using the techniques. It is thus necessary to remove particles of larger diameter from particle-laden stream for the better performance of miniaturized particle devices. For the compact packing of miniaturized devices a mini-cyclone is then needed. In this study, a ‘quarter-size’ mini-cyclone was developed to remove particles larger than 1.0 at a low flow rate of 0.3 lpm. The basic configuration of the mini-cyclone is referring to that of the Extra-Sharp-Cut cyclone (ESCC) series (L.C. Kenny and R.A. Gussman, 2000). Different from ESCC cyclone the base of the mini-cyclone is cylindrical rather than conical, and the cross section of the cyclone inlet is circular instead of rectangular. The performance of the mini-cyclone was evaluated based on the particle penetration and pressure drop. To acquire the penetration curve and consequently determine the 50% cutoff particle size, d50, of the prototype the upstream and downstream particle distributions of the mini-cyclone were measured by Scanning Mobility Particle Sizer (SMPS, TSI 3096) and Aerodynamic Particle Sizer (APS, TSI 3321). Potassium chloride particles were used as the challenging aerosol. Four different flow rates, i.e., 0.3, 1.2, 1.6, and 2.0 lpm were used in the experiment. In general, the d50 decreases with increasing the aerosol flowrate. The characteristic cutoff Stk0.5 (square root of the particle Stokes number) is about 0.15. Further, the pressure drops of the prototype mini-cyclone increase with the flow rate in a quadratic form. At 0.3 lpm the value is as low as 1.8 in H2O. It is also found that the performance of this newly designed mini-cyclone does not follow the design guideline proposed by Kenny and Gussman (2000). The detail of the cyclone design, experimental evaluation and the comparison with the design guideline of ESCC series cyclone will be given in this presentation.
Air Cleaner Effects on Improving Indoor Air Quality. Ying Xu (1), Suresh Raja (1), Andrea R. Ferro (1), Peter A. Jaques (1), Sean McMahon (1) Yang Qi (1), Philip K. Hopke (1), Cheryl Gressani (2), Larry E. Wetzel (2), (1) Clarkson University, (2) 2Air Innovations, Inc, North Syracuse

In 2007, the U.S. Centers for Disease Control and Prevention reported that 1 in 13 school-aged children suffer from asthma in the United States. Several reports have suggested that respiratory health is related to indoor air quality and air cleaning may be effective in alleviating asthma symptoms. Currently, there are no portable air cleaning devices that include an integrated energy recovery ventilator, air conditioner, and a High Efficiency Particulate Air (HEPA) filter. The HEPAiRxTM, a fully integrated unit from Air Innovations (AI), was tested in this study for its ability to improve indoor air quality and to relieve the symptoms of asthma in children from ages 5 -16 years. Indoor air quality was monitored in the bedrooms of thirty-two asthmatic children using AirAdvice indoor air quality (IAQ) multi-meters and condensation particle counters. Measurement parameters include temperature, relative humidity, particulate matter (0.5-10 um size range), CO, CO2 and total volatile organic compounds (VOC) concentrations. Statistically significant reductions in particulate matter (0.5-10 um size range), CO, CO2 and total VOC concentration were found due to the operation of HEPAiRxTM and the room dynamics for this cleaner were determined.
1C.01

We are developing a method to label specific chemical or biological aerosols on-the-fly with fluorescent markers using an electrospray. Labeling molecules, with affinities to specific surface epitopes and produce a detectable change in emission characteristics upon binding, will be used to coat aerosols in an air stream. Specifically targeted aerosols could be labeled in this manner, allowing single particle identification in near real-time using a simple laser-induced fluorescence technique. This method would permit the use of solutions containing mixtures of different markers to simultaneously detect/identify multiple types of chemical or biological particles.

In effect we would perform an immunoassay on the surface of individual particles as they flow, eliminating the need to sample into liquid or perform a washing process. The specifically labeled particles would then easily contrast among the dynamic ambient background of aerosols, which continues to be a formidable issue in the pursuit of rapid detection methods. Topics that are currently being investigated include the kinetics of molecular surface binding to an aerosol in flight, modeling geometries for efficient particle coating, and the control of charged aerosols in an airflow.

1C.02
Development of a dual-excitation-wavelength single-particle fluorescence spectrometer for monitoring atmospheric aerosol and detecting biological threats. Yong-Le Pan (1), Hermes Huang (1), Richard K. Chang(1), Steven C. Hill (2), Ronald G. Pinnick (2), (1) Department of Applied Physics, Yale University, (2) U.S. Army Research Laboratory

We report a dual-excitation-wavelength Single-Particle Fluorescence Spectrometer (SPFS) developed to measure two fluorescence spectra (excited by two different-wavelength UV laser pulses) from individual particles on-the-fly. The two fluorescence spectra are dispersed by a single spectrograph and recorded with a single 32-anode PMT array that can be read within 11 microseconds. Once a particle is detected to be approaching the sample region: a) the 351-nm laser fires and the fluorescence spectrum from 370 nm to 700 nm (in 22 channels) is recorded, b) the 32-anode PMT is read within 11 microseconds, and then c) the 263 nm laser fires and the fluorescence spectrum from 280 nm to 600 nm (in 20 channels) is recorded. The elastic scattering (at 263nm and 351nm, respectively) is also recorded for sizing each particle. A time stamp is also recorded (typically every 10 seconds). The SPFS employs a virtual-impactor-based concentrator to concentrate particles with sizes in the 1-10 micrometer range. When measuring urban atmospheric aerosol the typical count rates with the SPFS are a few ten to a few hundred particles per second, although the SPFS is capable of measuring many times faster rates. A brief development history of the SPFS system will also be presented along with some measurements from pure samples and atmospheric aerosols in New Haven, CT. The two spectra for each particle, obtained with dual-wavelength excitation, provide more information for understanding and monitoring atmospheric aerosol, and for discriminating between biological threats, and background aerosol.
1C.03  
Comparison of Electrostatic Field with BioSampler in Quantifying Airborne Allergens. Maosheng Yao (1), Shiqi Zhen (2), Huili Zhang (2), Shuofei Dong (1), (1) Peking University, Beijing, China (2) Jiangsu Center for Disease Prevention and Control, Nanjing, China

We have investigated the use of electrostatic field in quantifying airborne environmental allergens. When performing experiments, two 96-well plates filled with water were placed into the electrostatic sampler designed in our study. The combinations of different electrostatic fields, 2.5, 5, 7 kV/cm, and different sampling flow rates, 5, 12.5 L/min, were tested with the electrostatic sampler. As a reference, BioSampler operating at 12.5 L/min was simultaneously placed in the same environment. The sampling lasted for 30 min both for electrostatic sampler and BioSampler in each test. Allergens in the air samples collected were further analyzed using Enzyme-Linked Immunosorbent Assay (ELISA). The entire experiments were conducted twice in different environmental settings.

It was shown that the concentrations of airborne allergens such as Der p and Der f measured by electrostatic field were significantly higher than BioSampler under all combinations tested. At higher sampling flow rate, e.g., 12.5 L/min, electrostatic sampler was 3 times efficient than BioSampler. When the sampling flow rate was decreased to 5 L/min, the efficiency of electrostatic sampler increased to as much as 10 times. For the same sampling flow rate, the allergen concentrations measured by electrostatic sampler tended to decrease with decreasing electrostatic field. For higher flow rate such as 12.5 L/min, electrostatic field strength was observed to exhibit little influence on the efficiency, and the differences among the fields tested were not statistically significant. While for lower flow rate of 5, the effects of electrostatic field became stronger.

This study presents an advanced environmental allergen monitoring technology, which was shown as much as 10 times efficient than BioSampler. The developed technique can greatly improve biological exposure assessment and holds great promise for detecting and quantifying environmental bio-hazard.

1C.04  
Performance of an electrostatic sampler with superhydrophobic surface when collecting bacterial aerosols. Taewon Han, Hey-Reoun An, and Gediminas Mainelis, Bioaerosol Laboratory, Department of Environmental Sciences Rutgers, The State University of New Jersey

Compared to the inertia-based methods for bioaerosol collection, electrostatic precipitation offers better potential for maintaining integrity of the collected microorganisms. We have developed an electrostatic precipitator with superhydrophobic surface (EPSS), which features deposition of airborne particles on a narrow electrode (2.1 mm), from where they are removed by a small (5 uL) rolling droplet and are then available for analysis. The performance of the EPSS with polystyrene beads was evaluated in a previous study, while here we analyzed performance of the sampler with two commonly used bacteria: Pseudomonas fluorescens and Bacillus subtilis. The total cell count (TCC) collected by the EPSS was determined by acridine orange epifluorescence microscopy (AOEM) and Real-Time PCR (RT-PCR) and compared with particle concentration in the air to determine its collection efficiency. For the RT-PCR, species-specific standard curves were generated by comparing the RT-PCR output with cell counts obtained with AOEM.

By using AOEM, our tests have shown that at sampling flow rates of 2, 5, and 10 L/min and using water droplets of 5 and 40 uL, we achieved collection efficiencies ranging from 48% to 61% for P. fluorescens (aerodynamic diameter=0.82 micro-meter) and from 55% to 72% for B. subtilis (aerodynamic diameter=0.89 micro-meter), respectively. At a sampling rate of 10 L/min and using 5 uL collection droplet, the collection efficiency of EPSS when collecting P. fluorescens was on average 51% and 62%, as determined by AOEM and RT-PCR methods; when collecting B. subtilis, the values were 65% and 69%, respectively. For 5 uL droplet and both bacteria we achieved sample concentration rates as high as 1.3 million. The sampler's collection efficiency was about twice as high with test bioaerosols compared to non-biological particles of similar size. Our data show that the EPSS is able to achieve very high concentration rates when sampling bioaerosols.
1C.05
Reaerosolization Characterization in an Attempt to Improve Airborne Virus Sampling. Lindsey Riemenschneider (1), CHANG-YU WU (1), Dale Lundgren (1), Joseph Wander (3), Jin-Hwa Lee (1), Hsing-Wang Li (1), and Alex Theodore (2) , (1) University of Florida, Environmental Engineering Department (2) University of Florida, Chemical Engineering Department (3) Air Force Research Laboratory, Tyndall Air Force Base

Airborne virus outbreaks, including the influenza pandemic of 1918, the recent SARS pandemic, and the anticipated H5N1 outbreaks, plus the perceived threat of bioterrorism have led to heightened concern about the prevalence and potential effects of airborne viruses. However, current bioaerosol sampling methods are unable to effectively sample airborne viruses (20 to 300 nanometers). To address this problem, a novel Bioaerosol Amplification Unit has been designed and constructed to increase the size of the virus particles by condensational growth, thereby enhancing sampling recovery. To thoroughly evaluate the Bioaerosol Amplification Unit, reaerosolization of viral particles from the impinger must be investigated to assess its impact on the BAU's capability.

Reaerosolization as a function of flow rate and impinger concentration has been characterized. An impinger containing a known concentration of particles (MS2 bacteriophage or polystyrene latex particles) was operated at various flow rates with sterile air, and a scanning mobility particle sizer determined reaerosolization. Results indicate that reaerosolization increased as flow rate increased, due to the additional energy introduced to the system. However, increased concentration did not directly correspond to an increase in reaerosolization of virus particles. Rather, reaerosolization increased as concentration increased until it reached a concentration of approximately 10, PFU/mL, above which reaerosolization began to decrease. The phenomenon likely results from the aggregation of viral particles or the increase of surface tension or viscosity at high concentrations. Adjusting the surface tension by adding soap and increasing viscosity by adding a layer of heavy white mineral oil decreased reaerosolization. In summary, reaerosolization from an impinger could compromise the improved collection capability of the BAU and is a major mode of loss in airborne virus sampling with impingers in certain scenarios. Reaerosolization of viral-sized particles can be minimized by using the BioSampler and sampling over shorter periods of time.

2C.01
Hydrosol concentrator for Improved Detection of Bioaerosols. David Alburty (1) Pamela Murowchick (1) Zachary Packingham (1) Andrew Page (2) Viengsavanhong Elliott (1) Carol Pranulis (1), (1) AlburtyLab, Inc. (2) Page Applied Research, LLC

Following September 11, 2001, and the subsequent postal anthrax attacks, the importance of continuous aerosol monitoring has increased. Highly efficient aerosol collectors have been developed that can process hundreds of liters of air a minute and collect a high proportion of the aerosols in that air into a relatively small liquid sample.

In bioterrorism defense detection systems, an aerosol collector captures particles in the air and concentrates them into a liquid volume in the range of 1.5 ml to 15 ml. A portion of this sample is then transferred directly to a detector which analyzes the liquid and determines if any dangerous aerosols have been collected.

Advanced, rapid microbiological detectors used in these systems are capable of analyzing samples with volumes from around 40 ul to 200 ul of liquid at a time; that is 2% or less of a 10 mL sample from the collector. Usually, the remaining fluid is either archived or dumped to waste.

The hydrosol concentrator technology was developed so that a major portion of the particles found in a sample, such as in the 1.5 to 15 mL sample described above, could be delivered directly to a detector which analyzes the liquid and determines if any dangerous aerosols have been collected.

The concentrator has been demonstrated effective in concentrating biological particles including spores, vegetative cells, and DNA suspended in liquid. This method is suited primarily for the concentration of suspended biological particles such as proteins/toxins, viruses, DNA, and bacteria in the size range of approximately 0.1 nanometer to 20 microns diameter.

Given an initial sample of 1 to 20 mL, the concentrator efficiently concentrates the sample and delivers a sample as small as 4 microliters to the detector in less than 90 seconds. With an additional preconcentrator stage, the initial liquid input volume for concentration could be much larger, with a corresponding further increase in the concentration factor.
A two-stage circumferential slot virtual impactor (CSVI) was designed for bioaerosol sampling and concentration. The 1st and 2nd stage have inflows and minor port outflows of 100/10 L/min, and 10/1 L/min. Each stage could be operated independently with stable flow fields, high minor flow transmission efficiencies, and wide dynamic ranges to concentrate bioaerosol particles in the size range of interest, 1-10 micro-meter AD. Combined in a serial operation, the two-stage system had a total minor flow transmission efficiency above 50% for 2.6-13.5 micro-meter AD particles (>80% for 3.5-10 micro-meter AD), and a cutpoint of about 2.6 micro-meter. Operated at other flow rates of 67 and 150 L/min, the system can maintain stable flow and high transmission efficiency, which provides a flexible operation flow range and a method to adjust the cutpoint.

The pressure drop of the system, through the inlet and the major flow port of the 1st stage, was only about 500 Pa, corresponding to a pressure drop coefficient of 2.0 when the jet velocity at its slot was 21.7 m/s. The low pressure drop of the CSVI implies the two-stage system can be operated with very low power consumption.

Computational fluid dynamics (CFD) was used as primary technique in the CSVI system design to achieve stable flow and high transmission efficiency. Sheath flow was introduced through apex of a conical element, which was placed between the two stages to increase the transmission. Characterization dimensions and configuration strategies were analyzed to find their impacts on the overall performance of the system including the sizes of inlet tubes, diameter of the plenums, sheath flow effect etc. Numerical predictions were compared with experimental results and excellent agreement was achieved.

Increasing the collection efficiency of bioaerosol sampling systems for large (> 10 um AD) particles may result in increased detection capabilities due to the substantial biological mass contained in particles larger than 10 micrometers in aerodynamic diameter. However, the transport of coarse particulate is often thought to be limited to the first several hundred meters from the source due to relatively large gravitational settling velocities. There exists a need to model coarse particulate transport with an emphasis on the implications for bioaerosol sampling and detection. A transient two-dimensional convection-diffusion model was developed to simulate the release of biological aerosols in the lowest 50 meters of the atmospheric surface layer out to a distance of 5000 meters. Monin-Okhubov similarity theory and empirical relations determined by Businger (1971) were used to characterize the height dependent turbulent diffusivity and wind speed profiles. Gravitational settling was also included to determine the evolution of particle size distribution downwind of the source. Lognormal size distributions with initial count median aerodynamic diameters of 40, 10, and 2.5 micrometers and geometric standard deviations of 2, 1.6, and 1.2 were simulated as initial source releases for multiple atmospheric stability classes ranging from zero vertical diffusion to unstable stratification. The evolution in particle size distribution was calculated and used to determine the effective mass collection rate for different aerosol collector models. The effective mass collection rate was defined as the size integral of the product of the collector efficiency curve, particle size probability density function, and sampling flow rate. Two collectors with different collection efficiency curves were compared by forming the ratio of effective mass collection rates. The data suggest that significantly more bioaerosol mass can be collected by efficient collection of particles larger than 10 um AD.

2C.04
Ambient Aerosol Sampling Inlets for Flow Rates from 100 to 400 L/min. Mike Baehl, Sridhar Hari, BING GUO, and Andrew R. McFarland, Texas A&M University, College Station

A typical near-real-time bioaerosol detection system consists of a size selective inlet, a concentrator or collector (e.g., virtual impactor or cyclone), and some form of analyzer. The inlet is expected to have high penetration efficiency in the particle size range of interest, high robustness towards environmental effects, and minimal physical dimensions. In this study, aerosol sampling inlets that consist of a bell-shaped aspiration section and a fractionator (an inline real impactor or an inline virtual impactor) were tested to determine the inlet particle penetration of the inlet at various wind speeds. Experiments were also carried out to determine the effect of dust loading on the particle penetration of the inline real impactors and inline virtual impactors. Meanwhile, computational fluid dynamics (CFD) simulation for the aspiration section was carried out in an effort to improve the design.

The inlet was tested in a wind tunnel at wind speeds of 2, 8, and 24 km/h with particle sizes between 3 and 18 micrometers AD (aerodynamic diameter). Depending on the fractionator used, the exhaust aerosol flow rate through the inlet was 100, 300, or 400 L/min. The inlet showed wind-independent characteristics over the range of wind speeds. The aspiration section had greater than 85% penetration for particle sizes <= 10 micrometers AD. Under all conditions tested, the inlet had a cutoff of 11 +/- 0.5 micrometers AD. Dust loading was shown to have some effect on penetration for fractionators that did not have adequate design capabilities to retain the scalped coarse particles. CFD simulation results showed good agreement with experimentally measured particle penetration for the aspiration section.

3C.01
Bioaerosol Removal and Disinfection by Microwave Assisted Nanofiber Filtration. Qi Zhang (1), Myung-Heui Woo (1), James Welch (2), Hyoungjun Park (3), Chang-Yu Wu (1), Wolfgang Sigmund (3), (1) Department of Environmental Engineering Sciences, University of Florida (2) Department of Biology, University of Florida (3) Department of Materials Science and Engineering, University of Florida

Aerosolization of biological agents among other methods poses the biggest threat of biological attacks. Bioaerosol agents can be dispersed over a wide area in a short period of time. In this study, a HELP (High Efficiency-Low Pressure) air purification system for building ventilation was developed to provide protection from exposure to pathogenic bioaerosols. The system utilizes a combination of nanofiber filtration and microwave disinfection.

The quality of the HELP system was characterized by two phases of experiments. Phase I focused on the physical collection efficiency of the system. Polyacrylonitrile (PAN) nanofiber electrospun on activated carbon fiber (ACF) mats served as the filtration media. An ACF/PAN/ACF sandwich structure was used to protect the PAN layer from detachment. Compared to the glass fiber HEPA filter, the sandwich PAN nanofiber filter has a significantly better filter quality. Also, the filter quality of shorter-term electrospun PAN filters are better than that of longer-term electrospun ones. In phase II, microwave irradiation was applied to the system. Results showed that in less than 90 seconds, the survival of E. coli and MS2 coliphage collected on the filter became below the detection limit. Moreover, there was no E. coli penetration from the system detected. Experiments for other types of agents are also underway to explore the system's range of applicability.

The experimental results demonstrate the advantage of the microwave assisted HELP system for removal and deactivation of biological aerosol agents. Future works will focus on the performance of integrated collection and deactivation process by applying microwave energy during the bioaerosol collection process.

Acknowledgment
Financial support from Defense Threat Reduction Agency, Joint Science and Technology Office, Chemical and Biological Program, Contract number HDTRA1-01-C-0064 is gratefully acknowledged.
3C.02
Use of Zero-Valent Iron Nanoparticles in Inactivating Biological Agents. Minghui Diao and MAOSHENG YAO, Peking University, Beijing, China

This research investigated use of nanoscale zero-valent iron (NZVI) particles in inactivating bacteria and fungi including those prepared in lab and collected in the environments. NZVI particles were synthesized via chemical reaction using NaBH4 and Fe(NO3)3(9H2O). Microbial samples were subjected to the treatments of zero-valent iron nanoparticle suspensions with concentrations of 0.1, 1 and 10 mg/ml for 5 min. Field emission scanning electron microscope (FE-SEM) and UV-Vis photometer were used to study the characteristics of synthesized NZVI, iron suspensions and their inactivation phenomena.

FE-SEM images showed that the synthesized NZVI particles were spherical with a fairly uniform size of about 20-30 nm, and the iron oxides appeared in aggregates. The experimental results indicated that the inactivation rates depended on microbial species and the concentration of NZVI particles. In our study, 100% inactivation rate was achieved within 5 min both for Bacillus subtilis var. niger and Pseudomonas fluorescens when treated with 10 mg/ml iron nanoparticles under aerobic conditions. Inactivation effects on bacteria collected from the environments, 60% for water sample and more than 90% for air samples, were also observed by the same treatments. However, no inactivation effects were observed for fungi species including Aspergillus versicolor prepared in lab and those in environmental water samples. When directly treated with zero-valent iron nanoparticles under aerobic conditions, the surface of microbial species was quickly coated with yellow-brown iron oxides, which was responsible for the inactivation. UV-Vis spectra indicated that the coating on the bacterial surface was mainly ferric hydroxides (FeO(OH)).

Our study presents a multidisciplinary investigation about the inactivation effects of iron nanoparticles on bacteria and fungi, and their derivatives such as endotoxin and glucans. The results obtained herein could be used to guide the application of iron nanoparticles for remediation of environmental biological agents.

3C.03
Protection Factors Provided by Civilian Clothing Exposed to a Non-Biological Simulant During a Staged Evacuation. JONATHAN THORNBURG, Andrew Dart, Jeremy Seagraves, and Doug VanOsdell, RTI International

In the event of a terrorist attack with a biological, chemical, or radiological aerosol focused on the civilian population, people may move through the threat aerosol cloud during the evacuation. If this situation occurs, an important consideration for subsequent decontamination and preventative medical treatment options is how much of the aerosol deposited on a person's clothing and penetrated to their skin. This research calculated the protection factor provided by civilian clothing under various potential scenarios. The protection factor is the amount of aerosol deposited normalized by aerosol cloud concentration and exposure time.

Volunteers wearing normal clothing were exposed to a high concentration fluorescent aerosol cloud (median diameter of 2 micrometers) inside a large exposure chamber. Clothing ensembles were worn to simulate male and female casual and business clothing. The volunteer walked or jogged for 15 minutes inside the wind tunnel under constant environmental conditions to expose themselves to the aerosol. Following exposure, vacuum samples of the clothing and wash samples of the skin were collected to measure the fluorescent particle mass in each location. Multiple skin and clothing locations were sampled to completely characterize the range of calculated protection factors. Independent variables in the linear multivariate analysis were volunteer identification, clothing type, activity, and body location.

The linear multivariate regression determined the amount of aerosol deposited on the outer layer of clothing was influenced by the volunteer, their clothing, their activity, and the area of their body sampled. Similar statistical analysis determined the protection factor provided by the clothing was influenced by the clothing ensemble and body location. As expected, multiple layers of tightly fitted clothing provided higher protection factors for the torso. Much lower protection factors were calculated for the volunteer's legs because only a single layer of fabric provided protection.
3C.04
An Electrodynamic Balance for the Spectroscopic Study of Bioaerosol Fate in Simulated Ambient Environments. Joshua L. Santarpia, SHANNA RATNESAR, Kelly Brinkley, David Kitchen, Jerome Gilberry, Jason Quizon, Johns Hopkins University Applied Physics Laboratory

The atmospheric processes that affect the physical, chemical and biological properties of airborne microorganisms must be carefully studied and understood. Atmospheric oxidants such as ozone and hydroxyl radical have been shown to significantly reduce the viability of exposed Bacillus spores and other microorganisms in aqueous suspensions. The production of secondary organic species, from olefin-ozone interactions, on the surface of bioaerosol have also been used to explain loss in viability of aerosolized microorganisms. In order to study these processes, an octopole electrodynamic balance (EDB) has been developed to allow spectroscopic observation of single bioaerosol particles over extended periods of time. The EDB uses octopole electrodes to hold charged particles between two ring shaped electrodes and allows for x and y positoning and rotation of the particle being interrogated. The location of particles is observed and maintained using white-light shadow-grams onto two CCD cameras. Raman spectroscopy at 532 nm has been used to monitor changes in the chemical signature of the particles through optical ports located on the EDB. Additional optical ports provide a capability to make further spectroscopic measurements, such as ultraviolet light induced fluorescence spectroscopy. Terpenes, ozone, and hydroxyl radical can be introduced into the balance chamber through a Teflon flow-through system. Laboratory system design and preliminary measurements are discussed.

3C.05
Method and experimental facility for evaluating the inactivation of aerosolized microorganisms by a halogen-enriched filled nanocomposite material. SERGEY A. GRINSHPUN (1), Atin Adhikari (1), Chunlei Li (1), Tiina Reponen (1), Mirko Schoenitz (2), Edward Dreizin (2), Mikhaylo Trunov (3), (1) University of Cincinnati, Cincinnati, OH; (2) New Jersey Institute of Technologies, Newark, NJ; (3) Reactive Metals, Inc., Edison, NJ

Defeat of airborne biological agents, including highly-pathogenic viruses and bacteria, is a well-recognized objective. Some agents, e.g., bacterial spores, may survive considerable pressure and temperature stress. Consequently, viable microorganisms aerosolized by an explosion may be subjected to short- or long-range atmospheric transport and thus represent a great threat. Halogens are among the most effective biocidal materials; however, limited efforts have been directed to enable the tailored release of halogenated compounds as subproducts of the reaction of energetic formulations. A novel type of reactive filled nanocomposite material is under development in this effort and will serve as an energetic formulation additive generating such biocidal subproducts, leading to a drastic inactivation of airborne microbial species, including those known to be stress-resistant. To evaluate the efficiency of this approach, we developed a new bioaerosol exposure/sampling method and designed and built a state-of-the art experimental facility. The latter includes an aerosolization chamber, a flame chamber, in which a pellet of the new filled nanocomposite material is burned during the test, and a system for measuring the physical (real-time) and biological (collection and viability analysis) characteristics of aerosolized bio-particles up- and downstream of the flame chamber. The experimental protocol allows for testing over a period of minutes (necessary to perform meaningful bioaerosol sampling), representing a challenge because this time is considerably longer than typical combustion times. A specially designed scaling enables us to address this challenge. The method and set-up are being currently used to test the inactivation effect with airborne endospores of Bacillus subtilis (approx. 1 micro-meter) and MS2 viruses (approx. 0.03 micro-meter). This research was supported by US Defense Threat Reduction Agency's basic research program (Grant HDTRA1-08-1-0012).

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3C.06 Modeled Deposition of B. anthracis in the Human Lung.
JACKY A. ROSATI (1), James S. Brown (2), (1) U.S. Environmental Protection Agency (US EPA), National Homeland Security Research Center (NHSRC); (2) U.S. Environmental Protection Agency (US EPA), National Center for Environmental Assessment (NCEA)

In 2001, letters containing Bacillus anthracis were mailed to several locations throughout the country. This terrorist action resulted in the death of several individuals who inhaled the aerosolized anthrax spores. Since this time, there has been a great concern about bioterrorism agents such as B. anthracis being aerosolized to produce harm. There is also a concern about spore re-entrainment (and thus potential inhalation) as a result of human activity after an anthrax event occurs. This re-entrainment was seen in the contamination of the Hart Senate Office Building.

Little is understood about exposure concentration or dose required to acquire inhalational anthrax. After inhalation, the spores must germinate in the respiratory system for the disease to occur. This germination process can take up to 60 days. Knowledge about the concentration and location of anthrax spore deposition in the human respiratory system, as well as the concentration of spores that will subsequently clear will assist in assessing risk of acquiring the disease. As human experimental trials with inhaled anthrax are obviously not an option, theoretical modeling becomes an extremely important tool.

This work evaluated three current dosimetry models, modeling the deposition of B. anthracis in the adult human lung. These models include the Depos Model (Martonen, 1982), the ICRP model (ICRP, 1994) and the Multiple Path Particle Dosimetry Model (MPPD). Deposition fraction was calculated using each model, with efficiency calculations for diffusion, sedimentation and impaction to determine total deposition. The MPPD was used to calculate particle clearance from the lung. Model results, as well as a statistical comparison of model generated data will be presented.

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

3C.07 The Comparison of Different Strains of Avian Influenza A (H5N1) Infectivity at Mice and Chickens Aerosol Challenge.
Oleg V. Pyankov (1,2), ALEKSANDR S. SAFATOV (1), Sergei A. Kiselev (1), Olga G. Pyankova (1), Artem A. Sergeev (1), Olga K. Demina (1), Aleksandr A. Sergeev (1), Aleksandr N. Sergeev (1), Ilya G. Drozdov (1), Igor E. Agranovski (2), (1) Federal State Research Institution State Research Center of Virology and Biotechnology “Vector”, Novosibirsk Region, Koltsovo, Russia (2) Griffith School of Engineering, Griffith University, Brisbane, Australia

An avian influenza A subtype H5N1 outbreak caused a substantial economic damage in Asian and European countries. More than 150 million infected birds were slaughtered. According to the WHO data (April 2008 update), this virus killed > 240 humans worldwide. However, an amount of literature related to the aerosol infectivity of influenza A subtype H5N1 is very limited. The main scope of this project was to investigate the infectivity of a number of strains recovered at various locations across Eastern Europe.

Seven strains of studied virus recovered in different regions of Russia and one in Crimea, Ukraine, have been chosen for the study. A human influenza virus A/Aich/2/68 (H3N2) strain was used as control. A biological activity of all used strains was determined by Active Center Forming Units (ACFU) method. To perform the experiments, a particular virus suspension was placed into the Collison nebulizer and aerosolized to the aerosol chamber containing either 6 chickens or 10 mice. Two bioaerosol samplers in the chamber operated throughout the entire experiments to monitor viral concentration in the air carrier. Virus challenge doses were estimated using data on virus concentration, time of exposure and animals/birds minute breathing volume.

It was found that the infectivity of virus strains varied substantially when used for animals and birds at aerosol challenge. The values of both 50% aerosol lethal dose (ALD50) and 50% aerosol infectious dose (AID50) for mice were changing from about one to more than five log ACFU. The infectivity of the same strains when used for birds also varied by 2 - 4 log ACFU. However, the difference between ALD50 and AID50 for each strain was measured to be within the interval 0.2 - 1.5 log ACFU. The most virulent strains of avian influenza A; subtype H5N1 for mice and for chickens coincided as a rule.
The Effects of Gas-phase Ozone on Bacillus Spores.
JOSHUA L. SANTARPIA, Shanna Ratnesar, Jason Quizon, Albert Paul, George Murray, Nathan Hagan and Miquel Antoine, Johns Hopkins University Applied Physics Laboratory

Recent experiments have yielded interesting Raman observations and matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) of Bacillus atrophaeus (formerly globigii; Bg) exposed to gas-phase ozone in a low relative humidity environment. Raman spectra, at both 785 nm and 532 nm of unexposed and ozone exposed spores showed peaks typically associated with Bg. At both wavelengths, several features appear in the ozone exposed spores that are not present in the unexposed ones. Most noticeable is the region between 700 and 1200 cm⁻¹. This feature is apparent at both wavelengths, but is more prominent at 532 nm. Peaks in this region have been associated with matrix bound ozone. The work of Young and Setlow has indicated that the resistance of Bacillus spores to aqueous ozone is in the spore coat, and that oxidation of the inner membrane proteins (small acid soluble proteins; SASPs) is likely responsible for defects in spore germination leading to death. Further, the SASPs of Bg spores exposed to ozone were compared with those of unexposed spores using MALDI-MS. Spectra from unexposed control spores and ozone treated spores show the development of secondary peaks near the SASP peaks that indicate partial oxidation of these proteins. Initial viability experiments indicate a significant reduction in spore viability after similar exposures to gas-phase ozone. The change in Raman and MALDI-MS spectra suggests that some damage was done to the spores themselves, and that these techniques are a promising means to examine the processes involved in the interaction of biological aerosol with atmospheric oxidants. This has implications not only for the atmospheric fate of biological aerosol, but also for forensic sampling of biological material after an urban release or for the clean-up of biological contamination in urban areas.

Allergenic Potency of Alternaria alternata and Aspergillus fumigatus Spores is Influenced by Growth Temperature.
SWEE YANG LOW (1), Maosheng Yao (2), Jordan Peccia (1), (1) Yale University, (2) Peking University

Spores of the fungi Alternaria alternata and Aspergillus fumigatus are significant environmental aeroallergens. Common methods for specifically quantifying these allergens in the environment include qPCR spore counts, culture-based methods, and immunoassays targeting a single allergenic epitope on spore surfaces. However, in assessing exposure, these techniques neglect the allergenicity or potency per fungal spore, which is caused by the differential expression of various known protein epitopes that can bind to IgE in sensitized patients. Using a competitive immunoassay that targets human IgE-binding regions on spores, we have shown that the allergenicity per spore of Alternaria alternata and Aspergillus fumigatus conidia could decrease by as much as 6-7 times when growth temperatures increased from 14 degrees Celsius to 32 degrees Celsius. Conversely, corresponding culturability (total/culturable) spore counts indicate more abundant growth and faster germination rate of spores, and thus higher concentrations at a defined incubation period, with increasing growth temperatures. The effects of carbon dioxide levels on allergenicity of the fungal spores will also be presented. The results of our study indicate environmental conditions at growth influence the potency of allergenic fungal spores, and that allergenicity measurements should be considered alongside total spore measurements in order to improve the association of mold concentration with health outcomes.
3C.10
Relation of Aerodynamic Size and (1-3)-beta-D-glucan of Airborne Fungal Spores under Thermal Heat Exposure. Jae Hee Jung (1), Jung Eun Lee (2), Byung Uk Lee (3), Sang Soo Kim (1), (1) Korea Advanced Institute of Science and Technology, South Korea, (2) Seoul National University, South Korea, (3) Konkuk University, South Korea

Recently, indoor and outdoor air quality concerns have received increased public attention with a focus on fungal bioaerosols and their relation to adverse health problems. (1-3)-beta-D-glucans are major water-insoluble structural cell wall component of most fungi. Then, they have known as the indicator of total fungal biomass and fungal toxicity. In this study, we investigated the effect of applied thermal energy on the aerodynamic particle size and (1-3)-beta-D-glucan concentration of fungal bioaerosols (A. versicolor). For stable and reliable generation of fungal bioaerosols, we used a fungal bioaerosol generator with multi-orifice air jets and a rotating substrate designed in our recent research. And, a thermal electric heating tube system was developed in which bioaerosols were exposed to a high temperature environment for a very short period of time. As compared with normal temperature (17-21°C), the decrease ratio of aerodynamic geometric mean diameter (GMD) of A. versicolor fungal bioaerosol was about 7.7% at 400°C and about 34.5% at 700°C. On other hand, even though there was little variation in the GSD (<0.6%) of the fungal bioaerosols until about 500°C, their respective GSD increased as temperatures elevated above 500°C. An increase in surrounding temperature produced a significant decline in the (1-3)-beta-D-glucan concentration. The removal ratio of (1-3)-beta-D-glucan was found in ranges from 4.8 +/- 6.11% (200°C) to 32.2 +/- 2.27% (700°C). The total (1-3)-beta-D-glucan removal ratio was significantly correlated with the combined GMD reduce ratio of fungal particles. From surface morphology change of SEM pictures, we confirmed the effect of thermal heat treatment on GMD and (1-3)-beta-D-glucan variations of fungal bioaerosols.
A. Remer, L., 9B.10
Abbatt, J., 3I.06, 5E.01
Ada, E., 5C.10
Adachi, M., 9J.14
Adams, P., 10E.05, 10B.02, 5K.04, 9J.13
Adhikari, A., 7A.01, 3C.05
Agarwal, J., 10D.01
Agranovski, I., 3C.07
Agrawal, H., 9A.13, 3B.02
Ahmadi, G., 3D.01, 9C.13, 9J.07, 4C.03, 9J.16
Ahmed, K., 5D.11
Ahmed, T., 3I.11
Ahn, J., 9G.10, 3G.12
Ahn, K., 9G.10, 3G.12
Aiken, A., 8E.01, 2A.03, 7B.04, 2A.04, 3A.01
Alburty, D., 5C.16, 5C.16, 2C.01, 7C.05
Alexander, L., 9E.18, 2A.02
Alexander, M., 14C.02
Alfarra, M., 3A.01
Allen-Picolo, G., 9C.03
Almeria, B., 5A.04
Alshawa, A., 7A.06
Altieri, K., 5E.19
Amar, P., 5K.01, 3J.02
Amb, J., 5H.02
Amin, H., 12C.05, 7E.06
An, H., 1C.04
Anbar, A., 9A.17, 13B.04
Andelova, L., 3H.06
Andersen, M., 7E.05
Anderson, B., 14A.02, 9A.27
Anderson, J., 9L.01
Andrade, M., 2A.01, 9L.02
Andreeva, I., 5C.05, 3I.01
Andrews, E., 10B.01
Anisimov, M., 10E.01, 13C.02, 9E.03, 9I.03
Anlauf, K., 8B.04
Anthony, R., 5I.08
Antoine, M., 3C.08
Anwar, D., 8C.04
Apte, M., 11D.04
Archer, D., 4D.04
Archuleta, C., 5B.05
Arellanes, C., 4C.02
Arey, J., 5D.10
Arhami, M., 9D.03, 8B.02, 11C.04
Arnold, F., 10E.04
Armendariz, A., 3E.07
Asgharian, B., 5F.07
Atkinson, R., 5D.10
Auld, J., 5D.04, 5D.08
Ault, A., 8B.05
Aurela, M., 14B.01
Ayala, A., 9A.01, 9A.08, 8D.05, 9A.19, 9A.26, 10A.05
Backer, L., 7C.04
Bader, R., 8B.03
Bae, G., 9A.11, 9A.12, 9L.04
Bae, M., 6B.05, 3H.02, 9G.03, 5G.03, 3I.09, 7D.05
Baehl, M., 2C.04
Bahadur, R., 13C.01
Bahreini, R., 10B.05
Bairai, S., 6B.01
Baker, N., 5C.07, 3G.13, 3E.09, 9J.15, 9G.09
Balasubramanian, R., 9L.05

Balasubramanian, S., 3F.03
Baldauf, R., 8A.01
Balmori, R., 9D.12
Baltensberger, U., 3A.01
Baltensperger, U., 5D.02, 9B.07, 5D.07
Ban-Weiss, G., 10A.04, 10A.01
Banerjee, K., 12D.02, 5I.07
Barahona, D., 4B.04
Bare, C., 5C.07, 3G.13, 3E.09, 9J.15, 9G.09
Barnard, J., 6E.05, 5E.02
Baron, P., 8C.05
Barone, T., 9G.13, 4D.03
Barsanti, K., 8E.03
Barthelmie, R., 1B.05, 5B.03, 1B.04
Barton, C., 10C.02
Bateman, A., 7E.05
Baumgardner, D., 12B.06
Baumgartner, D., 7D.02
Baynard, T., 14D.04
Beckman, P., 5B.11
Beezhold, D., 7C.02
Begum, B., 1A.01
Belan, B., 5C.05, 3I.01
Belisle, C., 12A.04
Benassy, M., 9D.10
Bench, G., 14B.03
Bennett, J., 5D.04, 5D.08
Benson, A., 9E.06
Benson, D., 6E.03
Berg, M., 9K.04
Berisha, K., 3H.01
Bernardo-Bricker, A., 7B.01
Bertram, A., 5E.13
Betz, F., 4D.04
Beyersdorf, A., 14A.02, 9A.27
Bhargava, A., 14A.02, 9A.27
Bhave, P., 5D.06, 4A.04
Bika, A., 4D.02
Binkowski, F., 5K.06
Birch, E., 5C.11
Birky, B., 8D.03
Biswas, P., 3D.03, 4D.01, 7A.01, 9C.11, 2D.02, 4C.01
Biswas, S., 9A.01, 1A.01, 9A.07, 10A.03
Blachere, F., 7C.02
Black, D., 3E.08
Blake, D., 7E.05
Blankenship, R., 2D.02
Bohgard, M., 10C.03
Boies, A., 1D.03
Boman, J., 9I.02
Bonasoni, P., 5B.09
Bond, T., 6D.05, 1A.05, 9J.11
Bonilla, J., 5G.08
Bote, A., 5B.05
Bouvier-Brown, N., 14B.03
Bowen, L., 5I.04, 9G.08
Bowen, Sr., L., 9G.08
Boydston, J., 5I.04
Branis, M., 11C.02, 3H.06, 9C.12
Breysse, P., 5C.08
Bridgers, M., 5I.04
Brinkley, K., 3C.04, 3E.09
Brook, C., 14D.04, 10B.05
Broday, D., 14C.05
Broekhuizen, K., 5D.11
Brook, J., 8B.04
Brooks, S., 9I.01
Brown, J., 3C.06
Brown, S., 11B.03, 11A.03

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<table>
<thead>
<tr>
<th>Author</th>
<th>Paper Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buckley, A.</td>
<td>9L.09</td>
</tr>
<tr>
<td>Bunprapob, S.</td>
<td>1A.01</td>
</tr>
<tr>
<td>Buryak, G.</td>
<td>5C.05, 3I.01, 5E.20</td>
</tr>
<tr>
<td>Caceres, J.</td>
<td>9C.08, 9A.22</td>
</tr>
<tr>
<td>Cahill, C.</td>
<td>1B.02, 5B.07</td>
</tr>
<tr>
<td>Calzolari, F.</td>
<td>5B.09</td>
</tr>
<tr>
<td>Campos, T.</td>
<td>2A.03, 2A.02</td>
</tr>
<tr>
<td>Canagaratna, M.</td>
<td>2A.02, 7B.05, 3A.01</td>
</tr>
<tr>
<td>Canfield, N.</td>
<td>14C.02</td>
</tr>
<tr>
<td>Canuz, E.</td>
<td>9C.01, 9C.03</td>
</tr>
<tr>
<td>Cao, G.</td>
<td>5E.11, 12E.06, 5E.12</td>
</tr>
<tr>
<td>Capps, S.</td>
<td>6B.03</td>
</tr>
<tr>
<td>Caprez, C.</td>
<td>5D.07</td>
</tr>
<tr>
<td>Carbone, C.</td>
<td>13A.01, 3B.01, 5B.09</td>
</tr>
<tr>
<td>Carlton, A.</td>
<td>13E.03, 5D.06, 5E.19, 4A.04</td>
</tr>
<tr>
<td>Carrico, C.</td>
<td>2B.03, 5D.12</td>
</tr>
<tr>
<td>Carter, W.</td>
<td>9E.20</td>
</tr>
<tr>
<td>Casper, S.</td>
<td>9A.05</td>
</tr>
<tr>
<td>Cassee, F.</td>
<td>2B.02</td>
</tr>
<tr>
<td>Castranova, V.</td>
<td>3F.05</td>
</tr>
<tr>
<td>Castro, J.</td>
<td>13B.02</td>
</tr>
<tr>
<td>Casuccio, G.</td>
<td>3B.05</td>
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<tr>
<td>Ceburnis, D.</td>
<td>3B.01</td>
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<tr>
<td>Celik, I.</td>
<td>7C.02</td>
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<tr>
<td>Chakraborty, P.</td>
<td>5K.02</td>
</tr>
<tr>
<td>Chalupa, D.</td>
<td>3H.03</td>
</tr>
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<td>Chen, A.</td>
<td>5D.14</td>
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<td>Chen, C.</td>
<td>5E.08, 5E.09, 5E.07, 14E.01, 5E.06</td>
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<tr>
<td>Chen, M.</td>
<td>5D.14, 5E.06</td>
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<tr>
<td>Chang, H.</td>
<td>1D.02, 3D.15, 3D.16</td>
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<td>Chang, K.</td>
<td>5F.03</td>
</tr>
<tr>
<td>Chang, M.</td>
<td>10A.05</td>
</tr>
<tr>
<td>Chang, R.</td>
<td>9B.02, 1C.02, 13A.02</td>
</tr>
<tr>
<td>Chaudhary, A.</td>
<td>10A.02, 9A.19</td>
</tr>
<tr>
<td>Chein, H.</td>
<td>3D.08</td>
</tr>
</tbody>
</table>

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Clark, N., 7C.03
Clegg, S., 12E.03
Clements, A., 7B.03
Cocker III, D., 10A.02, 9A.19
Cocker, D., 9A.13, 4E.02, 3B.02, 6D.03, 6A.05, 14D.02, 9E.20, 7E.02
Coe, H., 9B.05
Coffey, C., 9G.12
Cohen, D., 1A.01
Collett Jr, J., 12B.01
Collett Jr., J., 3I.04
Collett, J., 3I.02, 5B.05, 8D.02, 5I.02, 11A.03, 13E.02
Collett, Jr J., 5D.09
Collett, Jr., J., 2B.01
Collins, A., 2D.02
Collins, D., 5D.11
Collins, J., 9A.26, 10A.05
Conner, T., 3B.05
Copan, W., 8D.05
Corporan, E., 14A.02, 9A.27
Corse, E., 6A.04
Corsi, R., 10C.05
Craig, L., 9I.04
Crespo-Hernandez, C., 5E.15
Crimmins, B., 1B.05, 5B.01
Cristofanelli, P., 5B.09
Cross, E., 7D.02, 8D.04
Crounse, J., 5D.14, 2A.03
Cubison, M., 10B.01, 7B.04, 2A.04
Curtis, D., 4C.02
Cziczo, D., 12B.05
Dabdub, D., 14E.05, 5D.10
Dagle, R., 14C.02
Daher, N., 5C.14
Dailey, B., 9E.06
Dal Maso, M., 10E.04
Dallmann, T., 8B.03
Dang, H., 3D.12
Daniel, J., 6B.03
Dann, T., 9D.02, 11B.04
Dart, A., 3C.03
Dass, S., 2D.03
Datta, S., 5G.08
Daukoru, M., 4D.01
Daum, P., 2A.02
Davidovits, P., 7D.02
Davidson, C., 13C.05
Davis, S., 7C.02
Davy, P., 1A.01
Day, D., 5I.02
de Bruijne, K., 12A.06, 9A.05, 3H.11
de Foy, B., 2A.04
de Vocht, F., 9A.23
DeCarlo, P., 5D.07, 5D.07, 8E.01, 2A.03, 7B.04, 2A.02, 2A.04, 3A.01
Deceusari, S., 13A.01, 5B.09, 5D.02, 14B.01
DeForest Hauser, C., 9E.17
Delfino, R., 9A.07, 11C.04
Delhomme, O., 9D.10, 3H.08, 3H.08, 3H.07, 7B.02
Demerjian, K., 6B.05, 3H.02, 9G.03, 5G.03, 3I.08, 3I.09, 7D.05
Demina, O., 3C.07
DeMinter, J., 13A.05
DeMott, P., 9B.03, 2B.03, 1B.03, 12B.05
Denero, S., 9A.24
Deng, W., 7A.05
Deye, G., 8C.05
Dhaniyala, S., 9I.06, 12D.01, 5L.06, 12D.02, 5I.07, 9H.01, 11D.05, 13D.04, 9G.06, 9A.28, 5B.02
Diamond, M., 4A.02

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AAAR hereby grants contributing authors full rights to use of their own abstracts
Diao, M., 3C.02
Dibb, J., 5B.11
Dickens, C., 5C.13, 5C.13
Dikken, D., 3E.02
Dimitrova, R., 9L.01
Ding, X., 14B.04
Do, J., 3G.12
Docherty, K., 6E.04, 5G.04, 7B.04, 2A.04, 3A.01, 14B.03
Dommen, J., 9B.07, 5D.07, 3A.01
Donahue, N., 9E.13, 13E.01, 5D.03, 6A.02, 7E.03, 3L.05, 8D.01, 9E.12
Dong, S., 1C.03
Doo, S., 9L.03
Dooley, B., 9I.01
Dorsey, J., 12A.03
Doyle-Eisele, M., 12A.06
Dreizin, E., 3C.05
Drozdov, I., 3C.07
Du, H., 9J.10, 9J.10, 14A.03, 14A.03
Dubey, P., 13D.04
Duchi, R., 5B.09
Dunlea, E., 2A.03, 7B.04, 3A.01
Dulissy, J., 9B.07, 3A.01
Durbin, T., 10A.02, 9A.19
Dutton, S., 11B.02
Duvall, R., 3B.03, 11B.05, 3B.05
Easter, R., 6E.05, 5E.02
Eatough, D., 7B.04
Eberly, S., 11B.06
Ebersviller, S., 12A.06, 9A.05, 3H.11
Eden, R., 3B.02
Edergton, E., 14B.04
Edgerton, E., 6B.02
Edney, E., 6A.04, 7E.01, 8E.04, 4A.04, 5E.14
Edwards, J., 11C.05
Ehara, K., 9G.07
Ehn, M., 10E.04
Ehrhardt, J., 11A.02
Ehrman, S., 2D.03
Eichinger, W., 3H.04
Eidhammer, T., 12B.05
Eiguren-Fernandez, A., 7C.06
Eisele, F., 10D.02
Eisner, A., 11C.05
Ellenbecker, M., 5C.10
Elperin, T., 5K.03
Elzey, S., 9G.15
Emel'yanova, E., 5C.05, 5E.20
Emery, M., 9K.07, 11E.05
Emmanuel, J., 2D.03
Eninger, R., 7A.01
Epstein, S., 9E.13, 13E.01
Erickson, K., 9G.11
Erupe, M., 6A.05, 12E.02, 3B.06
Ervens, B., 10B.01, 5E.19
Evans, D., 5C.11
Evans, G., 9J.12, 9E.07, 9D.02, 8A.02, 11B.04, 12A.02, 9C.02
Eversole, J., 1C.01
Ezekoye, O., 12D.06, 2C.03
Fabian, P., 12D.04
Facchini, M., 13A.01, 3B.01, 5B.09, 5D.02, 14B.01
Facciola, N., 11C.01
Farhana, B., 1A.03, 1A.02
Farmer, D., 14B.03
Farnoud, A., 3E.07
Farnsworth, J., 10D.01
Fast, J., 2A.02
Faulhaber, A., 7D.06
Fei, Z., 7A.02
Feingold, G., 10B.01, 14B.05  
Felton, D., 31.08, 31.09  
Fennel, D., 12D.03  
Ferguson, S., 12D.04  
Fernandez de la Mora, J., 9K.06  
Fernandez Garcia, J., 5A.06  
Fernandez, E., 13A.02  
Fernando, H., 9L.01  
Ferro, A., 12C.01, 9C.13, 9C.14, 9C.06, 10C.04, 10C.04, 4E.04  
Fine, P., 3B.02, 3I.12  
Finessi, E., 3B.01, 5B.09, 5D.02, 14B.01  
Finlay, W., 6C.01, 3G.05, 3G.08  
Finlayson-Pitts, B., 14E.05, 12E.04  
Firmansyah, D., 9K.08  
Fisher, M., 7C.02  
Fissan, H., 5C.12, 11E.02, 9K.03, 13D.02  
Flagan, R., 5D.14, 10B.04, 14B.05  
Flanagan, J., 31.10  
Flocke, F., 2A.02  
Fominykh, A., 5K.03  
Forman, M., 5F.05  
Fotner, E., 2A.04  
Fountoukis, C., 14E.02  
Frank, B., 3H.02, 9G.03, 9G.04, 5J.01, 7D.05  
Frank, N., 31.04  
Franklin, L., 4D.02  
Fraser, M., 7B.03, 9D.11  
Frazer, D., 3F.05  
Fritz, P., 5J.01  
Froines, J., 8A.05  
Frost, G., 6B.03  
Fruin, S., 11A.05, 11A.06  
Fu, H., 3F.09  
Fung, D., 7C.06, 9L.07  
Furukawa, T., 1E.03  
Fusco, P., 7D.05  
Fuzzi, S., 5B.09  
Gaeggeler, K., 5D.07  
Gaffney, J., 2A.04  
Galarneau, E., 4A.02  
Gallagher, M., 9A.23, 12A.03  
Gallavardin, S., 12B.05  
Gant, B., 9B.04  
Gao, H., 9A.24  
Gao, P., 2E.03  
Garbuzenko, O., 3F.02  
Garcia, J., 11B.02  
Garrick, S., 13C.03, 13C.03, 4E.01  
Gaston, C., 8B.05  
Gates, H., 10B.04, 14B.05  
Geller, M., 8A.05  
George, I., 9B.07, 31.06  
Gerald, T., 6A.04  
Geyh, A., 5G.08, 5C.08  
Ghauri, B., 1A.02  
Ghiviriga, I., 5E.10  
Gichuru Gatari, M., 91.02  
Gidwani, A., 6D.02  
Gilardoni, S., 9E.10, 14E.03  
Gilberry, J., 3C.04, 5C.07, 9J.15, 9G.09  
Gilmour, M., 3E.05  
Giraud, R., 10C.02  
Girshick, S., 1D.03, 10E.03, 11E.01, 2D.01  
Giulianelli, L., 5B.09  
Glen, A., 91.01  
Goldstein, A., 5I.05, 8D.01, 7B.04, 14B.03, 5G.05  
Gomez, A., 7A.05, 5A.04  
Gong, L., 9A.03  
Gong, W., 4A.01
<table>
<thead>
<tr>
<th>Name</th>
<th>Abstracts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goohs, K.</td>
<td>5I.01, 5H.03, 5H.02, 9F.01</td>
</tr>
<tr>
<td>Graham, L.</td>
<td>8B.04</td>
</tr>
<tr>
<td>Gramsch, E.</td>
<td>9A.22</td>
</tr>
<tr>
<td>Grand, C.</td>
<td>9D.10</td>
</tr>
<tr>
<td>Graney, J.</td>
<td>11B.05</td>
</tr>
<tr>
<td>Grassian, V.</td>
<td>9G.15</td>
</tr>
<tr>
<td>Gressani, C.</td>
<td>10C.04, 4E.04</td>
</tr>
<tr>
<td>Grycers, B.</td>
<td>3G.05</td>
</tr>
<tr>
<td>Grieshop, A.</td>
<td>6A.03</td>
</tr>
<tr>
<td>Griffin, R.</td>
<td>13B.01, 5D.10, 3I.07, 5B.11, 5B.04</td>
</tr>
<tr>
<td>Grimm, H.</td>
<td>9L.10</td>
</tr>
<tr>
<td>Grinshpun, S.</td>
<td>7A.01, 3C.05</td>
</tr>
<tr>
<td>Grits, B.</td>
<td>4B.02</td>
</tr>
<tr>
<td>Gross, D.</td>
<td>7D.01, 9D.06</td>
</tr>
<tr>
<td>Gross, S.</td>
<td>5E.13</td>
</tr>
<tr>
<td>Grover, B.</td>
<td>7B.04</td>
</tr>
<tr>
<td>Gucwa, K.</td>
<td>9J.06</td>
</tr>
<tr>
<td>Guddmundsson, A.</td>
<td>10C.03</td>
</tr>
<tr>
<td>Guha, S.</td>
<td>14D.03</td>
</tr>
<tr>
<td>Gundel, L.</td>
<td>11D.04</td>
</tr>
<tr>
<td>Guo, B.</td>
<td>2C.04, 1D.04</td>
</tr>
<tr>
<td>Gupta, M.</td>
<td>2D.03</td>
</tr>
<tr>
<td>Gupta, S.</td>
<td>9D.07</td>
</tr>
<tr>
<td>Gustafsson, ?</td>
<td>9D.04</td>
</tr>
<tr>
<td>Gustafsson, O.</td>
<td>2B.04</td>
</tr>
<tr>
<td>Gysel, M.</td>
<td>9B.05, 9B.07</td>
</tr>
<tr>
<td>Ha, G.</td>
<td>5C.01</td>
</tr>
<tr>
<td>Hadley, O.</td>
<td>9J.11</td>
</tr>
<tr>
<td>Hagan, N.</td>
<td>3C.08</td>
</tr>
<tr>
<td>Hagen, D.</td>
<td>14A.01</td>
</tr>
<tr>
<td>Hagler, G.</td>
<td>8A.01</td>
</tr>
<tr>
<td>Haglund, J.</td>
<td>12D.06, 2C.03</td>
</tr>
<tr>
<td>Hagwood, C.</td>
<td>11E.03</td>
</tr>
<tr>
<td>Hall, W.</td>
<td>6A.01</td>
</tr>
<tr>
<td>Hallbauer, E.</td>
<td>5D.12</td>
</tr>
<tr>
<td>Ham, W.</td>
<td>3H.09</td>
</tr>
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<td>Han, B.</td>
<td>3G.03, 9G.02, 13D.03, 3G.02</td>
</tr>
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<td>Han, T.</td>
<td>12D.03, 1C.04</td>
</tr>
<tr>
<td>Han, Y.</td>
<td>3H.05</td>
</tr>
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<td>Hanford, K.</td>
<td>9L.06</td>
</tr>
<tr>
<td>Hanley, T.</td>
<td>5H.01</td>
</tr>
<tr>
<td>Hannigan, M.</td>
<td>11B.02, 3I.12</td>
</tr>
<tr>
<td>Hao, W.</td>
<td>5D.09</td>
</tr>
<tr>
<td>Hari, S.</td>
<td>2C.04</td>
</tr>
<tr>
<td>Harley, R.</td>
<td>10A.04, 10A.01</td>
</tr>
<tr>
<td>Harman, C.</td>
<td>7A.06</td>
</tr>
<tr>
<td>Harman, W.</td>
<td>5I.01</td>
</tr>
<tr>
<td>Harper, M.</td>
<td>9G.05</td>
</tr>
<tr>
<td>Harris, A.</td>
<td>13C.05</td>
</tr>
<tr>
<td>Harrison, R.</td>
<td>8B.01</td>
</tr>
<tr>
<td>Hart, M.</td>
<td>1C.01</td>
</tr>
<tr>
<td>Hartmann, J.</td>
<td>5G.08</td>
</tr>
<tr>
<td>Hartsell, B.</td>
<td>6B.02</td>
</tr>
<tr>
<td>Hasan, M.</td>
<td>8C.02</td>
</tr>
<tr>
<td>Hase, A.</td>
<td>10D.01</td>
</tr>
<tr>
<td>Hastie, D.</td>
<td>5D.04, 5D.08</td>
</tr>
<tr>
<td>Hatakeyama, S.</td>
<td>5B.10</td>
</tr>
<tr>
<td>Hatfield, M.</td>
<td>12C.05, 7E.06</td>
</tr>
<tr>
<td>Hawley, H.</td>
<td>3I.08</td>
</tr>
<tr>
<td>He, J.</td>
<td>9L.05</td>
</tr>
<tr>
<td>He, M.</td>
<td>9G.06, 9A.28</td>
</tr>
<tr>
<td>He, S.</td>
<td>5K.01, 3I.02</td>
</tr>
<tr>
<td>Heaton, K.</td>
<td>6A.01</td>
</tr>
<tr>
<td>Hedquist, B.</td>
<td>9L.01</td>
</tr>
<tr>
<td>Hennigan, C.</td>
<td>13E.04</td>
</tr>
<tr>
<td>Henning, S.</td>
<td>9B.07</td>
</tr>
<tr>
<td>Henricksen, D.</td>
<td>7E.05</td>
</tr>
<tr>
<td>Henry, C.</td>
<td>8D.02, 5I.05</td>
</tr>
<tr>
<td>Henshaw, D.</td>
<td>9L.09</td>
</tr>
<tr>
<td>Heo, J.</td>
<td>5C.04</td>
</tr>
</tbody>
</table>
Herb, J., 9E.05, 6E.01
Herckes, P., 9B.01, 9A.17, 13B.04, 5G.07
Hering, S., 3I.05, 8D.01, 8D.02, 14B.03, 11D.03, 5G.05
Heringa, M., 5D.07
Hernez, M., 12C.02
Hernandez, M., 12C.02
Herner, J., 9A.01, 9A.08, 8D.05, 11A.06, 9A.19, 9A.26, 10A.05
Herod, D., 9D.02, 11B.04
Herrera Peraza, E., 3A.02
Hersey, S., 5D.14, 14B.05
Hershey, D., 5J.01
Hess, P., 1A.05
Hesse, D., 5C.15
Hesterberg, T., 9A.15
Heymsfield, A., 4D.01
Hildebrandt, L., 5D.03
Hill, S., 9B.02, 1C.02, 13A.02
Hillamo, R., 14B.01, 14B.01
Hindle, M., 3F.01
Hinds, W., 7C.06, 9L.07
Hitchman, A., 5C.15
Hixson, M., 3H.10
Hodzic, A., 2A.02
Hogan, Jr., C., 7A.01
Hogrefe, O., 6B.05, 3H.02, 9G.03, 9G.04, 7D.05
Holden, A., 3I.02
Holloway, J., 10B.05
Holm, J., 1D.01
Holmen, B., 9A.14, 9A.18
Holsen, T., 12D.01, 5I.06, 12D.02, 5I.07, 11A.02
Holve, D., 9A.16
Hong, W., 3G.02
Hopke, P., 12C.01, 12C.01, 13D.02, 13C.02, 5G.01, 10E.01, 9D.01, 5F.06, 5F.06, 13C.02, 5G.01, 9E.11, 1A.01, 9H.01, 1A.03, 9C.06, 5F.04
Horst, M., 5E.10
Hotchi, T., 3E.08
Houyoux, M., 4A.04
Hovorka, J., 8A.04, 9J.04, 5C.02, 9G.01, 9D.01, 9C.12
Howard Reed, C., 12C.03
Howard, R., 14A.02, 9A.27
Hsiao, T., 2E.01, 2E.04, 4E.03
Hsieh, W., 5K.08, 5K.08
Hsu, Y., 3D.08, 8D.03
Hu, J., 13B.05
Hu, S., 9A.01, 9A.07, 8B.02, 8D.05, 4C.04, 11A.05, 2C.02, 9A.26, 9A.26, 10A.05, 10A.05
Hu, X., 4B.03
Huai, T., 9A.19, 9A.26, 10A.05
Huang, C., 3E.07
Huang, D., 1D.05
Huang, H., 9B.02, 1C.02, 13A.02
Huang, R., 5C.10
Huang, S., 5F.03
Hubbard, J., 12D.06, 2C.03
Hubbe, J., 2A.02
Hudda, N., 9G.02, 12A.01, 13D.03
Hudson, J., 9B.09
Huey, G., 10B.05
Huff Hartz, K., 12C.05, 12C.05, 7E.06
Huffman, J., 7B.04, 2A.04, 3A.01
Huggins, J., 9E.17
Huh, J., 5B.08
Hunter, H., 5E.03
Husain, L., 1A.03, 1A.02, 3I.11
Hutchings, J., 9B.01
Hwang, J., 3G.12, 9A.11
Hyde, P., 9L.01
Hytychova, A., 11C.02
Iida, K., 10D.04, 10B.03
Imamura, T., 5D.01
Imre, D., 14D.01
Ireson, R., 9A.15
Irvin, M., 7C.04
Isakov, V., 9A.24
Isaxon, C., 10C.03
Jacobson, C., 1C.01
Jacobson, M., 4B.01
Jaenicke, R., 5C.05
Jang, H., 1D.02, 3D.15, 3D.16
Jang, M., 5E.10, 5E.11, 12E.06, 5E.12
Janisko, S., 5G.09
Jaoufi, M., 6A.04, 7E.01, 8E.04, 4A.04, 5E.14
Jaques, P., 12C.01, 9C.06, 2E.03, 10C.04, 4E.04
Jaspers, I., 12A.06, 9A.05, 3H.11
Jayaram, V., 4E.02, 6D.03, 10A.02
Jayne, J., 7D.02, 2A.02, 8D.04, 7D.06
Jeffries, H., 12A.06, 9A.05, 3H.11
Jennerjohn, N., 7C.06, 9L.07
Jeon, K., 9G.10, 3G.12
Jeong, C., 9J.12, 9D.02, 8A.02, 11B.04, 12A.02
Jeong, S., 3G.01, 3G.02
Jha, V., 9B.09
Jhang, Y., 9A.09, 9C.07
Jia, Y., 7B.03, 9D.11
Jiang, J., 4C.01
Jicha, M., 5F.05
Jimenez, J., 10B.01, 4A.03, 8E.01, 2A.03, 7B.04, 2A.02, 7B.05, 2A.04, 3A.01, 14B.03, 7D.06
Jin, H., 9A.12
Jobson, T., 1B.05
Johansson, C., 9D.04
John, A., 10C.03
John, K., 11A.01
Johnson, B., 14C.02
Johnson, K., 6D.03, 10A.02, 9A.19
Johnston, M., 7D.04, 6A.01
Jonsson, H., 10B.04, 14B.05
Jordan, C., 5D.10
Jorquera, H., 13B.02
Jung, C., 9J.08, 3G.10
Jung, E., 9H.03
Jung, H., 6D.02, 9A.19
Jung, J., 9J.02, 3C.10, 5D.05, 3D.06, 3H.05, 5C.01, 9J.13
Junge, J., 12C.05, 7E.06
Junninen, H., 10E.04
Jur?nyi, Z., 9B.07
Kadla, J., 3G.05
Kajii, Y., 5B.10
Kaleel, R., 3B.03, 3B.05
Kameel, R., 6E.03, 9E.06
Kaminski, H., 9K.03
Kammer, R., 10C.03
Kaneyasu, N., 5B.10
Kang, C., 5G.10
Kang, K., 9G.10, 3G.12
Kang, M., 3D.14
Kang, S., 13D.05, 3G.12
Kang, Y., 5D.05
Kapetanovic, S., 3E.06
Karlsson, J., 10C.03
Karna, S., 11A.01
Karydis, V., 4A.03, 14E.02
Kasumba, J., 3H.03
Kato, S., 5B.10
Katoshevski, D., 13C.04, 8C.01, 14C.05

Katzenstein, A., 3B.02
Kautzman, K., 5D.14
Keck, L., 9L.10
Kelkar, V., 7C.01
Kennedy, N., 7C.06, 9L.07
Kenski, D., 2B.01
Kerekes, R., 3G.05
Kerminev, V., 10E.04
Kesavan, J., 5C.08
Khakoo, R., 7C.02
Khan, A., 1A.02, 3I.11
Khlystov, A., 8E.05, 5E.17, 13A.04, 11A.04
Kim Oanh, N., 1A.05
Kim, B., 3D.16
Kim, C., 4C.04, 4C.04
Kim, G., 3G.04
Kim, H., 5C.04, 5D.05, 5C.01, 3G.03, 9G.02, 5B.08, 3G.02
Kim, J., 11E.06, 9A.20, 5A.07, 5A.07, 3D.16
Kim, K., 5B.12, 9J.02, 5A.01, 5A.01, 3D.09, 5A.02, 5A.02, 5B.08, 9L.03
Kim, M., 3D.09, 9E.17
Kim, S., 1D.02, 3C.10, 5A.01, 5D.05, 9K.01, 9H.02, 3G.04, 9H.03, 9H.03, 5A.02, 1E.04, 5C.01, 5C.01, 1E.02, 11E.04, 3D.15, 9K.07,
Kim, T., 13D.05, 9E.01, 3D.09, 9K.08, 3D.16, 9L.03, 9L.04
Kim, W., 5D.05
Kim, Y., 5B.12, 3G.01, 9J.02, 3D.04, 9J.08, 13D.05, 5D.05, 5J.02, 3E.04, 3G.03, 9G.02, 3G.02
Kimbell, J., 6C.03
Kimmel, J., 7B.04, 3A.01
King, S., 8E.01
Kinney, P., 9A.24
Kirchstetter, T., 10A.04, 9J.11, 10A.01
Kirkpatrick, B., 7C.04
Kiselev, A., 9B.07
Kiselev, S., 3C.07, 5E.20
Kitchin, D., 3C.04
Kittelson, D., 3E.01, 3E.02, 4D.02, 9A.19
Kleeman, M., 13B.01, 13B.05, 3H.09, 3H.10, 13A.05
Kleindienst, T., 6A.04, 7E.01, 8E.04, 4A.04, 5E.14
Kleinman, L., 2A.02
Kleinstreuer, C., 5F.01
Kleinsteuer, C., 6C.02
Klingbeil, B., 7D.06
Knapp, D., 2A.03, 2A.02
Knopf, D., 5E.13, 5E.04, 5E.05, 5E.05
Kochevar, S., 3G.14
Koehler, K., 5I.08
Kok, G., 7D.02, 10D.03, 12B.06
Koutrakis, P., 12D.04, 5G.10, 9C.08
Kovenja, V., 9L.03
Kozawa, K., 9A.08, 11A.05, 11A.06
Kraby, J., 5J.05
Kranendonk, L., 9G.13
Krantz, Q., 3E.05
Krasovitov, B., 5K.03
Krecl, P., 9D.04
Kreidenweiss, S., 3I.02, 9B.01, 5E.06, 5D.09, 1B.03, 5D.12, 14E.04, 12B.05
Krebsberg, N., 3I.05, 8D.01, 14B.03, 11D.03, 5G.05
Kreuzer, H., 14C.02
Kroll, J., 8E.01, 7D.02, 3A.01
Krudysz, M., 8A.05, 12A.01, 31.12
Krumins, V., 12D.03
Krus, M., 9D.04
Krusa, M., 2B.04
Ku, B., 8C.05, 9K.06, 5C.11

Kuang, C., 10D.04, 10B.03
Kuehn, T., 5C.12, 2E.02
Kuhlbusch, T., 5C.12, 11E.02, 9K.03, 10C.03
Kulkarni, P., 8C.05, 8C.05
Kulmala, M., 14B.01, 10E.04
Kulshrestha, A., 9C.10
Kumar, P., 5K.07
Kumar, R., 7C.01
Kuo, Y., 5F.03
Kuroda, S., 3D.11
Kwak, J., 7D.03
Kwamena, N., 9L.06
Kwon, Y., 9G.10, 3G.12
Laaksonen, A., 10E.04
Lack, D., 14D.04
LaCroix, D., 2C.02
Laj, P., 5B.09
Lala, G., 6B.05, 3H.02, 9G.03
Lall, A., 14D.03, 14D.03, 1D.05
Lam, C., 3G.08
Lam, N., 9C.03
Lambe, A., 9E.13, 3I.05, 8D.01
Lance, S., 9B.12
Lander, O., 7C.02
Landis, M., 11B.05
Lane, D., 9E.14, 9E.15
Larriba, C., 5A.05
Larson, T., 9A.15
Laskin, A., 7E.05, 2A.04, 14E.04
Laskin, J., 7E.05
Lau, A., 5E.08
Lau, P., 5E.09
Lau, Y., 6D.05
Lawson, D., 9A.15
Leavey, A., 9A.23
Leck, C., 2B.04
Lee, A., 5E.08, 14E.01
Lee, B., 3C.10, 5A.01, 5E.18, 5I.02
Lee, C., 8C.04, 1E.01
Lee, D., 3E.04, 3D.06, 3D.07, 9K.01, 9H.02, 6C.05, 9K.08
Lee, H., 3D.04, 2D.04
Lee, J., 9C.05, 9E.14, 9E.15, 3C.10, 8C.04, 1C.05, 1E.01
Lee, K., 5E.09, 9K.01, 9H.02
Lee, L., 7A.02
Lee, M., 3G.04
Lee, S., 12D.01, 5I.06, 6E.03, 9E.06, 13B.03, 5E.16, 3G.11, 9A.11, 9A.12, 9L.04, 9L.08
Lee, T., 9G.05, 12B.01, 11A.03
Lee, W., 8B.04
Lee, Y., 5K.04
Lehtinen, K., 10E.04
Lei, W., 4A.03, 14E.02
Lersch, T., 3B.05
Levin, E., 5D.09
Lewandowski, M., 6A.04, 7E.01, 8E.04, 4A.04, 5E.14
Lewis, G., 11D.03
Lewis, K., 5D.09
Lewis, S., 5D.13
Li, C., 3C.05
Li, H., 1C.05, 1E.01
li, l., 13D.01
Li, M., 5D.07, 3I.08, 12A.04
Li, S., 4A.01, 3D.05, 6D.01, 8B.04
Li, Y., 5E.08, 4D.01, 5E.09, 8B.01, 9D.05
Li, Z., 6C.02
Liao, K., 5K.01, 3J.02
Liggio, J., 4A.01, 8B.04
Lilienfeld, P., 5I.01

Lim, C., 9A.20
Lim, H., 3D.16
Lim, J., 9A.20
Lim, K., 3G.11, 3G.06, 3G.09
Lim, Y., 6E.04, 5D.10
Lin, G., 9K.02
Lin, H., 1C.01
Lin, J., 3E.10
Lin, M., 13A.04, 11A.04
Linak, W., 3E.05
Lindsley, W., 7C.02
Ling, T., 5E.07
Lippmann, M., 10C.01
Lipsky, E., 4D.04
Liscinsky, D., 14A.02, 9A.27
Liu, L., 9A.15
Liu, S., 9E.10
Llewellyn, Z., 5I.04
Lloyd, J., 7D.04
Lobo, P., 14A.01
Logue, J., 3I.05
Longest, W., 9J.01, 5F.02, 3F.01
Longley, I., 9A.23, 12A.03
Lopez, G., 9A.22
Lopez, M., 5E.04
Lottmann, A., 9D.10
Lovejoy, E., 14D.04
Low, S., 3F.06, 3C.09
Lu, G., 5A.03, 3D.13
Lun, X., 5B.10
Lunden, M., 10A.04, 10A.01, 10A.01, 3E.08, 3E.08
Lundgren, D., 1C.05, 8D.03
Ma, B., 3D.05
Ma, X., 14D.05, 14D.03, 1D.05
Mack, L., 5D.09
Madronich, S., 2A.02
Mahmood, A., 1A.04
Mainelis, G., 12D.03, 1C.04, 3F.02
Majestic, B., 7D.01, 9A.17, 13B.04
Makar, P., 4A.02, 4A.01, 9E.19, 8B.04
Malloy, Q., 6A.05, 14D.02, 7E.02
Malm, W., 3I.02, 5D.09, 5I.02
Mang, S., 7E.05
Manninen, H., 10E.04
Manomaiphiboon, K., 5K.01, 3J.02
Manthena, S., 9C.14
Mao, J., 3G.05
Mao, S., 5A.03, 3D.13
Mara, S., 9A.08, 11A.05
Marchenko, V., 5E.20
Margulies, J., 5C.08
Marinoni, A., 5B.09
Mark, T., 5B.05
Markowicz, A., 1A.01
Markwitz, A., 1A.01
Marley, N., 2A.04
Marple, V., 12D.05
Martin, C., 12A.03
Martin, R., 3B.06
Martin, S., 5B.06, 9B.08, 8E.01, 9E.04, 3I.13
Marx, D., 9C.28
Masih, J., 9C.10
Massey, D., 9C.10
Massling, A., 5D.12
Massoli, P., 14D.04
Matross, D., 14B.03
Matsunaga, A., 6E.04
Mauldin, L., 1B.05
<table>
<thead>
<tr>
<th>Author Name</th>
<th>Session Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>May, A.</td>
<td>12D.01, 5I.06</td>
</tr>
<tr>
<td>Mazurek, M.</td>
<td>3I.08, 3I.08, 12A.04</td>
</tr>
<tr>
<td>Mazzoleni, L.</td>
<td>13E.02</td>
</tr>
<tr>
<td>McAddy, E.</td>
<td>9A.21</td>
</tr>
<tr>
<td>McAughey, J.</td>
<td>5C.13</td>
</tr>
<tr>
<td>McCormick, A.</td>
<td>10B.03</td>
</tr>
<tr>
<td>McCracken, J.</td>
<td>9C.01</td>
</tr>
<tr>
<td>McDevitt, J.</td>
<td>12D.04</td>
</tr>
<tr>
<td>McDow, S.</td>
<td>3I.08, 12A.04</td>
</tr>
<tr>
<td>McFarland, A.</td>
<td>2C.04, 2C.02</td>
</tr>
<tr>
<td>McFiggans, G.</td>
<td>9B.05</td>
</tr>
<tr>
<td>McGrath, C.</td>
<td>5C.13</td>
</tr>
<tr>
<td>McGuire, M.</td>
<td>9D.02, 11B.04</td>
</tr>
<tr>
<td>McInnis, J.</td>
<td>8D.04</td>
</tr>
<tr>
<td>McKay, M.</td>
<td>7B.04</td>
</tr>
<tr>
<td>McKinney, W.</td>
<td>3F.05</td>
</tr>
<tr>
<td>McLaughlin, J.</td>
<td>9I.16</td>
</tr>
<tr>
<td>McMahon, S.</td>
<td>10C.04, 4E.04</td>
</tr>
<tr>
<td>McMeeking, G.</td>
<td>5D.09, 5D.12</td>
</tr>
<tr>
<td>McMurry, P.</td>
<td>2D.01, 9K.05, 10D.04, 10B.03, 10D.02</td>
</tr>
<tr>
<td>McWhinney, R.</td>
<td>5E.01</td>
</tr>
<tr>
<td>Meade, B.</td>
<td>7C.02</td>
</tr>
<tr>
<td>Mei, F.</td>
<td>14C.01, 3D.02</td>
</tr>
<tr>
<td>Meiritz, M.</td>
<td>13A.05</td>
</tr>
<tr>
<td>Mendoza, A.</td>
<td>14C.02</td>
</tr>
<tr>
<td>Mentele, M.</td>
<td>5I.05</td>
</tr>
<tr>
<td>Merritt, C.</td>
<td>1C.01</td>
</tr>
<tr>
<td>Meskhidez, N.</td>
<td>9B.10</td>
</tr>
<tr>
<td>Metzger, A.</td>
<td>3A.01</td>
</tr>
<tr>
<td>Miake-Lye, R.</td>
<td>14A.02, 9A.27</td>
</tr>
<tr>
<td>Middlebrook, A.</td>
<td>10B.05</td>
</tr>
<tr>
<td>Mifflin, A.</td>
<td>9E.04</td>
</tr>
<tr>
<td>Mihalic, J.</td>
<td>5G.08, 5C.08</td>
</tr>
<tr>
<td>Mihele, C.</td>
<td>8B.04</td>
</tr>
<tr>
<td>Mikheev, V.</td>
<td>5C.15</td>
</tr>
<tr>
<td>Milford, J.</td>
<td>11B.02</td>
</tr>
<tr>
<td>Miller, S.</td>
<td>11C.01, 11B.02</td>
</tr>
<tr>
<td>Miller, W.</td>
<td>9A.13, 4E.02, 3B.02, 6D.03</td>
</tr>
<tr>
<td>Millet, M.</td>
<td>9D.10, 3H.08, 3H.07, 7B.02</td>
</tr>
<tr>
<td>Milton, D.</td>
<td>12D.04</td>
</tr>
<tr>
<td>Minguillon, M.</td>
<td>9D.03</td>
</tr>
<tr>
<td>Minko, T.</td>
<td>3F.02</td>
</tr>
<tr>
<td>Minyard, M.</td>
<td>5I.04</td>
</tr>
<tr>
<td>Miracolo, M.</td>
<td>4D.04, 7E.03, 9E.12</td>
</tr>
<tr>
<td>Mitchell, M.</td>
<td>11A.02</td>
</tr>
<tr>
<td>Mitchem, L.</td>
<td>9I.06</td>
</tr>
<tr>
<td>Miyoshi, T.</td>
<td>5B.10</td>
</tr>
<tr>
<td>Modesto-Lopez, L.</td>
<td>2D.02</td>
</tr>
<tr>
<td>Modesto, L.</td>
<td>3D.03</td>
</tr>
<tr>
<td>Moharreri, A.</td>
<td>9J.06, 9J.06</td>
</tr>
<tr>
<td>Mohr, C.</td>
<td>3A.01</td>
</tr>
<tr>
<td>Moission, R.</td>
<td>8B.05</td>
</tr>
<tr>
<td>Molenar, J.</td>
<td>5B.05</td>
</tr>
<tr>
<td>Molina, L.</td>
<td>4A.03, 14E.02, 2A.04</td>
</tr>
<tr>
<td>Montoya, L.</td>
<td>5J.01, 3F.08</td>
</tr>
<tr>
<td>Montzka, D.</td>
<td>2A.03, 2A.02</td>
</tr>
<tr>
<td>Moore, K.</td>
<td>8A.05, 12A.01, 3B.06</td>
</tr>
<tr>
<td>Moore, M.</td>
<td>5E.19, 14E.04</td>
</tr>
<tr>
<td>moore, r.</td>
<td>10B.05, 10D.03, 9B.12</td>
</tr>
<tr>
<td>Moosmiller, H.</td>
<td>5D.09</td>
</tr>
<tr>
<td>Moran, M.</td>
<td>4A.01, 8B.04</td>
</tr>
<tr>
<td>Moretti, F.</td>
<td>13A.01, 14B.01</td>
</tr>
<tr>
<td>Morrison, G.</td>
<td>10C.05</td>
</tr>
<tr>
<td>Moss, O.</td>
<td>3F.11, 3F.07, 3F.04</td>
</tr>
<tr>
<td>Mulholland, G.</td>
<td>14D.05, 11E.03, 11E.04, 14D.03, 9K.07, 11E.05</td>
</tr>
<tr>
<td>Mun, J.</td>
<td>13D.05</td>
</tr>
<tr>
<td>Murowchick, P.</td>
<td>7C.05</td>
</tr>
<tr>
<td>Name</td>
<td>Session References</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Murphy, D.</td>
<td>14D.04, 6B.03</td>
</tr>
<tr>
<td>Murphy, S.</td>
<td>10B.04, 14B.05</td>
</tr>
<tr>
<td>Murray, G.</td>
<td>3C.08</td>
</tr>
<tr>
<td>Na, K.</td>
<td>5G.02</td>
</tr>
<tr>
<td>Nadykto, A.</td>
<td>9E.05, 6E.01</td>
</tr>
<tr>
<td>Nakao, S.</td>
<td>14D.02, 7E.02</td>
</tr>
<tr>
<td>Nakatani, E.</td>
<td>9J.14</td>
</tr>
<tr>
<td>Napelenok, S.</td>
<td>4A.04</td>
</tr>
<tr>
<td>Nash, D.</td>
<td>3F.07, 3F.04</td>
</tr>
<tr>
<td>Nasr, H.</td>
<td>9J.16</td>
</tr>
<tr>
<td>Nazaroff, W.</td>
<td>9C.09, 12C.04</td>
</tr>
<tr>
<td>Negrín Juárez, R.</td>
<td>9B.10</td>
</tr>
<tr>
<td>Nemitz, E.</td>
<td>12A.03</td>
</tr>
<tr>
<td>Nenes, A.</td>
<td>14E.02, 4B.04, 10B.04, 10B.05, 13E.05, 5K.07, 5K.08, 10D.03, 9B.12</td>
</tr>
<tr>
<td>Newburn, M.</td>
<td>9E.18, 14C.02</td>
</tr>
<tr>
<td>Ng, N.</td>
<td>7B.05</td>
</tr>
<tr>
<td>Ng, S.</td>
<td>8D.04</td>
</tr>
<tr>
<td>Ni, B.</td>
<td>1A.01</td>
</tr>
<tr>
<td>Nielsen, D.</td>
<td>9A.14, 9A.18</td>
</tr>
<tr>
<td>Nielsen, J.</td>
<td>10C.03</td>
</tr>
<tr>
<td>Nieminen, T.</td>
<td>10E.04</td>
</tr>
<tr>
<td>Nigam, A.</td>
<td>4E.02</td>
</tr>
<tr>
<td>Nilsson, E.</td>
<td>3B.01</td>
</tr>
<tr>
<td>Ning, Z.</td>
<td>9A.06, 9G.02, 13D.03</td>
</tr>
<tr>
<td>Nissenson, P.</td>
<td>14E.05</td>
</tr>
<tr>
<td>Nizkorodov, S.,</td>
<td>7E.05, 7A.06</td>
</tr>
<tr>
<td>Noble, S.</td>
<td>9B.09</td>
</tr>
<tr>
<td>Noblitt, S.</td>
<td>8D.02</td>
</tr>
<tr>
<td>Noga, M.</td>
<td>6C.01</td>
</tr>
<tr>
<td>Noll, J.</td>
<td>5G.09</td>
</tr>
<tr>
<td>Nolte, C.</td>
<td>5K.06</td>
</tr>
<tr>
<td>Norbeck, J.</td>
<td>5G.02</td>
</tr>
<tr>
<td>Norris, D.</td>
<td>2D.01</td>
</tr>
<tr>
<td>Norris, G.</td>
<td>3B.03, 11B.05, 11B.05, 3B.05</td>
</tr>
<tr>
<td>Northcross, A.</td>
<td>9C.01, 9C.03</td>
</tr>
<tr>
<td>Northway, M.</td>
<td>2A.04, 3A.01</td>
</tr>
<tr>
<td>Novoselac, A.</td>
<td>11C.06</td>
</tr>
<tr>
<td>O'Dowd, C.</td>
<td>13A.01, 3B.01</td>
</tr>
<tr>
<td>O'Lenick, C.</td>
<td>9A.05</td>
</tr>
<tr>
<td>O'Shaughnessy, P.</td>
<td>3D.14</td>
</tr>
<tr>
<td>Oakes, M.</td>
<td>7D.01</td>
</tr>
<tr>
<td>Ober dorster, G.</td>
<td>4C.01</td>
</tr>
<tr>
<td>Ober Reit, D.</td>
<td>9G.11</td>
</tr>
<tr>
<td>Obrist, D.</td>
<td>5D.09</td>
</tr>
<tr>
<td>Offenberg, J.</td>
<td>6A.04, 7E.01, 8E.04, 4A.04, 5E.14</td>
</tr>
<tr>
<td>Ogren, J.</td>
<td>10B.01</td>
</tr>
<tr>
<td>Oh, H.</td>
<td>5A.07</td>
</tr>
<tr>
<td>Oh, Y.</td>
<td>9K.01, 9H.02</td>
</tr>
<tr>
<td>Okuyama, K.</td>
<td>1D.02</td>
</tr>
<tr>
<td>Oldham, M.</td>
<td>3F.11, 5F.02</td>
</tr>
<tr>
<td>Olenick, C.</td>
<td>12A.06, 3H.11</td>
</tr>
<tr>
<td>Olfert, J.</td>
<td>10D.05, 10D.05</td>
</tr>
<tr>
<td>Olkin, S.</td>
<td>3I.01</td>
</tr>
<tr>
<td>Olson, B.</td>
<td>12D.05</td>
</tr>
<tr>
<td>Olson, M.</td>
<td>8B.02, 8B.03</td>
</tr>
<tr>
<td>Olszynka, K.</td>
<td>6B.01</td>
</tr>
<tr>
<td>Onasch, T.</td>
<td>14A.02, 7D.02, 2A.02, 3A.01, 8D.04, 9A.27</td>
</tr>
<tr>
<td>Ondov, J.</td>
<td>7B.01</td>
</tr>
<tr>
<td>Orf, M.</td>
<td>1A.04</td>
</tr>
<tr>
<td>Orisini, D.</td>
<td>7D.05</td>
</tr>
<tr>
<td>Orland, R.</td>
<td>14C.05</td>
</tr>
<tr>
<td>Orsini, D.</td>
<td>5G.03</td>
</tr>
<tr>
<td>Ortega, J.</td>
<td>2A.02</td>
</tr>
<tr>
<td>Osmondson, B.</td>
<td>9G.11</td>
</tr>
<tr>
<td>Otani, Y.</td>
<td>1E.03, 1E.03, 3D.10</td>
</tr>
<tr>
<td>Oyama, B.</td>
<td>9L.02</td>
</tr>
<tr>
<td>Oyola, P.</td>
<td>9C.08, 9A.22</td>
</tr>
<tr>
<td>Ozturk, F.</td>
<td>11B.01</td>
</tr>
</tbody>
</table>
Pabroa, P., 1A.01
Packwood, D., 14E.05
Padro, L., 10B.04, 9B.12
Page, A., 14E.05
Pagels, J., 10C.03
Pakbin, P., 12A.01
Pan, X., 7E.05
Pan, Y., 9B.02, 1C.02, 13A.02
Panchenko, M., 5C.05, 3I.01
Pandey, J., 3H.12
Pandis, S., 4A.03, 14E.02, 5D.03, 6B.04, 5E.18, 9J.13
Pandit, G., 1A.01
Pankow, J., 8E.02, 8E.03
Park, B., 3G.04
Park, C., 5G.02
Park, H., 3G.10, 3G.11, 3G.06, 3G.09, 3C.01
Park, J., 9G.14, 9L.03
Park, K., 7D.03, 9B.06, 11E.06, 9G.14
Park, S., 9A.08, 11E.06, 9A.11, 9A.12
Parsons, M., 2B.03
Patel, M., 9A.24
Pati, R., 2D.03
Patterson, M., 3I.02
Pettibone, A., 3H.12
Pierce, J., 10E.05, 10B.02, 5E.18
Pinder, R., 5D.06
Pinnick, R., 9B.02, 1C.02, 13A.02
Place, P., 5B.04
Platnick, S., 9B.10
Poehl, P., 2C.02
Polidori, A., 9A.06, 9A.07, 7B.06, 2B.02, 11C.04
Pongprueksa, P., 9A.24, 9A.24
Poulim, L., 5D.12
Pouliot, G., 4A.04
Prather, K., 14E.04, 12B.03, 12B.04, 12B.05, 8B.05
Pratsinis, S., 9K.05
Pratt, K., 12B.03, 12B.05
Praveen, M., 2B.04
Prenni, A., 2B.03, 1B.03, 12B.05
Presto, A., 9E.13, 9E.13, 7E.03, 7E.03, 9E.12
Prevot, A., 14B.02, 8A.03, 8A.03, 5D.07, 2A.04, 3A.01
Price, O., 5F.07
Prinsell, M., 5D.11
Protus, T., 5G.08
Pryor, S., 1B.05, 5B.03, 1B.04
Puchkova, L., 5C.05
Pui, D., 5C.12, 11E.02, 1E.04, 1E.02, 13D.02, 9K.07, 11E.05
Pun, B., 12E.01, 9D.12
Puppala, J., 9C.11
Purdy, C., 7C.03, 7C.03
Pyankov, O., 3C.07
Pyankova, O., 3C.07
Qi, C., 13D.02, 13D.02  
Qi, L., 2D.01, 6A.05, 14D.02, 7E.02  
Qi, Y., 10C.04, 4E.04  
Qian, J., 9C.13, 9C.14  
Quant, F., 9G.11  
Quizon, J., 3C.08, 3C.04, 5C.07, 9J.15, 9G.09  
Quraishi, T., 1A.04  
Rahnama, M., 9J.09  
Raife, J., 13B.03  
Raja, S., 12C.01, 1A.03, 9C.06, 5B.05, 10C.04, 4E.04  
Ramirez, D., 11A.01  
Ramos-Bonilla, J., 5C.08  
Ranjan, M., 11D.05  
Rastogi, N., 5G.06, 7D.01  
Ratnesar, S., 3C.08, 3C.04, 5C.07, 9J.15, 9G.09  
Rattigan, O., 6B.05, 3I.08, 3I.09  
Ravi, L., 11E.01  
Ray, A., 5E.03  
Raymond, T., 12B.02  
Reagan, J., 9A.24  
Reddy, C., 14B.04  
Redwine, K., 9J.05  
Reff, A., 5H.01, 11B.06  
Reid, J., 9L.06  
Renbaum, L., 7E.04, 12E.05  
Rengasamy, S., 3G.07  
Reponen, T., 7A.01, 3C.05  
Reznikova, I., 3I.01  
Rhoads, K., 5G.03, 7D.05  
Richardson, M., 9B.03  
Richter, R., 5D.07  
Rieger, P., 10A.05  
Riemenschneider, L., 1C.05  
Riemer, N., 5E.05, 6E.05, 5E.02  
Riipinen, I., 10E.04  
Rinaldi, M., 13A.01, 3B.01, 5B.09  
Rinkleff, P., 5B.07  
Rissman, T., 10C.02  
Roberts, G., 14E.04  
Roberts, J., 1D.03, 1D.01, 10D.02  
Roberts, P., 11A.03  
Robertson, W., 9A.19, 9A.26, 10A.05  
Robinson, A., 9E.13, 6A.03, 4D.04, 7E.03, 31.05, 8D.01, 9E.12  
Rocklage, J., 12D.05  
Roden, C., 6D.05, 9J.11  
Rodhe, H., 2B.04  
Rogers, D., 12B.05  
Rogge, W., 7B.01  
Romanovskiy, M., 9J.03  
Rosati, J., 3C.06, 11C.05  
Roselle, S., 5K.06  
Rosen, J., 13A.02  
Rosenoern, T., 8E.01  
Rossner, A., 1B.05  
Rostami, A., 6C.02  
Rowchowdhury, U., 13E.02  
Ruda-Eberenz, T., 5C.11  
Ruehl, C., 13E.05  
Ruiz-Mercado, I., 9C.03  
Ruiz, P., 9C.08, 9C.08, 9A.22  
Rule, A., 5G.08, 5C.08  
Russell, A., 3J.02  
Russell, A., 5K.01  
Russell, L., 13C.01, 9E.10, 9E.10, 14E.03  
Rutter, A., 8B.03  
Ryu, J., 9A.20  
S., 9E.06  
Saarikoski, S., 14B.01
<table>
<thead>
<tr>
<th>Author</th>
<th>Paper Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sabaliauskas, K.</td>
<td>12A.02, 9C.02</td>
</tr>
<tr>
<td>Safai, P.</td>
<td>2B.04</td>
</tr>
<tr>
<td>Safatov, A.</td>
<td>5C.05, 5C.05, 3C.07, 3I.01, 5E.20</td>
</tr>
<tr>
<td>Safarneek, J.</td>
<td>11C.02</td>
</tr>
<tr>
<td>Sage, A.</td>
<td>8D.01, 5E.15</td>
</tr>
<tr>
<td>Sagona, J.</td>
<td>12A.04</td>
</tr>
<tr>
<td>Saha, A.</td>
<td>9I.01</td>
</tr>
<tr>
<td>Sahu, M.</td>
<td>9C.11</td>
</tr>
<tr>
<td>Salcedo, D.</td>
<td>2A.04</td>
</tr>
<tr>
<td>Saleh, R.</td>
<td>8E.05, 5E.17, 11A.04</td>
</tr>
<tr>
<td>Salinas, R.</td>
<td>11A.01</td>
</tr>
<tr>
<td>Salmanzadeh, M.</td>
<td>9C.15, 9J.09</td>
</tr>
<tr>
<td>Samburova, V.</td>
<td>14A.05</td>
</tr>
<tr>
<td>Samy, S.</td>
<td>14A.05</td>
</tr>
<tr>
<td>Santarpia, J.</td>
<td>3C.08, 3C.04, 5C.07, 3G.13, 3E.09, 9J.15, 9G.09</td>
</tr>
<tr>
<td>Santos, F.</td>
<td>1A.01</td>
</tr>
<tr>
<td>Santoso, M.</td>
<td>1A.01</td>
</tr>
<tr>
<td>Sarin, M.</td>
<td>2B.04</td>
</tr>
<tr>
<td>Sarwar, G.</td>
<td>4A.04</td>
</tr>
<tr>
<td>Sassi, M.</td>
<td>8B.04</td>
</tr>
<tr>
<td>Sato, K.</td>
<td>5D.01</td>
</tr>
<tr>
<td>Satsangi, V.</td>
<td>2D.03</td>
</tr>
<tr>
<td>Sawant, A.</td>
<td>6D.03</td>
</tr>
<tr>
<td>Saylor, R.</td>
<td>6B.02</td>
</tr>
<tr>
<td>Schauer, J.</td>
<td>8B.02</td>
</tr>
<tr>
<td>Schauer, J.</td>
<td>9A.01, 9A.06, 9D.03, 5G.06, 7D.01, 2B.02, 1A.04, 8D.05, 9D.06, 8B.03, 7B.04, 9A.26, 2A.04, 13A.05</td>
</tr>
<tr>
<td>Schauer, J.</td>
<td>5A.01, 9A.06, 9D.03, 5G.06, 7D.01, 2B.02, 1A.04, 8D.05, 9D.06, 8B.03, 7B.04, 9A.26, 2A.04, 13A.05</td>
</tr>
<tr>
<td>Scheelke, E.</td>
<td>6C.05</td>
</tr>
<tr>
<td>Schichtel, B.</td>
<td>3I.02</td>
</tr>
<tr>
<td>Schoenfelder, J.</td>
<td>3H.04</td>
</tr>
<tr>
<td>Schoenitz, M.</td>
<td>3C.05</td>
</tr>
<tr>
<td>Schroeter, J.</td>
<td>6C.03</td>
</tr>
<tr>
<td>Schurman, M.</td>
<td>5I.02</td>
</tr>
<tr>
<td>Schwab, J.</td>
<td>6B.05, 3H.02, 9G.03, 5G.03, 3I.08, 3I.09, 7D.05</td>
</tr>
<tr>
<td>Schwandner, F.</td>
<td>5B.05</td>
</tr>
<tr>
<td>Schwarz, J.</td>
<td>10B.05</td>
</tr>
<tr>
<td>Schwegler-Berry, D.</td>
<td>3F.05</td>
</tr>
<tr>
<td>Seagraves, J.</td>
<td>3C.03</td>
</tr>
<tr>
<td>Seigneur, C.</td>
<td>9D.12</td>
</tr>
<tr>
<td>Seinfeld, J.</td>
<td>5D.14, 10B.04, 14B.05</td>
</tr>
<tr>
<td>Seitzinger, S.</td>
<td>5E.19</td>
</tr>
<tr>
<td>Seneviratne, S.</td>
<td>1A.01</td>
</tr>
<tr>
<td>Seo, J.</td>
<td>9E.01</td>
</tr>
<tr>
<td>Sergeev, A.</td>
<td>5C.05, 3C.07, 3C.07, 3C.07, 3I.01, 5E.20</td>
</tr>
<tr>
<td>Seshadri, S.</td>
<td>12D.03, 3F.02</td>
</tr>
<tr>
<td>Seto, T.</td>
<td>1E.03</td>
</tr>
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<td>Sewell, H.</td>
<td>5B.05</td>
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<td>Sexton, K.</td>
<td>12A.06, 9A.05, 3H.11</td>
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<td>Shafer, M.</td>
<td>5G.06, 7D.01, 2B.02, 8D.05, 8B.03, 9A.26</td>
</tr>
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<td>Shair Singh, K.</td>
<td>9E.07</td>
</tr>
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<td>Shakked, T.</td>
<td>8C.01</td>
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<td>Shakya, K.</td>
<td>3I.07</td>
</tr>
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<td>Shanley, K.</td>
<td>4C.03, 4C.03</td>
</tr>
<tr>
<td>Sheesley, R.</td>
<td>2B.04, 9D.04, 13A.05</td>
</tr>
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<td>5C.14</td>
</tr>
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<td>12B.01</td>
</tr>
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<td>Shihadeh, A.</td>
<td>5C.14</td>
</tr>
<tr>
<td>Shilling, J.</td>
<td>8E.01</td>
</tr>
<tr>
<td>Shim, S.</td>
<td>3G.01, 3G.02</td>
</tr>
<tr>
<td>Shimono, A.</td>
<td>5B.10</td>
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<td>Shin, H.</td>
<td>3D.09</td>
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<td>Shin, W.</td>
<td>13D.02, 9K.07, 11E.05, 3G.02</td>
</tr>
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<td>Shin, Y.</td>
<td>13D.05</td>
</tr>
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<td>Shrivastava, M.</td>
<td>6D.02, 6D.02</td>
</tr>
<tr>
<td>Si, X.</td>
<td>9J.01</td>
</tr>
</tbody>
</table>

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Siddique, N., 1A.01
Sie, C., 9A.09, 9C.07
Siegel, J., 10C.05
Sigmund, W., 3C.01
Sihto, S., 10E.04
Sillanpää, M., 8B.02
Silva, P., 6A.05, 12E.02, 3B.06
Simonenkov, D., 31.01
Singer, B., 3E.08
Singh, A., 2D.03
Sioutas, C., 8A.05, 9A.01, 9A.06, 9D.03, 9A.07, 2B.02, 10A.03, 3G.03, 9G.02, 8B.02, 11C.04, 12A.01, 13D.03, 9A.26, 10A.05
Sipila, M., 10E.04
Skarnovich, M., 5E.20
Skrehot, P., 5C.02
Slaven, J., 9G.05
Slowik, J., 3I.06, 5E.01
Smetannikova, M., 5E.20
Smith, G., 7E.04, 12E.05
Smith, K., 9C.01, 9C.03
Smith, M., 9E.04
Snyder, D., 9D.06, 8B.03, 7B.04, 13A.05
Sokolik, I., 5K.07
Son, S., 4E.03, 11D.06
Song, C., 14D.01, 9E.20, 9E.18, 9E.18
Song, D., 3G.01, 3G.02
Song, Q., 3D.05, 6D.01, 6D.01
Sorensen, C., 9K.04
Sorooshian, A., 10B.04, 14B.05
Sosa, G., 2A.04
Souza, J., 14A.02, 9A.27
Spackman, R., 10B.05
Spaulding, A., 1B.05, 5B.03
Spears, M., 11D.04
Spielvogel, J., 9L.10
Springston, S., 2A.02
Sreenath, A., 10D.01
Srirama, P., 6C.05
Srivastav, R., 2D.03
Stahlmecke, B., 11E.02, 9K.03
Stanier, C., 13B.03, 3H.04
Stankova, Z., 8A.04
Stanley, N., 5C.12
Steiger, M., 5D.07
Stevens, N., 9A.14
Stevens, T., 9A.18
Stone, E., 1A.04, 7B.04, 2A.04
Storey-Bishoff, J., 6C.01
Storey, J., 9G.13, 4D.03, 5D.13
Stratmann, F., 9B.07, 5D.12
Straus, D., 7C.03
Strawbridge, K., 8B.04
Stroud, C., 4A.01, 9E.19, 8B.04, 8B.04
Su, G., 5F.02
Su, W., 6C.04
Subramanian, R., 1A.05, 12B.06
Sueper, D., 8E.01, 7B.04, 2A.04, 3A.01
Suh, H., 5G.10
Sullivan, A., 3I.02, 2B.01, 3L.04
Sullivan, R., 14E.04
Sun, L., 9E.11
Sun, Y., 7D.05, 13E.02, 3A.01
Sun, Z., 12A.04
Sunling, G., 8B.04
Suriyawong, A., 4D.01
Surratt, J., 5D.14
Swain, K., 10C.02
Swanson, J., 3E.01, 3E.02
Switzer, T., 3B.03, 3B.05
Swihart, M., 3D.12
| Syla, A., 5C.06, 5C.06, 3H.01, 5C.03, 5C.03 | Tinnerberg, H., 10C.03 |
| Szidat, S., 2A.04 | Titcombe, M., 10D.02 |
| Tabor, D., 3E.05 | Tjoa, T., 11C.04 |
| Tacina, K., 14A.02, 9A.27 | Tobias, D., 7A.06 |
| Tagaris, E., 5K.01, 3J.02 | Tolmachev, G., 3I.01 |
| Tagliavini, E., 14B.01 | Toohey, D., 11C.01 |
| Tahiryslaj, S., 9E.08, 9E.08 | Toom-Sauntry, D., 8B.04 |
| Takahama, S., 9E.10, 14E.03 | Toro, C., 9C.08 |
| Takahata, K., 9G.07 | Tovstoy, V., 1E.05 |
| Takami, A., 5B.10 | Trimborn, A., 7D.02, 2A.04, 3A.01 |
| Takeuchi, Y., 1E.03 | Tritscher, T., 9B.07, 5D.07 |
| Tan, Y., 13E.03, 5E.19 | Trombley, J., 5I.04 |
| Taneja, A., 9C.10 | Trunov, M., 3C.05 |
| Tang, W., 2E.02 | Tsai, C., 11D.01, 9K.02 |
| Tanner, D., 10B.05 | Tsai, D., 7A.04 |
| Tanner, R., 6B.01 | Tsai, S., 5C.10, 3D.08 |
| Tarlov, M., 7A.04 | Tseng, C., 9C.04 |
| Teffera, S., 3B.02 | Tsimpidi, A., 4A.03, 14E.02 |
| Teinila, K., 14B.01 | Tu, W., 3E.10, 3E.10 |
| Tepper, F., 1E.01 | Tuchman, A., 8C.04 |
| Tewksbury, E., 6C.03 | Tumolva, L., 9B.06 |
| Theiss, T., 4D.03 | Turco, R., 10E.02 |
| Theodore, A., 1C.05 | Turner, J., 9D.05, 9D.06, 3B.03, 11B.05, 3B.05, 3J.03 |
| Thewlis, R., 7C.02 | Turpin, B., 13E.03, 5E.19 |
| Thiansathit, W., 1A.05 | Twohy, C., 12B.03, 12B.05, 12B.06 |
| Thimmaiah, D., 9J.04, 9G.01, 9D.01 | Ulbrich, I., 4A.03, 2A.03, 7B.04, 7B.05, 2A.04, 3A.01 |
| Thimsen, E., 3D.03, 2D.02 | Underwood, J., 7A.06 |
| Thoma, E., 8A.01 | Upadhyay, N., 5G.07 |
| Thomas, J., 14E.05, 4D.03 | Utell, M., 3H.03 |
| Thomas, R., 12A.03 | VanDyke, M., 5I.08 |
| Thornburg, J., 3C.03 | VanOsdell, D., 3C.03 |
| Thornhill, K., 14A.02, 9A.27 | Vedal, S., 11B.02 |
| Tian, J., 7B.05 | Vedantham, R., 11B.05 |
| Tian, L., 5F.04 | Veilleraud, C., 9D.10 |
| Timko, M., 14A.02, 9A.27 |

Veith, S., 10C.02
Verburg, P., 6D.04
Verma, V., 9A.01, 2B.02
vogt, m., 9A.10
Vogt, R., 5E.15
Volckens, J., 5I.08
Volkwein, J., 5G.09
Vorontsov, A., 5E.20
Voss, P., 2A.02
Vrbova, J., 8A.04
Vuillermoz, E., 5B.09
Vuong, T., 1A.01
Wade, K., 11B.03
Wagener, S., 9K.03
Wagner, A., 12C.05, 7E.06
Wagner, J., 8C.03
Wagner, M., 3G.13
Wagstrom, K., 6B.04
Waheed, S., 1A.01
Wall, S., 8C.03
Wallace, L., 12C.03
Wander, J., 8C.04, 1C.05
Wang, B., 5E.04
Wang, F., 12C.03
Wang, J., 3D.05, 11E.02, 1E.04, 1E.02, 10D.05, 2A.04, 9K.07, 11E.05
Wang, L., 6E.02
Wang, T., 12B.01
Wang, W., 12B.01
Wang, X., 12B.01, 10D.01, 11A.02
Wang, Y., 11A.01, 9A.09, 9C.07, 8B.05
Wang, Z., 8C.03
Wanmin, G., 8B.04
Waring, M., 10C.05
Warren, B., 6A.05, 9E.20, 7E.02
Watson, J., 6D.04
Weaver, C., 9A.15
Weber, R., 5G.06, 7D.01, 7B.04
Wehrle, G., 5D.07
Wehrli, M., 2A.04
Wei, Z., 3F.08
Wei, Z., 3F.08
Weimer, S., 8A.03
Weingartner, E., 9B.07, 5D.07
Weinheimer, A., 2A.03, 2A.02
Weinstock, L., 5H.01
Weitkamp, E., 8D.01
Welch, J., 3C.01
Welch, W., 9A.13, 4E.02, 3B.02
Wen, X., 4B.03
Wendt, J., 3E.05
Wennberg, P., 5D.14, 2A.03
Weschler, C., 9C.09, 12C.04
West, B., 4D.03
West, M., 6E.05, 5E.02
West, R., 3B.05
Westerberg, B., 5C.15
Wetzel, L., 10C.04, 4E.04
Wetzel, M., 10C.02
Wex, H., 5D.12
Wexler, A., 4B.02, 12E.03, 6C.05
Wey, C., 14A.02, 9A.27
white, w., 6B.03
Whitefield, P., 14A.01
Wiedinmyer, C., 2A.04
Wiens, B., 4A.01, 8B.04
Williams, B., 7B.04, 14B.03, 5G.05
Williams, D., 11B.02
Williams, L., 7D.02, 8D.04, 8D.04
willis, r., 3B.03, 3B.05
Wimolwattanapun, W., 1A.01

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Winer, A., 11A.05, 11A.06
Winijkul, E., 1A.05
Winstead, E., 14A.02, 9A.27
Wold, C., 5D.09
Wolfson, J., 12D.04
Wolfson, M., 5G.10
Wollny, A., 14D.04
Won, J., 3G.01
Wong, B., 3F.07, 6C.03, 3F.04
Woo, C., 2D.04
Woo, D., 9L.04
Woo, J., 5K.01, 3J.02
Woo, M., 3C.01
Woodside, R., 12A.06, 9A.05
Worley, C., 8B.03
Worsnop, D., 14B.01, 8E.01, 7D.02, 2A.02, 7B.05, 2A.04, 3A.01, 8D.04, 7D.06
Worton, D., 3I.05, 8D.01, 14B.03, 5G.05
Wright, M., 9L.09
Wu, C., 11D.01, 8C.04, 1C.05, 3C.01, 8D.03, 1E.01
Wu, J., 11D.02
Wu, Y., 7A.02, 3E.10
Wyslouzil, B., 7A.02
Xi, J., 9J.01
Xia, A., 9E.19
Xu, B., 9A.02, 9A.03
Xu, L., 14B.04
Xu, Y., 12C.01, 9C.06, 10C.04, 4E.04
Yadama, G., 9C.11
Yamamoto, H., 3D.10
Yang, J., 14D.01
Yang, L., 13A.03, 9E.16
yang, x., 7A.03
Yao, M., 1C.03, 3C.02, 3C.09, 5I.03
Yao, Q., 3D.05, 6D.01

yao, x., 9J.12, 9E.07
Yeung, M., 14E.01
Yi, O., 5C.04
Yi, S., 5C.04, 5B.08
Yim, H., 1D.04, 1D.04
Yin, L., 5I.03
Ying, Q., 13B.01, 13B.05, 12A.05
Yli-Juuti, T., 10E.04
Yokoyama, N., 9J.14
Yoon, J., 9G.10, 3G.12
You, S., 2D.04
Young, L., 6E.03, 9A.09, 9C.07
Yu, F., 9J.10, 14A.03, 5K.05, 10E.02, 9E.05, 6E.01
Yu, J., 3D.04
Yu, L., 13A.03, 9E.16, 3F.03
Yu, Y., 12E.04
Yu, Z., 14A.02, 9A.27
Yue, Y., 6D.01
Yun, J., 13D.05
Zachariah, M., 14D.05, 9E.02, 5K.02, 7A.04, 11E.04, 14D.03, 1D.05
Zamankhan, P., 9H.01
Zauscher, M., 8B.05
Zavala, M., 4A.03, 14E.02
Zaveri, R., 6B.02, 6E.05, 14D.01, 5E.02, 9E.18, 2A.02
Zelenyuk, A., 14D.01, 14D.01, 9E.18
Zeng, T., 3I.03
Zhang, H., 1C.03, 5I.03
Zhang, K., 9A.24, 9A.25
Zhang, M., 11A.02
Zhang, Q., 9A.04, 6B.05, 3H.02, 3C.01, 7B.05, 7D.05, 13E.02, 3A.01
Zhang, R., 6E.02, 2A.04
Zhang, X., 3D.01, 9C.13
Zhang, Y., 9C.05, 4B.03, 12A.05
Zhang, Z., 5F.01
Zhao, G., 9H.01
Zhao, J., 10D.02
Zhao, Y., 14B.03
Zhao, Z., 13B.05
Zhen, S., 1C.03, 5I.03
Zheng, J., 2A.04
Zheng, M., 14B.04
Zheng, W., 2A.02
Zhou, L., 9E.02
Zhou, M., 5I.03
Zhou, Y., 11D.02, 7C.04
Zhu, Y., 11A.01, 9A.02, 9A.03, 9A.04
Zhuang, Y., 4D.01
Zielinska, B., 14A.05, 9A.15
Ziemann, P., 6E.04, 5D.10, 3A.01, 7D.06
Ziemba, L., 5B.11