Plenary.1: AEESP Lecture

Lessons from the Workplace: Hazards from Exposure to Engineered Nanomaterials. THOMAS PETERS, *U of Iowa*

Unique exposures may result when raw nanomaterials are produced or handled and when objects that contain nanomaterials are manipulated in the production of commercial products. Exposures in the workplace are often many times higher than those that occur via environmental release or that may be experienced by consumers of products that contain nanomaterials. Professionals trained in the field of industrial hygiene hold the responsibility to assess and mitigate exposures to nanomaterials in the workplace. This job is challenging due to limited health-based occupational exposure limits, exposure equipment that has been designed for more traditional exposures, and control methods that are generally untested for their effectiveness to control nanoparticle exposures. An overview will first be presented to summarize the state-of-the-art in the primary activities central to the practice of industrial hygiene (anticipation, recognition, evaluation, and control) in the context of workplaces where nanomaterials are present. Special emphasis will be placed on the advantages and disadvantages of various state-of-the-art methods used to assess exposures to engineered nanomaterials will be presented. A series of case studies will be used to illustrate how these methods can be applied in occupational settings to assess worker exposures. Lastly, a discussion will be presented to help translate the lessons learned from the workplace to more broadly address hazards from engineered nanomaterials in any environment.

Plenary.2: Friedlander Lecture

Solarthermal Chemical Processing Using Particle Flow Reactors – Challenges and Opportunities. ALAN WEIMER, *University of Colorado*

Lewis and Nocera (Proceedings of the National Academy of Sciences of the United States of America. 2006;103(43):15729-35) make a compelling case for solar energy powering the planet. While the world energy consumption rate is projected to double from 13.5 TW in 2001 to 27 TW by 2050 and to triple to 43 TW by 2100, more sunlight strikes the earth in 1 hr (4.3 x 10^20 J) than all of the energy currently consumed on the planet in 1 yr (4.1 x 10^20 J in 2001). Hence, “the sun has a unique role in sustainable energy production, in that it is the undisputed champion of energy; the resource base presented by terrestrial insolation far exceeds that of all other renewable energy sources combined”.

Concentrated solar energy can be used to reach high temperatures and drive strongly endothermic chemical reactions such as direct water splitting, metal oxide reduction for water splitting cycles, metal oxide carbothermal reduction, and pyrolysis or gasification of cellulosic biomass or other carbonaceous material. The efficiencies for such processes are typically higher than those of competing solar technologies because the energy from the sun is used to directly drive chemical reactions instead of first being converted to another energy form, e.g. electricity.

Fine particle flow transport reactors are often used for chemical processing at temperatures above 1200oC where radiation heat transfer to the fine solids flowing through the reaction tube drives rapid reaction and the heating of gases that are transparent to radiation. This presentation will review several solarthermal processes in which fine powders are transported and will identify challenge areas of interest for researchers in the field of aerosol science and engineering.

Plenary.3

Studying Aerosol Processes, One Particle at a Time.

JONATHAN P. REID, *University of Bristol*

Aerosol particles are dynamic, changing in size, composition and temperature as chemical and physical transformations occur. To fully characterise and understand the dynamical processes occurring, measurements must be able to access a wide range of lengthscales and timescales, spanning from the nanometre to the millimetre, and from nanoseconds to days. Although we must always remember that aerosols display collective ensemble behaviour, studying the mechanistic details of processes at the single particle level can provide important insights into the processes that influence the dynamics of the whole population. Over the decades, both electrodynamic and optical levitation techniques have demonstrated their value in isolating individual particles for study. When coupled with non-intrusive spectroscopic probes, temporal changes in size, composition and morphology can be followed. Indeed, in recent years we have shown that it is possible to manipulate multiple particles simultaneously using aerosol optical tweezers and to compare their properties directly in situ, bridging the gap between single particle and ensemble studies. In this talk, we will explore the advantages of studying aerosol processes, one particle at a time. More specifically, examples will be given of how processes, such as the evaporation and condensation of water from aerosol particles, can be resolved at the nanometre lengthscale, providing insights into the surface and bulk limited mechanisms and kinetics of hygroscopic growth. The timescales that must be accessed for such measurements span the range from millisecond to days, and are applicable to the inhalation of drugs to the respiratory tract through to the condensation kinetics of water on secondary organic aerosol. The dynamics occurring during the coalescence of aerosol particles will also be explored, with concomitant measurements of particle viscosity spanning almost 12 orders of magnitude. We will also see how the details of chemical aging of organic aerosol can be explored at the single particle level over timescales of days. Finally, the use of optical tools for manipulating aerosol particles to initiate controlled chemical transformations and to probe optical extinction will be introduced.

Plenary.4

Secondary Organic Aerosols: Are Laboratory Chambers Mimicking the Atmosphere?

LYNN RUSSELL, *Scripps Institution of Oceanography*

Carbonaceous components contribute about half of the submicron atmospheric aerosol, but our knowledge of their composition and sources has lagged behind that of the inorganic components because of the diversity of organic compounds and the complexity of their mixtures. These particles include directly emitted “primary” particles and “secondary” particles from the photochemical oxidation of volatile organic compounds. The last decade has provided new measurement techniques that have allowed the identification and chemical characterization of both primary carbonaceous particle types and three categories of secondary organic aerosol (SOA) sources – fossil fuel combustion, biofuel and biomass burning, and marine and terrestrial biogenic vapor fluxes. Laboratory-based chamber studies have clearly demonstrated important differences in the SOA from these three types of precursors. Now, by comparing the chemical signatures of SOA composition formed from fossil fuel, biomass burning, and biogenic precursors to the components of atmospheric particles identified in multiple field campaigns as secondary, we provide evidence of the potential contributions of particles similar to those produced in SOA chambers to ambient compositions during those campaigns.

1AC.1

Adsorption-Based Chemical Thermodynamics of Atmospheric Aerosols: Towards Reduced Parameterization, Temperature Dependence, and Organic Solvents. CARI DUTCHER, Caitlin Asato, Anthony Wexler, Simon Clegg, *University of California, Davis*

The calculation of gas/liquid/solid equilibrium by soluble aerosols, and their water uptake as functions of temperature and relative humidity, is central to atmospheric chemistry (e.g., new particle formation, the behavior of cloud condensation nuclei, cloud formation, visibility, air quality, and climate). Using statistical mechanics and multilayer adsorption isotherms, we recently developed a transformative method for capturing thermodynamic properties of multicomponent aerosols over the entire concentration range (i.e., 0 to 100% relative humidities).[1] Now, we explore improvements of the model to include reduced parameterization, temperature dependence, and organic phases. Starting with the apparent radial dependence in the multilayer adsorption of solvent molecules on a solute, in this work, the values of the energies of adsorption are related to known analytic short-range dipole-dipole and ion-dipole Coulombic electrostatic relationships. In the case of non-electrolytes or organic molecules, the physical properties necessary to calculate the energies of adsorption are the dipole moments of the solvent and the solute and the intermolecular solute-solvent and solvent-solvent bond lengths. For ionic solutions, the ionic charge types, ionic-solvent bond lengths and solvent-solvent bond lengths are the necessary parameters to calculate the energy of adsorption parameter. The majority of these physical properties, with the exception of the solute-solvent intermolecular bond lengths, are available in the literature, resulting is significant reduction of adjustable parameters as well as activity coefficient predictions for solutes and mixtures for which there are no activity data. Further implications for systems of mixed charge types and mixed-solvents as well as parameter temperature dependence are explored. Finally, a practical discussion of the thermodynamic model for key atmospheric systems, such as sulfuric acid containing aqueous solutions, to extreme low water activity and temperatures will be given.

[1] Dutcher et al. J. Phys. Chem. (2011, 2012, 2013).

1AC.2

Functional Group Distributions in Photolytically Generated Organic Aerosol. Alicia Kalafut-Pettibone, Joseph Klems, W. SEAN MCGIVERN, *National Institute of Standards and Technology*

Secondary organic aerosol (SOA) particles consist of complex mixtures of oxygenated organic compounds for which the identification and quantification of individual chemical species is intractable. However, knowledge of the nature of the oxygenated functional groups can provide valuable insight into the sources, oxidative aging, and cloud condensation nucleus propensity of collected particles. Toward this end, we have applied a recently developed high-performance liquid chromatography/ultraviolet-visible spectroscopy (HPLC/UV-VIS) methodology for determining functional group distributions through chemical derivatization to synthetic organic aerosol samples. Previously, our group has characterized three derivatization reagents that are specific to hydroxyl (OH), non-acid carbonyl (C=O), and carboxylic acid (COOH) moieties and enhance both ultraviolet absorption response and electrospray (ESI) ionizability for mass spectrometry. The functional group specificity and linearity of the ultraviolet response of these derivatization substituents allows the relative concentrations of the individual moieties to be determined. The enhanced ionizability, due to the presence of moderately basic nitrogen in the derivatization reagents, allows organic aerosol samples to be effectively studied using mass spectrometry, despite the often poor ESI ionizability of typical SOA constituents. In the present work, this derivatization methodology has been applied to extracts of filter-collected samples of particles derived from the 254 nm photodissociation of 1-iodooctane. The resulting product spectrum is complex, showing several chromatographically resolved peaks and a broad unresolved mixture. Triple-quadrupole mass spectrometry has been used to identify these individual compounds and the concentrations of the OH, C=O, and COOH moieties in the complex mixture. The products are derived from a single 1-octyl radical isomer, and these results will be used to constrain a model of the particle formation mechanism focusing on conversion of the octyl peroxy radicals to octoxy radicals and subsequent decomposition, isomerization, and termination by reaction with oxygen.

1AC.3

Aerosol Phase Chemistry of Isoprene Derived Epoxides Evaluated Using Density Functional Theory. IVAN PILETIC, Edward Edney, Libero Bartolotti, *U.S. Environmental Protection Agency*

Epoxides have been detected as important intermediates during atmospheric isoprene oxidation. Their subsequent reactions in the particle phase lead to the production of low volatility compounds detected in ambient aerosols. In this work, we apply density functional theory to computationally assess the reactivity of isoprene derived epoxides in the condensed phase. The M062x density functional and 6-311++G** basis set are applied to reacting molecular clusters in a dielectric continuum model to simulate the aerosol condensed phase. The relative barriers and energies of epoxide reactions such as hydrolysis, organosulfate formation, organonitrate formation and oligomerization are determined. In particular, the relative rates of 2-methyl-2,3-epoxybutane-1,4-diol (isoprene epoxide – IEPOX) and 2-methyl-2,3-epoxypropanoic acid (methacrylic acid epoxide - MAE) are discussed. Both epoxides are important in organic aerosol formation under low and high NOx conditions respectively.

1AC.4

New, Experimentally Based, Secondary Organic Aerosol Paradigm Removes Discrepancies between Models and Data.ALLA ZELENYUK, Dan Imre, ManishKumar Shrivastava, Evan Abramson, Lawrence Kleinman, Jerome Fast, Stephen Springston,*Pacific Northwest National Laboratory*

Significant fraction of atmospheric aerosols, which affect climate and health, are comprised of secondary organic aerosols (SOA). A number of resent studies that utilized independent methods for SOA characterization have shown SOA particles to be highly viscous semi solids and nearly non-volatile, rather than, as the models assume, equilibrated rapidly mixing and evaporating solutions. However, doubts as to whether these laboratory results are pertinent to atmospheric conditions remain. Here we present analysis of the detailed spatial distributions of organic aerosol (OA) loadings observed during the Mexico City 2006 MILARGO field campaign. We compare OA loadings measured repeatedly at the same locations and find that the patterns of OA spatial distributions are in close agreement with predictions by our newly constructed model, which treats SOA as non-volatile semisolids, and preclude presumptions of gas-particle equilibrium that form the basis of commonly accepted models. Field data provide direct evidence that the time scale, on which particles must respond by evaporation to maintain equilibrium, is orders of magnitude faster than measured evaporation rates. Moreover, the experimental data and model simulations indicate that in this new paradigm, loadings significantly increase due to well understood mechanism, reducing persistent discrepancies between measured organic aerosol loadings and model predictions, bringing them to within levels consistent with uncertainties in measurements and emissions. SOA loadings predicted by our newly developed comprehensive 3-D model that treats SOA as non-volatile semi-solid and includes fragmentation and multi-generation chemistry are in good agreement with measurements over the entire 3-D experimental domain over the Mexico City Plateau.

1AC.5

Implications of Low Volatility SOA and Gas-Phase Fragmentation Reactions on SOA Loadings and their Spatial and Temporal Evolution in the Atmosphere.

MANISHKUMAR SHRIVASTAVA, Alla Zelenyuk, Dan Imre, Richard Easter, Josef Beranek, Rahul Zaveri, Jerome Fast, *Pacific Northwest National Laboratory*

We investigate issues related to volatility and multigenerational gas-phase aging parameterizations affecting the formation and evolution of secondary organic aerosol (SOA) in models. We show that when assuming realistic values for the mass accommodation coefficient, experimentally observed SOA evaporation rates imply significantly lower “effective volatility” than those derived from SOA growth in smog chambers, pointing to the role of condensed phase processes and suggesting that models need to use different parameters to describe the formation and evolution of SOA. We develop a new, experimentally driven paradigm to represent SOA as a non-absorbing semi-solid with very low “effective volatility”. We modify both a box model and a 3D chemical transport model, to include simplified parameterizations capturing the first order effects of gas-phase fragmentation reactions, and investigate the implications of treating SOA as a non-volatile, non-absorbing semi-solid (NVSOA). Box model simulations predict SOA loadings decrease with increasing fragmentation, and similar SOA loadings are calculated in the traditional, semi-volatile (SVSOA) approach and with the new paradigm (NVSOA) before evaporation reduces loadings of SVSOA. Box-model-calculated O:C ratios increase with aging in both the SVSOA and the NVSOA paradigms. Consistent with box model results, 3D model simulations demonstrate that predicted SOA loadings decrease with the addition of fragmentation reactions. The NVSOA paradigm predicts higher SOA loadings compared to the SVSOA paradigm over nearly the entire 3D modeling domain, with larger differences close to the surface and in regions where higher dilution favors SVSOA evaporation.

1AC.6

Constraining the Range of Product Chemical Formulas, Volatilities, and Reaction Mechanisms of SOA-forming Reactions.

JESSE KROLL, Kelly Daumit, James Hunter, Sean Kessler, *MIT*

The formation and evolution of secondary organic aerosol (SOA) is characterized by reactions that can change both the carbon oxidation state (OS_C) of and the number of carbon atoms (n_C) in a molecule, resulting in dramatic changes to the volatility and other key properties of the molecule. However such changes can be hard to predict due to the very large number of chemical transformations and reaction products that are possible. Here the full range of possible products from a given SOA precursor are described, using a simple three-dimensional chemical space (defined by O/C, H/C and n_C), combined with fundamental rules governing atmospheric oxidation. This range of products is pathway-independent, and thus holds for any possible formation mechanism: gas-phase oxidation, particle-phase chemistry, oxidation in liquid water, etc. One benefit of this chemical space, which is closely related to other recently-proposed (and mostly two-dimensional) spaces, is that few assumptions about the distribution of functional groups are necessary in order to determine the volatility (c*) of a given organic species. Thus the predominant phase of the species is determined directly from its location in this three-dimensional space. We use this approach to constrain the underlying mechanisms of a number of different oxidation systems recently studied in our laboratory, including the gas-phase oxidation of volatile precursors, the heterogeneous oxidation of low-volatility species, and the oxidation of water-soluble species within liquid-water aerosol particles.

1AC.7

Volatility-Resolved Measurements of the Amount and Oxidation State of Gas-Phase and Particulate Organic Compounds in a Forested Environment. JAMES HUNTER, Eben Cross, Anthony Carrasquillo, Patrick Hayes, Pedro Campuzano-Jost, Douglas Day, Brett Palm, LaxmiNarasimha Yatavelli, Harald Stark, Samantha Thompson, Jose-Luis Jimenez, Scott Herndon, Douglas Worsnop, Jesse Kroll, *MIT*

The volatility and degree of oxidation of organic aerosol can significantly alter its impacts on air quality, climate and human health. Much remains to be understood about these key properties and how they evolve over the full life cycle of aerosol particles, including initial formation through emission or oxidation processes. Here we describe measurements of organic volatility and oxidation state in a ponderosa pine forest in the Colorado Rocky Mountains during the BEACHON-RoMBAS campaign. Measurements of intermediate and semivolatile organic compounds (IVOCs and SVOCs) using a cryogenic preconcentration-electron impact mass spectrometry (CP-EI) technique are combined with organic acid measurements from the MOVi-CIMS and aerosol volatility measurements from a thermo-denuder HR-AMS system to yield organic composition over 19 orders of magnitude in volatility (from $\log C^* = -9$ to $+8$). In addition to organic aerosol, this volatility range includes gas-phase biogenic emissions that act as aerosol precursors (i.e. mono and sesquiterpenes) as well as a complex mixture of gas-phase oxidation products. This data is mapped into a 2D volatility basis set, enabling the entire relevant range of volatility and oxidation state to be viewed simultaneously. This approach allows possible pathways to be proposed and visualized for carbon originating in the gas phase to lead to the observed distribution of condensed and gas-phase oxidation products. Further constraints are placed on these complex, dynamic processes by tracking changes in the VBS distribution at different times of day, and by comparison with key laboratory oxidation experiments.

1AP.1

Ethanol/Water Binary Nucleation Rates in Supersonic Laval Nozzles: Analyses via the First and Second Nucleation Theorems. Shinobu Tanimunra, Alexandra Manka, Harshad Pathak, Ashutosh Bhabhe, Kelley Mullick, BARBARA WYSLOUZIL, *The Ohio State University*

Pressure trace measurements and small angle X-ray scattering measurements were combined to measure the vapor-liquid nucleation rates of EtOH/H_2O mixtures. By using two supersonic Laval nozzles with different expansion rates, nucleation rates were varied under isothermal conditions. Thus, the sizes, compositions, and excess energies of the critical clusters could be determined. These results in turn yield a relationship between the surface energy and the composition of the critical clusters.

1AP.2

Size-Dependent Condensation of Organics – Parameterization for Nanoparticle Growth.

SILJA HÄKKINEN, Hanna Manninen, Taina Yli-Juuti, Joonas Merikanto, Maija Kajos, Tuomo Nieminen, Stephen D'Andrea, Ari Asmi, Jeffrey Pierce, Markku Kulmala, Ilona Riipinen, *University of Helsinki*

One of the biggest challenges in current large-scale atmospheric models is to accurately present nanoparticle growth by biogenic and anthropogenic secondary organics. Accurate estimation of atmospheric nanoparticle growth is important in order to improve the prediction of the concentrations of cloud condensation nuclei (CCN). In our work we introduce a semi-empirical parameterization of size-dependent sub-20 nm particle growth that distributes atmospheric organics to nanoparticles according to their size. The parameterization includes particle condensational growth by sulfuric acid, secondary organics from monoterpene oxidation ($SORG_{MT}$) and an additional condensable non-monoterpene organics (“background”). Nanoparticle growth in three size classes, 1.5 to 3 nm, 3 to 7 nm and 7 to 20 nm, was investigated. The performance of the parameterization as well as the experimental parameters (weighting factors for distributing the $SORG_{MT}$ and the concentration of the background species) for the parameterization were determined using extensive field data obtained from six temperate continental European sites. In our analysis there were altogether 7 years of data from Hyytiälä (Finland) and around one year of data from other measurement stations. The parameterization was able to reproduce the observed nanoparticle growth rates and to capture the seasonal pattern observed in the ambient nanoparticle growth. The contribution of $SORG_{MT}$ to nanoparticle growth was strongly dependent on particle size – weighting factors for distributing $SORG_{MT}$ were 0 for the smallest particles (1.5 to 3 nm) and approaching 1 for the 7 to 20 nm particles. The contribution of the background species was also important, especially for the very smallest particles, its concentration being similar to that of the $SORG_{MT}$ and sulfuric acid. The “background” is suggested to be formed in the oxidation process of biogenic organics in the presence of anthropogenic pollution.

1AP.3

Adsorption of Organic Molecules may Explain Enhanced Growth of Nucleated Clusters and New Particle Formation.

JIAN WANG, Anthony Wexler, *Brookhaven National Laboratory*

New particle formation (NPF) in the atmosphere influences the concentrations of atmospheric aerosols, and therefore their impact on climate. New particle formation is a two-stage process consisting of homogeneous nucleation of thermodynamically stable clusters followed by growth of these clusters to a detectable size (> 3 nm). Due to the large coagulation rate of clusters smaller than 3 nm with the pre-existing aerosol population, these clusters must grow quickly in order to survive and form new particles. Previous modeling and field studies indicated that condensation of low-volatility organic vapor may play an important role in the initial growth of the clusters. However, due to the small size of the clusters and the relatively high vapor pressure and partial molar volume of even highly oxidized organic compounds, the strong Kelvin effect may prevent typical ambient organics from condensing on these clusters. Earlier studies did not consider that adsorption of organic molecules on the cluster surface, due to the intermolecular forces between the organic molecule and cluster, may occur and substantially alter the growth process under sub-saturated conditions. Using the Brunauer-Emmett-Teller (BET) isotherm, we show that the adsorption of organic molecules onto the surface of clusters may significantly reduce the saturation ratio required for condensation of organics to occur, and therefore may provide a physico-chemical explanation for the enhanced initial growth by condensation of organics despite the strong Kelvin effect. The effect of adsorption on initial cluster growth rate and new particle formation will be discussed.

1AP.4

Evaporation and Growth of Multiphase Droplets. ASIT RAY, Haohua Tu, *University of Kentucky*

The evaporation and growth of multiphase droplets is of interest in many natural and industrial processes. We present theoretical analysis and experimental data on growth and evaporation of layered droplets of partially miscible components as well as droplets containing dispersed salt particles. Experiments were conducted on single layered droplets suspended in an electrodynamic balance under controlled atmospheres. A suspended droplet was illuminated by a laser beam, and light scattering intensity from the droplet was monitored in the planes parallel and perpendicular to the incident light polarization plane. The size of a droplet (i.e., the core and outer radii for a layered droplet) as a function of time was determined using a resonance based light scattering technique. In addition, the mass of the particle was determined from the d.c. voltage required to maintain the particle at the centre of the balance. The experimental results obtained from layered droplets of various partially miscible systems show that for some systems the core evaporation rate increases, while for other systems the rate exhibits a maximum with increasing layer thickness. The theoretical analysis suggests that the evaporation rate of a core droplet covered with an immiscible layer to increase, decrease or exhibit a maximum with increasing layer thickness. The decrease in the evaporation rate can only be observed for core droplets of volatile compounds, a requirement not satisfied by the binary systems involved in the study. The results from droplets hydrophobic compounds containing dispersed water soluble particles show that salt particles gradually absorb water as the relative humidity in the surrounding atmosphere increases, and the growth rate rapidly increases as the relative humidity approaches the deliquescence relative humidity of the salt involved. During the period of lowering of humidity, water evaporates rapidly and then slowly, while salt remains in the solution phase at a humidity level below the recrystallization point.

1AP.5

Measuring the Atmospheric Organic Aerosol Volatility Distribution: A Theoretical Analysis. ELENI KARNEZI, Ilona Riipinen, Spyros Pandis, *Carnegie Mellon University*

Organic compounds represent a significant fraction of the atmospheric aerosol mass. Even if most of these compounds are semi-volatile in atmospheric concentrations, the ambient organic aerosol volatility is quite uncertain. Understanding the partitioning between gas and aerosol phases has been recognized as one of the major challenges in our effort to quantify the rates of formation and atmospheric fate of organic particulate matter. The most common volatility measurement method relies on a thermodenuder (TD). The aerosol passes through a heated tube where its more volatile components evaporate leaving the less volatile behind in the particulate phase. The typical result of a thermodenuder measurement is the mass fraction remaining (MFR), which depends among other factors on the organic aerosol (OA) vaporization enthalpy and the accommodation coefficient. We use a new method combining forward modeling, introduction of ‘experimental’ error and inverse modeling with error minimization for the interpretation of existing TD measurements. We try to estimate simultaneously the OA volatility distribution, its effective vaporization enthalpy and the mass accommodation coefficient; we calculate the uncertainty range of each property and show that existing TD-based approaches cannot estimate reliably the OA volatility distribution. We propose an improved method, using both TD and isothermal dilution measurements. We evaluate this experimental approach using the same model and show that it is suitable for studies of OA volatility in the lab and the field.

1AP.6

The Evaporation Loss of Fine Particles in the Multi-Filter PM10-PM2.5 Sampler (MFPPS).

CHUN-NAN LIU, Shi-Fan Lin, Chuen-Jinn Tsai, *Naitional Chiao Tung University*

Field studies were conducted at NCTU campus to determine the evaporation loss of fine particles (PM2.5) collected by the multi-filter PM10-PM2.5 sampler (MFPPS). A porous metal denuder (PMD) was installed in one of the channels of the MFPPS and used as a reference sampler for determining the evaporation loss. The MFPPS was collocated with a dichotomous sampler (Dichot, Andersen, Model SA-241), a WINS PM2.5 sampler (Thermo, Model 2000-FRM), and a tapered element oscillating microbalance with filter dynamic measurement system (TEOM-FDMS, Thermo, Model 1405-DF). Totally, twenty 24-h samples were obtained. Results show that during the sampling process, the evaporation in PM2.5 is severe, which ranges from 6.2 to 56.7 % in PM2.5 concentration and the percentage decreases with an increasing PM2.5 concentration. The evaporated concentration of NH4+, NO3- and Cl- accounts for 13.2 ± 10.7, 5.2 ± 4.9 and 2.2 ± 2.0 % in PM2.5 concentration, respectively, or 49.6 ± 19.5, 61.7 ± 23.6 and 79.5 ± 9.4 %, in the concentration of each species, respectively. After 24-h conditioning, PM2.5 concentration was decreased by 3.1 ± 3.6 %, which was calculated from the differences in inorganic ion concentrations obtained immediately after sampling and those after 24-h conditioning. If the filter samples were conditioned for over 24 hours, PM2.5 concentration was further decreased by 2.1 ± 2.83, 3.6 ± 4.04, 5.5 ± 5.7, and 6.9 ± 5.56 % after 48, 72, 96, and 120-h conditioning, respectively, compared to that after only 24-h conditioning. Based the TEOM-FDMS data, it can be concluded that the sampling artifact concentration determined by the PMD is underestimated by 13.8 ± 10.3 %, due to the lack of the artifact concentration of the particulate organic carbon (POC). In the future, the POC artifact will be determined by installing the VOC denuder in one of the sampling channels of the MFPPS.

1AP.7

Summer-time Volatility Measurement of Ultrafine Particles in the Midwestern United States: Field Measurement from Bondville, IL and Iowa City, IA.

ASHISH SINGH, Robert Bullard, Charles Stanier, *University of Iowa*

Volatility measurement of ultrafine particles (10-100 nm) provides important information about particle formation pathways and thermodynamic properties, and can assist in constraining chemical composition. Bondville, IL and Iowa City, IA are two Midwestern U.S. sites where particle nucleation and extensive secondary sulfate and organic aerosol formation have been reported. Furthermore, the volatility of UFPs using V-TDMA has not been reported for many sites in the Midwest. Consequently, the relative contributions of organic and inorganic constituents to particle growth in the UFP size ranges, and the presence or absence of non-volatile particle cores in 10-100 nm particles, has not been determined. Summer volatility measurement in Iowa City showed 20% residual volume at 260 0C for the total particle population. In contrast, size resolved volatility at nuclei mode detected less than 2% residual volume. Preliminary data also shows diurnal patterns and little residence time sensitivity.

This study will present results for UFP volatility from preliminary measurements (Iowa City, 2012) and a 2013 sampling campaign (summer, Bondville, IL). Temporal variability of size resolved volatility; including diurnal, weekday-weekend, and month-to-month variability will be investigated. The mixing state of UFPs will be investigated using size resolved volatility at 80-260 0 C and its variability will be explained. The contribution of non-volatile core to volatility profiles will also be determined. VTDMA results will be interpreted with respect to pollutant trace gases and particulate times series (e.g. CO, SO_2 and NO_x, NH_3 and BC). The non-volatile core will be investigated to identify the possible anthropogenic sources.

In addition to field measurements, a computational model (size resolved, fully dynamic aerosol model with volatility basis set) will be used to explain observations and to infer possible chemical compositions of the aerosol, as well as fractions of volatile, semi-volatile to non-volatile species.

1BA.1

Interactions of Airborne Microbial Communities with Clouds: A Perpective from Metagenomic Analysis.

NATASHA DELEON-RODRIGUEZ, Terry Lathem, Bruce Anderson, Andreas Beyersdorf, Luke Ziemba, Michael Bergin, Athanasios Nenes, Kostantinos Kostantinidis, *Georgia Institute of Technology, Atlanta, GA*

Microbial cells are thought capable of influencing cloud formation and precipitation. Their small size and membrane composition allow them to have higher atmospheric residence time. Several species of bacteria are good ice nucleators, owing to the presence of an outer-membrane protein that serves as a nucleation center. The impact of bacterial cells on cloud formation however remains poorly characterized. Most studies to date were conducted on Earth surface (high mountains) and assessed only the small subunit ribosomal rRNA gene; microbial communities at higher altitudes remain essentially uncharacterized. To study the bacterial communities in the upper and lower troposphere, samples from high altitudes (over 10km) and two major tropical hurricanes were collected on board the DC3 aircraft during the NASA Genesis and Rapid Intensification Processes campaign and samples from low altitudes on board the P3B aircraft during the NASA Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality campaign. Metagenomic sequencing was performed for four samples, three high altitudes and one low altitude using Ilumina-GAII sequencing technology. Taxonomic analysis showed that Proteobacteria is the most abundant phylum in the atmosphere, but that Bacteroidetes and Actinobacteria are the second most abundant in the high and low altitude samples, respectively. To understand how bacterial cells may influence cloud formation, the inaZ gene was search in all metagenomes. We found the presence of this gene in the low altitude sample. This result was consistent with the present of Pseudomonas, which account for approximately 5% of the total community of this sample. Pseudomonas sp. are known to be one of the best ice nucleation in the atmosphere. Metagenomic analysis of bacterial communities in the atmosphere would provide quantitative insights in the distribution of proteins related to cloud formation and cloud chemistry.

1BA.2

Primary Biological Aerosols as Cloud Condensation Nuclei.

FRANCIS POPE, Paul Griffiths, Markus Kalberer, Michael Herzog,*University of Birmingham, UK.*

Primary biological aerosols (PBAs) represent a significant fraction of the total atmospheric aerosol mass burden. The low number density of PBA precludes a significant direct effect on the radiative budget of the Earth. However, the large particle size of PBA should allow them to have a significant indirect radiative effect on cloud processes if they are wettable. In particular, PBA may preferentially activate as cloud condensation nuclei (CCN) when compared to the smaller background aerosol. This effect will be most pronounced under pristine conditions where the background aerosol concentrations are small and of low hygroscopicity. Recent measurements of high PBA concentration within the Amazon (Huffman et al. 2012) suggest that this region may be particularly important for PBA-cloud interactions, and hence a potential feedback between the atmosphere and biosphere could be established (Pöschl et al. 2010).

This study investigates the ability of primary biological aerosol (PBA) to influence cloud formation and precipitation dynamics. In particular, pollen grains and fungal spores have been studied using a combined laboratory and modelling approach. The laboratory studies assessed the hygroscopicity, wettability and activation of the particles. The model output data suggests that under certain atmospheric conditions the activation of PBA can significantly interfere with the activation of the fine aerosol mode thus changing cloud dynamics. This work expands upon our previously published results on pollen activation (Pope 2010, Griffiths et al. 2012).

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1BA.3

Potential Impact of Microbial Activity on the Oxidant Capacity and the Organic Carbon Budget in Clouds. Mickaël Vaitilingom, Laurent Deguillaume, Virginie Vinatier, Martine Sancelme, Pierre Amato, Nadine Chaumerliac, ANNE-MARIE DELORT,*Clermont Université, Institut de Chimie de Clermont-Ferrand*

Within cloud water, microorganisms are metabolically active; so they are suspected to contribute to atmospheric chemistry. This paper is focused on the interactions between microorganisms and Reactive Oxygenated Species present in cloud water since these chemical compounds are driving the oxidant capacity of the cloud system. For this, real cloud waters with contrasting features (marine, continental, urban) were sampled at the puy de Dôme mountain (France). They exhibit high microbial biodiversity and complex chemical composition. These media were incubated in the dark and subjected to UV-light radiation in specifically designed photo-bio-reactors. The concentrations of hydrogen peroxide (H2O2), organic compounds and the ATP/ADP ratio were monitored during the incubation period. Microorganisms remained metabolically active in the presence of hydroxyl radicals (•OH) photo-produced from H2O2. This oxidant and major carbon compounds (formaldehyde and carboxylic acids) were biodegraded by the endogenous microflora. This work suggests that microorganisms could play a double role in atmospheric chemistry: first, they could directly metabolize organic carbon species; second they could reduce the available source of radicals due to their oxidative metabolism. Consequently, molecules such as H2O2 would be no longer available for photochemical or other chemical reactions, decreasing the cloud oxidant capacity.

Vaïtilingom M., Deguillaume L., Vinatier L., Sancelme M., Amato P., Chaumerliac N. and Delort A-M (2013). Potential impact of microbial activity on the oxidant capacity and the organic carbon budget in clouds. Proceedings of the National Academy of Sciences USA, 110 (2), 559-564.

1BA.4

Measurement and Observation of the Hygroscopic Growth Properties of Biological Aerosols. SHANNA RATNESAR-SHUMATE, Elizabeth Corson, Jonathan Eshbaugh, Sean Kinahan, Joshua Santarpia, *The Johns Hopkins Applied Physics Laboratory*

There are many mechanisms by which primary biological aerosols may undergo chemical or physical changes in the atmosphere. Fluctuations in RH may influence aerosolized biological organism viability, facilitate chemical reactions, lead to shifts in size, and affect aerosol transport. It is important to understand the hygroscopic nature of biological aerosols including spores, vegetative bacteria, viruses and proteins. The hygroscopic growth, as indicated by changes in the aerodynamic diameter, of several biological organisms and other materials often associated with biological aerosol particles was measured at The Johns Hopkins University Applied Physics Laboratory to determine the behavior of these particles during both humidification and drying. Changes to the size distribution of biological aerosols are measured by using three Aerodynamic Particle Sizer® (APS) spectrometers separated by two Nafion® tubes in series in which the RH is controlled. Using this method, the hygroscopic properties of sodium chloride, polystyrene latex beads, and sodium nitrate aerosols were compared against those reported in previous literature in order to characterize the ability of the new method to accurately predict the deliquescence and efflorescence of aerosol particles. Hygroscopic measurements ranging from 20% to 85% RH were taken of Bacillus thuringiensis Al Hakam, Bacillus thuringiensis kurstaki, Bacillus globigii, MS2 Phage, Pseudomonas fluorescens and Pseudomonas syringae. Hygroscopic growth measurements of the supernatent material from each biological aerosol type were were also made, to isolate any hygroscopic growth due soley to the material in the supernatent. Additionally, the hygroscopic properties of several materials often found in biological aerosol particles were measured, including: phosphate buffered saline (PBS), glucose, Cab-O-Sil®, and Tween 20®. Results of the characterization process and the measured hygroscopic properties of different types of biological organisms are discussed.

1BA.5

Studies of the Impacts of Biological Particles on Clouds and Precipitation in Aircraft and Sea Spray Studies. KIMBERLY PRATHER, Paul DeMott, Vicki Grassian, Timothy Bertram, Grant Deane, Matthew Ruppel, Douglas Collins, Andrew Ault, *University of California, San Diego*

Aerosols can modify cloud microphysical properties including droplet size and water phase, and thus can alter precipitation efficiency. In particular, dust aerosols which originate from various deserts around the world, have been shown to serve as effective ice nuclei (IN) and potentially enhance precipitation in mixed-phase clouds. IN are atmospheric particles that catalyze the freezing of supercooled cloud droplets, producing ice crystals that would not form otherwise at warmer, mixed-phase cloud temperatures. Some types of biological aerosols such as bacteria have also been shown to serve as effective IN at relatively warm temperatures, however recent modeling studies have concluded they are of minor importance to global IN concentrations and precipitation processes. In general, the specific sources of the biological particles that serve as ice nuclei are poorly understood and most studies have focused on the ice nucleation activity of terrestrial biological particles. The role of the ocean in producing biological particles which impact clouds is far less understood. This presentation will describe in-situ cloud measurements made in aircraft studies using single particle mass spectrometry to probe the chemical composition of cloud nuclei. This study shows the presence of biological markers in mixed phase clouds and their impact on ice formation and precipitation processes. Results will be presented from laboratory ocean-atmosphere wave flume studies aimed at better understanding marine sources of ice nuclei. These studies use natural seawater and control biological conditions of the seawater to probe how seawater composition impacts the composition and the ice nucleation ability of the resulting sea spray aerosol.

1BA.6

Marine Biological Ice Nuclei – Estimation of Sources and Significance for Marine Clouds. SUSANNAH BURROWS, Corinna Hoose, Ulrich Pöschl, Mark Lawrence, Paul DeMott, Xiaohong Liu, Po-Lun Ma, Phil Rasch, *Pacific Northwest National Laboratory*

Particles associated with marine biological activity have been proposed as a possible source of ice nuclei (IN) to the marine boundary layer. Using a combination of satellite data and parameterizations of sea spray emissions, we will argue that the region in which marine biogenic IN are most likely to influence IN concentrations is the remote Southern Ocean, where sea spray emissions and biological activity are strong, and continental aerosols are scarce.

Although concentrations of marine biogenic IN emissions are expected to be small, a large fraction of clouds in the Southern Ocean region contain super-cooled liquid and so these clouds may be particularly sensitive to changes in the concentration of ice nuclei. At the same time, continental aerosol that can act as IN is transported episodically from desert source regions to the remote ocean, often in a well-defined plume that lies above boundary-layer clouds.

To investigate and contrast the sensitivity of marine clouds to ice nuclei and cloud condensation nuclei from local marine sources and remote continental sources, we have performed simulations of marine clouds and their interactions with marine and continental aerosols using a cloud-resolving model. We present preliminary results from these simulations and suggest avenues for further research.

1BA.7

Studies on the Relation of Ice Nuclei from Sea Spray to Ocean Biological Cycles. PAUL DEMOTT, Kimberly Prather, Thomas C. Hill, Taehyoung Lee, Chung Hwang, Yukata Tobo, Douglas Collins, Matthew Ruppel, Jessica Axson, Christopher Lee, Camille Sultana, Bruce Moffett, *Colorado State University*

Far less is known about the emission of ice nucleating aerosols from the oceans than from land, yet the potential influence of marine aerosols on supercooled cloud properties and radiative transfer are great over vast remote oceanic regions. We recently reported on number concentrations of ice nuclei (IN) from laboratory-produced and ambient sea spray aerosols. Here we document new experiments to study variations in the IN activity of sea spray aerosols occurring as the result of marine biological processes that affect the chemical complexity and biological content of aerosols, and on further studies of the relation between IN concentrations and the diversity of biological particles found during marine boundary layer sampling.

Phytoplankton bloom conditions were reproduced in laboratory studies, and nurtured through successional stages dominated by bacteria and then viruses, to examine the impact on aerosols formed by realistic sea spray generation. IN concentrations active in the condensation/immersion freezing regime were measured in real-time below -25C, and filter collections were processed offline to quantify immersion freezing IN concentrations to as warm as -5C. IN increased up to 50 times in accord with chlorophyll-a concentrations during blooms. Aerosol compositions measured simultaneously by single particle aerosol mass spectrometry and IN compositions measured by scanning electron microscopy are under analyses.

Offline analyses of aerosols collected during the July 2012 Korea Polar Research Institute’s research vessel cruise over the Pacific basin from approximately 40N to 65N latitude indicate markedly varied IN number concentrations and contributions of labile (presumably biological) IN ranging from 0 to 85%. Initial pyrosequencing results suggest variably diverse communities of aerosol prokaryotes present during the cruise, with terrestrial influence in most cases. These data will be compared to meteorological, aerosol mass spectrometer, and IN data to discern a picture regarding the role of biological aerosols in the marine boundary layer.

1IA.1

Ultrafine Particles Emitted from Scented Markers. Cha-Chen Fung, Shi Shu, YIFANG ZHU, *UCLA*

Recent studies found an increase in ultrafine particles (UFPs diameter < 100 nm) concentration inside classrooms during art activities. Art products (e.g. scented markers) containing ozone reactive terpenes are possible sources. Experiments using scented markers were conducted inside a stainless steel chamber with air sample ports and fans to control air exchange rate and mixing. Ozone was supplied to the chamber from a UV lamp ozone generator. A scented marker was used to color an area of 24 cm by 18 cm on a sheet of A4 paper inside the chamber via a glove port while UFP number concentration, size distribution, and ozone concentrations were measured. Twelve different scents from three brands of markers were tested and only the lemon scent from one brand produced UFPs. Calculated emission rates ranged from 2.4×10^6 – 5.7×10^7 particles/second. Particle size measurements revealed unimodal distributions in the range of 20 – 30 nm. Experiments at decreasing ozone concentrations showed a critical point (50 ppb), below which no UFPs were detected above background. Model simulation revealed that drawing with the lemon-scented marker emitted ozone-reactive VOCs, most likely limonene, in the order of 10 - 100 microgram, which yielded in the same order of magnitude of secondary organic aerosols (SOA). These findings suggest that not all scented markers contain reactive terpenes, and substituting products can reduce children’s exposure to UFPs.

1IA.2

Impact of Air Exchange Rates on Aerosol Mass Fractions Describing Indoor-Generated Secondary Organic Aerosol.

Somayeh Youssefi, MICHAEL WARING, *Drexel University*

Secondary organic aerosol (SOA) formation due to the oxidation of reactive organic gases (ROG) is often parameterized with the aerosol mass fraction (AMF), which is the mass ratio of SOA produced to parent ROG reacted. The AMF is not constant and depends on the organic aerosol mass concentration. Most often, AMF curves are determined in batch systems. However, indoor settings undergo unintentional and intentional ventilation air exchange processes that lead to indoor air residence times of ~0.25 to 5 h and hence are better approximated as a continuous flow mixed reactor (CFMR) system. Little work has been done to evaluate ‘dynamic AMFs’ in CMFR systems over the range of typical indoor residence times for transient injections of reactant compounds. These dynamic AMFs may differ in magnitude from traditional ‘batch AMFs’ because of the shorter time for precursors to react, the flushing of gas- and SOA-phase products from the system with the exhaust air, and differences in deposition rates. In this work, dynamic AMFs for d-limonene ozonolysis were measured in a CFMR chamber system at three different air exchange rates and at different initial ozone:d-limonene ratios. Higher air exchange rates led to decreases in the observed AMFs and size-distributions with smaller median diameters and geometric standard deviations. Also, the AMF increased as the ozone:d-limonene ratio increased, potentially due to heterogeneous reactions. This study provides a framework to predict SOA formation indoors due to d-limonene ozonolysis over the range of typical air exchange rates and ozone:d-limonene ratios common to indoor environments.

1IA.3

Emissions of Secondary Organic Aerosol Initiated by Surface Reactions between Ozone and Squalene.

Chunyi Wang, MICHAEL WARING, *Drexel University*

Squalene is a low volatility compound that is prevalent on human skin and on indoor surfaces due to human desquamation. Ozone/squalene surface reactions initiate the generation of numerous volatile and semivolatile products, some of which may lead to secondary organic aerosol (SOA) formation. To investigate that possibility, 13 steady state chamber experiments were conducted to measure the SOA formation due to ozone reactions with squalene sorbed to glass, at chamber ozone mole fractions of 57–500 ppb for two relative humidity (RH) conditions of 20 and 50%, in the absence of seed particles. The size distributions, mass and number secondary emission rates (SER), aerosol mass fractions (AMF), and aerosol number fractions (ANF) of formed SOA were quantified. The surface AMF and ANF are defined as the change in SOA mass or number formed, respectively, per ozone mass consumed by ozone/squalene surface reactions. All experiments but one exhibited appreciable nucleation and subsequent SOA mass formation. Mass formation parameters increased monotonically with ozone, more notably for the higher RH experiments. Similar to the traditional gas phase AMF, the surface AMF was a function of the chamber aerosol concentration, and a multiproduct model was fit to the results using ‘volatility basis set’ parameters. Number formation was strong at low ozone/low RH conditions, implying that these conditions favored nucleation. Based on an estimate of the time scales for desorption of compounds formed on the surface, nucleating species are thought to be formed by reactions that initiated on the surface and are completed in the gas phase after the initial product desorption. The mass formation results were extrapolated to explore the importance of this mechanism in real indoor spaces; likely environments influenced are those with high occupant densities and low air exchange rates.

1IA.4

Particulate Reactive Oxygen Species in Retail Stores in Austin, Texas. SHAHANA KHURSHID, Kerry Kinney, Jeffrey Siegel, *The University of Texas at Austin*

Precursors to reactive oxygen species (ROS) are ubiquitous in indoor environments. Despite this, there is little information in the literature on the indoor concentrations of ROS. This study reports on the ROS concentration in retail stores, since they present an environment where large numbers of people may be exposed to stocks of consumer goods, several of which emit reactive organic compounds. Almost eight million people work as retail salespeople and cashiers in the U.S., and 43% of the population shops daily in retail stores. Sampling was conducted in five retail stores in Austin, Texas, including grocery, furniture and general merchandise stores. ROS on $PM_{2.5}$ was assessed as particles in this size range can carry ROS deep into the lungs, potentially leading to the greatest health effects. In addition to indoor and outdoor concentrations of ROS on $PM_{2.5}$, ventilation rates and indoor and outdoor air quality parameters were also assessed at the stores. The indoor concentration of ROS on $PM_{2.5}$ (expressed in terms of a representative ROS, hydrogen peroxide (H_2O_2)) ranged from 0.02 nanomoles H_2O_2/m^3 air sampled (at a general merchandise store) to 3.36 nmoles/m^3 (at a grocery store). The indoor ROS concentration at all stores was seen to vary from day to day, possibly due to changes in indoor activities, ventilation rates, and outdoor pollutant concentrations. The mean indoor concentration of ROS on $PM_{2.5}$ (1.09+/-0.93 nmoles/m^3) was not significantly different from the outdoor concentration (1.12+/-1.09 nmoles/m^3), although this may be partially due to high variation. The range of concentrations measured in retail stores was similar to that in a residential sample. Given that the indoor concentrations of ROS are similar to those in outdoor environments, and that people spend the bulk of their time in indoor environments, it is important to note that indoor exposure to ROS likely dominates total exposure.

1IA.5

Characterize the Size Distribution of Walking-induced Particle Resuspension. YILIN TIAN, Andrea R. Ferro, *Clarkson University*

Walking-induced particle resuspension has received significant attention as a contributor of indoor particulate matter exposure. Resuspension of micron size particles has been well characterized by previous studies. However, there is still a knowledge gap regarding the lower end of the resuspended particle size distribution. The lack of information in submicron particle resuspension has been possibly due to high background concentration or instrumentation limitation, as optical particle instruments have commonly been used. This study aimed to characterize the lower end of the resuspended particle size distribution by conducting a chamber study using a mechanical foot to mimic human walking. Particle resuspension from cut pile carpet and vinyl flooring were tested. House dust collected from residences was used to soil the floorings. A Model 1000XP Wide Range Particle Spectrometer (WPS™) was used to measure the airborne concentration of particles range from 0.05 to 10 microns. Preliminary results showed that the smallest particles resuspended due to shoe-floor contact were about 0.1 micron in diameter from both flooring types, which extends the size range (0.3-25 micron) reported in previous studies.

1IA.6

Seasonal and Environmental Factors Associated with Microbes Living in Our Homes. PATRICIA KEADY, Shelly Miller, Noah Fierer, Joanne B. Emerson, Jonathan Awerbuch, Oluwaseun Oyatogan, Suraj Prabhu, Kangqian Wu, Allie James, Rob Dunn, Holly Menninger, *University of Colorado Boulder*

Using relatively-low-cost, high-throughput DNA sequencing techniques, investigators can explore the diversity of bacterial and fungal microbes found inside buildings. The objective of this research is to identify factors within the home environment that influence the community of bacteria and fungi found within the home. The study spans one year to evaluate temporal variation and seasonal relationships. The study population consists of 15 single-family residences on the northern front range of Colorado, with between 2 to 5 non-smoking occupants. The homes vary in age, design, heating and ventilation systems, type of fuel source, rural or urban location, and the number of children, pets, and plants. Hypotheses that result from detailed consideration of these houses will be compared to ongoing work in over a thousand homes spread across a wide geographical area. In this way they will be tested across many more houses and contexts both in a general sense and with regard to the abundance and diversity of particular taxa.

Twice each season the research team visited the study homes to conduct detailed 24-hour measurement of indoor and outdoor air quality, and collect air and surface samples for microbial DNA sequencing using the Illumina HiSeq platform. Air quality data included temperature, relative humidity, carbon dioxide, carbon monoxide, ozone and particulate concentration (PM10/PM2.5). Surface swab samples were taken from six locations: top of an exterior door sill, top of an interior door sill, kitchen surface where food is prepared, used pillowcase, floor surface near the indoor air sampling station, and face of a HVAC air filter. The air filter was replaced (or cleaned) at the start of each season. Investigators documented the building infrastructure with a walk-through inspection. Volunteer participants completed a questionnaire and activity diary for the sample period. This presentation focuses on findings from the winter through summer season investigation.

1IA.7

Modeling of Indoor Particles with Resuspension via Human Activity for a Commercial Building. KYUNG SUL, James Farnsworth, Andrea R. Ferro, *Clarkson University*

Because people spend most of their time indoors, investigation of indoor pollution is important for examining human exposure. Human activity is known as a significant source of indoor particles via resuspension. However, most investigations on particle resuspension have taken place in the laboratory or in the residence. In this study, a materials balance model was developed to simulate particulate matter (PM) concentration in indoor air for an occupied commercial building. The model includes resuspension from human activity and infiltration of particles from outdoor air as the primary sources of indoor PM. The number of employee occupants in each targeted area as a function of time was considered as a factor for the resuspension term, along with the resuspension fraction (fraction of particles emitted per footstep), stepping frequency, and floor loading. Entry and exit of employees from key card data was used to count the occupancy in each room. The concentration for each particle size bin was calculated and compared with measured number concentrations of particles from optical particle counters. Concentrations from the simulation results showed good agreement with the measured data.

1IM.1

Application of a Drift tube Ion Mobility Spectrometer (DTIMS) for Aerosol Particle Size Distribution and Vapor Uptake Measurements. DEREK OBERREIT, Peter McMurry, Christopher Hogan Jr., *University of Minnesota*

Described in this presentation, we have developed a prototype drift tube ion mobility spectrometer (DTIMS) which provides modest to high resolution measurements of aerosol particle electrical mobility distributions. This device differs from traditional drift tube devices in that it is able to sample pre-charged aerosol particles and has sufficient sensitivity to be used at the concentration levels typically found in ambient aerosols. Laboratory tests show that the resolving power of the device approaches 10 and that it is able to obtain size distribution measurements in less than 5 seconds. The measurement speed and resolution of the device make it an ideal candidate for investigating vapor uptake by small aerosol particles, particularly those formed during new particle formation events in the atmosphere. Traditionally, such uptake measurements have been performed with two differential mobility analyzers in tandem. However, due to poor transmission efficiency in these systems along with degrading resolving power with increasing particle mobility, the measurements have been limited to particle sizes greater than 5 nm. Measurements of water vapor uptake by hygroscopic aerosol particles using the DTIMS in tandem with a DMA have been made under laboratory and field conditions for particle diameters ranging from 3nm to 7nm. The results show the degree of water vapor uptake has a strong dependence on size and composition of the particles and is dependent on the water activity of a saturated solution of the particle material. Finally, we demonstrate that through the use of non-linear electric fields in the DTIMS drift region, either instrument resolution or transmission can be optimized.

1IM.2

Online Characterization of Nanoparticle Growth during Flame Aerosol Synthesis. ARTO GROEHN, Sotiris E. Pratsinis, Karsten Wegner, *ETH Zurich*

A method for online characterization of nanoparticle growth in aerosol reactors is presented. By combining a differential mobility analyzer (DMA), an aerosol particle mass analyzer (APM) and a condensation particle counter (CPC) the average agglomerate size and structure as well as the number and size of primary particles can be determined [1, 2]. Here, this approach was applied to study agglomerate growth during production of zirconia nanoparticles by flame spray pyrolysis at rate of 30 g/h [3].

Nanoparticles were sampled from the reactor plume at temperatures up to 1500 K and particle concentrations up to 10^{18} /m^3, with a probe allowing continuous aerosol extraction and rapid dilution with quench air that effectively suppressed coagulation. Primary particle growth was shown to be completed at 75 mm above burner as a constant primary particle diameter was observed for all radial and downstream axial positions. Such homogeneity indicates well mixed conditions in the high temperature region of the flame where sintering takes place. As expected, the average agglomerate size was found to increase with axial distance from the burner. However, larger agglomerates were observed at the fringes of the aerosol plume attributed to prolonged residence time due to lower gas velocity there. Results were compared against off-line particle size characterization by nitrogen adsorption and thermophoretic sampling/transmission electron microscopy as well as model predictions [3].

The detailed spatial characterization of particle growth helps to better understand and optimize the flame aerosol process. Furthermore, such real-time particle diagnostics can assist control of nanoparticle manufacturing processes and assure product quality.

[1] Park, K., Cao, F., Kittelson, D.B., McMurry, P.H. (2003), Environ. Sci. Technol. 37, 577.
[2] Eggersdorfer, M.L., Gröhn, A.J., Sorensen, C.M., McMurry, P.H., Pratsinis, S.E. (2012), J. Colloid. Interface Sci. 387, 12.
[3] Gröhn, A.J., Pratsinis, S.E., Wegner, K. (2012), Chem. Eng. J. 191, 491.

1IM.3

Performance Study of a Miniature, Corona-based Unipolar Aerosol Charger for Compact Particle Sizers. SIQIN HE, Da-Ren Chen, Paul Greenberg, *Washington University in St. Louis*

As the rising concern of the health effect due to the exposure of ultrafine particles, A low-cost, ultrafine particle sizer enabling to measuring spatial distribution of particles is in high demand. In our group, the low-cost sizers are developed based on the electrical mobility classification technique, of which an aerosol charger is an essential component for each unit. To improve the charging performance while covering the particle size ranging from 10 to 500 nm, a new prototype of miniature unipolar aerosol charger was designed and constructed and in this study.

By challenging the prototype with DMA-classified neutral particles, the extrinsic charging efficiency of the charger was significantly improved by 20% for the whole size range when compared with that developed by Qi et al (2008). And 100% extrinsic charging efficiency for particles was achieved for the sizes larger than 80 nm. The experimental result of this study will be presented in this talk.

1IM.4

Near Real-time Measurement of Carbonaceous Aerosols Using Microplasma Spectroscopy: Application to Measurement of Carbon Nanomaterials. LINA ZHENG, Pramod Kulkarni, M. Eileen Birch, Gregory Deye, Dionysios Dionysiou, *Centers for Disease Control and Prevention, NIOSH*

We extend the application of our aerosol spark emission spectroscopy system (J. Anal. At. Spectrom., 2012, 27, 1101) to measurement of engineered carbon nanomaterials. The system incorporates coaxial electrodes that preconcentrate the incoming aerosol particles for subsequent analysis using spark emission spectroscopy in near real-time. Preconcentration is accomplished through focused electrostatic deposition of charged aerosol particles onto the tip of a cathode. Following deposition, a pulsed high voltage is applied, forming a pulsed spark discharge (plasma) with energy ranging from 50-300 mJ/pulse. The particulate matter collected on the cathode tip is ablated, atomized and electronically excited by the spark plasma, resulting in atomic emissions that are subsequently recorded using a broadband optical spectrometer for element identification and quantification. The total particulate carbon determined is a good surrogate measure of carbon nanomaterials when particulate organic carbon (OC) and elemental carbon (EC) from other sources are absent or minimal, or correction for the bias can be made. The system was calibrated and detection limit were determined for total carbon using carbon emission at 247.85 nm (C I) and carbonaceous test aerosols. To improve the selectivity for carbon nanomaterials, the cathode was heated to minimize the contribution of condensed OC. The detection limit for total carbon, measurement selectivity, results compared with EC obtained by NIOSH Method 5040, and application to near real-time measurement of single- and multi-walled carbon nanotubes will be presented and discussed.

1IM.5

Comparison of Half Mini DMA and Nano DMA for Measurement of Size Distributions in Electrospray and a Flame Aerosol Reactor. YANG WANG, Jiaxi Fang, Tandeep Chadha, Wei-Ning Wang, Pratim Biswas, *Washington University in St. Louis*

Compared to conventional Differential Mobility Analyzers (DMA), Half-Mini DMA has advantages of high resolution and low diffusion loss during the classification of sub 3nm charged aerosols due to its ability to achieve high sheath flow rates (up to ~700 lpm) while maintaining laminar flow. In this work, the accuracy of the Half Mini DMA and the commercialized Nano DMA (TSI model 3085) was compared in measurement of size distributions of sucrose particles and flame aerosols, both of which had large concentration under 6 nm. In measurement of sucrose particles generated by electrospray, good agreement between the Half Mini DMA and Nano DMA was obtained in size ranges over 3 nm. However, a relatively higher number concentration was observed by the Half Mini DMA for sub 3 nm particles, indicating that Half Mini DMA has lower diffusion losses in the sub 3 nm size range. For measurements conducted in a premixed methane-air flame aerosol reactor, size distributions of TiO2 particles below 3 nm were measured with high repeatability by a Half Mini DMA-electrometer. In addition, higher particle concentrations in this size range were obtained as compared to the Nano DMA. Additionally, a much smaller standard deviation for the Half Mini DMA in measuring low concentration aerosols was observed due to its flexibility in tuning the sheath and aerosol flow ratio. The size distribution measurements of flame aerosols in the sub 6 nm range could provide significant information in particle formation processes. Future work on flame aerosol measurements with the Half Mini DMA will be performed and this will enable the design and operation of reactors for material synthesis and pollutant control.

1IM.6

Real-Time Nano-Aerosol Monitoring System: RTNAMS. MARIA D. KING, Victor Ugaz, Ray Pierson, John Haglund, Yassin Hassan, *Texas A&M University*

Despite the increasing prevalence of nanomaterials in a wide range of everyday products and applications, the health risks associated with environmental exposure to these materials remain poorly understood. Efforts to assess safe exposure limits and establish correlations between aerosolized nanomaterials and potential health risks critically depend on the ability to effectively sample nanoaerosols from room-sized volumes and quantitatively characterize their size, chemical species, and concentration. We have established a real time in-line collection, detection and speciation system called the Real-Time Nano-Aerosol Monitoring System (RTNAMS) for the continuous monitoring of nanoparticles. The Low Cutpoint (LCP) Wetted Wall Cyclone (WWC) continuously collects nano- and larger aerosols from the environment at 300 LPM, using a surfactant (Tween-20) in its collection fluid continuously eluting and dispersing the agglomerated nanoparticles into solution. During laboratory trials the test materials Ti, Al, Cu, Fe, Zn and Si nanoparticles were released into a flowcell using the Collison atomizer and RTNAMS was allowed to sample these materials. Within the LCPWWC a “Skimmer pump” creates a vacuum that draws the sample laden collection fluid at 100 microliter/min into a de-gassing reservoir where it accumulates for 3 minutes prior to injection into the RTNAMS analysis devices, the TAMU-microchannel and the NanoSight-LM20. In the microchannel co-flowing aqueous streams containing Al particle-laden suspension and a fluorescent dye solution result in complexation with the nanoparticles, producing an easily detectable fluorescent plume and exhibiting intense interfacial fluorescence upon complexation. The opposite effect occurs with Ti nanoparticles, resulting in fluorescence quenching. Different reactivity with fluorescent dye enables the quantitation and speciation of the nanoparticles. The microchannel is also able to distinguish particle size information from the fluorescence. In the LM20 the sample was automatically sized, quantitated, and reported using the imaging software. Mass spectrometry was used for reference quantitation. Environmental RTNAMS nanoaerosol sampling and analysis was also performed at different locations, in mass transit centers, classrooms, agricultural fields and processing plants.

1IM.7

Evaluation of a Twin-head Electrospray System for Nanoparticle Exposure Study. QIAOLING LIU, Da-Ren Chen, *Virginia Commonwealth University*

Because of its capability to generate/dispersing un-agglomerate particles in the sizes ranging from nanometers to micrometers, electrospray has been proposed in a wide range of applications, including material synthesis, drug delivery, particle encapsulation, nanoparticle exposure study and many others. Particles produced by electrospray are highly charged in the same polarity. Highly charged particles are easily deposited during the transportation by electrostatic effect. Charge reduction for electrosprayed particles is thus important to keep particles airborne. The charge reduction is often accomplished by exposing sprayed particles in a bipolar ion environment, generated by either AC-corona discharging or radioactive sources. An AC-corona discharger requires an AC power supply with two independent voltage outputs. Gradually rigorous regulation of using the radioactive sources prevents users from accessing them. The alternative and simple solution to the above dilemma is to use twin-head electrospray, in which one spray head produces positively charged particles and the other produces negatively charged ones. The collision of oppositely charged particles in the twin-head electrospray process reduces electrical charges on colliding particles. In this study, the performance of a new twin-head electrospray system (THES) was evaluated for animal exposure study. Nanoparticle suspensions of TiO2, ZnO and NiO were used in this evaluation. The detail result of this study will be presented in this talk.

1RA.1

Ground Based Observations of New Particle Formation during the PEGASOS - SUPERSITO Joint Campaign in the Po Valley. STEFANO DECESARI, M. Cristina Facchini, Claudio Carbone, Stefania Gilardoni, Angela Marinoni, Paolo Cristofanelli, Gian Paolo Gobbi, Amar Hamed, Ari Laaksonen, Hanna Manninen, Tuukka Petäjä, Johannes Groess, Laurent Poulain, Michela Maione, Vanes Poluzzi, *CNR-ISAC*

During the PEGASOS-SUPERSITO field campaign held in the Po Valley (Italy) in June-July 2012, new particle formation (NPF) was observed on 87.5% of the days at the rural station of San Pietro Capofiume (SPC), which is consistent with the observed climatology for this site. On average, the formation and growth rates estimated by the DMPS were also high: 6 cm3 s-1 and 7 nm/h, respectively. The fast particle growth from 2 to 3 nm made the DMPS and ion spectrometers (NAIS) record the start of nucleation nearly simultaneously. This happened in the first two hours following sunrise, before the mixing layer development, in an atmospheric layer characterized by reduced ozone concentrations, high NOx and relatively high anthropogenic VOC levels (200 ppt of toluene). Nucleation rate (J3) peaked in windy, dry days and showed a negative correlation with condensation sink (CS). Accurate calculations of ambient (humid) CS were performed based on aerosol chemical composition and hygroscopicity measurements. The comparison of nucleation events in SPC with those recorded at other Po Valley stations distant 40 – 100 km indicates that NPF occurred over vast sectors of the plain, although the events did not start always simultaneously, probably because of differences in CS levels or in the local boundary layer meteorology. New particle formation was also observed at a nearby mountain station (Monte Cimone, 2165 m a.s.l), where a much lower frequency (35 %) occurred in comparison with the low-altitude stations. This was unexpected because, even if anthropogenic VOC concentrations are much lower in Monte Cimone than in San Pietro Capofiume, the emissions of biogenic VOCs are higher over the Apennines and temperature and CS lower. The experiment provides a nice opportunity to investigate NPF in contrasting environments in respect to anthropization level and emission patterns.

1RA.2

Quantitative and Time-Resolved Nanoparticle Composition Measurements during New Particle Formation. BRYAN R. BZDEK, Andrew Horan, M. Ross Pennington, Joseph DePalma, Murray Johnston, *University of Delaware*

The elemental composition of 20 nm diameter nanoparticles during new particle formation (NPF) days was measured quantitatively and with high time resolution in a rural/coastal environment with the Nano Aerosol Mass Spectrometer (NAMS). Nanoparticle chemical composition was dynamic during NPF days, and changes in composition did not necessarily correlate with changes in aerosol mass or number concentration. During NPF, nanoparticle composition shifts towards a more inorganic composition. Relative to previous measurements during NPF with NAMS, in this study we identify time-dependent chemical composition changes that are related to different stages of NPF. The particle phase sulfur mole fraction during NPF is quantitatively explained by condensation of sulfuric acid. This is a remarkable observation as it validates existing models describing the sulfuric acid contribution to NPF and it demonstrates the importance of developing models to explain satisfactorily incorporation of other species (e.g. nitrogen-containing and carbonaceous matter) into growing nanoparticles. Nitrogen is shown to exist in excess of that required to neutralize sulfuric acid, indicating a substantial, additional nitrogen-based growth process. Carbonaceous matter is the most abundant component of the growing nanoparticles, although it is the inorganic components that are preferentially enhanced. The results will be compared to observations made by NAMS during NPF in other environments. Although certain aspects (such as the contribution of sulfuric acid to nanoparticle growth) appear to be general characteristics of NPF, other aspects (such as the identity of certain growth species) may be relevant only in certain environments.

1RA.3

Use of Long-Term, Co-Located, Vertical and Ground-based Particle Number Concentration Data to Examine Nucleation Intensity Patterns in a Rural Continental Environment. ROBERT BULLARD, Charles Stanier, John Ogren, Patrick Sheridan,*University of Iowa*

Long-term records of aerosol number, nucleation event frequency, and vertical profiles of number concentration are valuable to the atmospheric modeling community but are rare. The extensive data record from multiagency monitoring assets at Bondville, IL can contribute important information on long term and vertically resolved patterns in these parameters. Highly time-resolved particle number concentration data have been measured for nearly twenty years by the NOAA ESRL Global Monitoring Division. Furthermore, vertically-resolved aerosol counts and other aerosol parameters are available from more than 300 flights of the NOAA Airborne Aerosol Observatory (AAO).

As documented in Asmi et al. 2013, the monthly average particle count has a statistically significant decrease from 1994 – 2012, and this is likely linked to decreases in SO_2 mixing ratios. Relationships between a number of particle-number metrics (diurnal patterns, frequency and size of peaks in number concentration over time, and monthly and daily average concentrations) are analyzed with respect to available mixing ratios of precursor gases (SO_2 and NH_3) and indicators of particle mass and surface area. Considering monthly diurnal average patterns, the highest peaks in number concentration occur during the late spring months (April, May, June) with slightly lower peaks during the fall months (September, October). The diurnal pattern of aerosol number has a midday peak and the timing of the peak is seasonal (earlier in warmer months, later in colder months). Furthermore, the average diurnal peak height has a decreasing trend from 1994-2012 in all months except for April, May, and June. Average vertical profiles show a nearly monotonic decrease with altitude in all months, with peak magnitudes also occurring in the spring and fall. Historical data will be compared to preliminary size distribution data taken during a 2013 field campaign in Bondville, IL.

1RA.4

Long-term Interannual Variability of Aerosol Sources Impacting Mauna Loa Observatory, Hawaii. LAUREN POTTER, Sonia Kreidenweis, Molly Morman, Barry Huebert, Steven Howell, John Zhuang, Nicole Hyslop, Warren White, *Colorado State University*

Located in the remote Pacific Ocean at an elevation of nearly 4 kilometers above sea level, Mauna Loa Observatory (MLO) is an ideal and unique measurement site for ground-based, free tropospheric observations. This study will make use of two long-term Mauna Loa Observatory aerosol datasets to identify contributions of long distance influence from both natural (biogenic and volcanic) and anthropogenic aerosol sources. The first dataset is obtained from a collection of daily filter samples collected from 1989-2009 during nighttime downslope (free-tropospheric) transport conditions obtained by the University of Hawaii at Manoa and analyzed for total aerosol-phase concentrations of NO_3^-, SO_4^{2-}, MSA, Cl^-, oxalate, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. The second dataset consists of recently analyzed $PM_{2.5}$ filter samples obtained at the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network Mauna Loa Observatory location (MALO). The IMPROVE sampler was run during overnight hours only for continuous three and four day time periods and covers the time period from 1988-2010. Filters were weighed to determine total $PM_{2.5}$ mass and analyzed for the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb. We identified seasonal and interannual variability in aerosol concentrations from both datasets at Mauna Loa Observatory and further investigated these patterns using HYSPLIT and EPA PMF model analyses to identify relevant aerosol sources. The data reflect changes in large scale circulation patterns that impact transport efficiency to this receptor site, in addition to changes in source emission strength. In this work we focus on the impacts of circulation changes on the variability and trends in the observations.

1RA.5

Chemical and Molecular Characterization of Free Tropospheric Aerosol Sampled at the Pico Mountain Observatory, Azores. LYNN MAZZOLENI, Katja Dzepina, Claudio Mazzoleni, Paulo Fialho, Sumit Kumar, Bo Zhang, Swarup China, Seth Olsen, R. Chris Owen, Kendra Wright, Judith Perlinger, Noel Urban, Louisa Kramer, Michael Dziobak, Detlev Helmig, Jacques Hueber,*Michigan Tech*

Improved characterization of free tropospheric aerosol optical, chemical and morphological properties is essential to further our understanding of the aerosol lifecycle and the aerosol-climate implications. Free tropospheric aerosols were studied at the Pico Mountain Observatory, located on top of the Pico volcano in the Azores, Portugal (2225 m asl; 38.47°N, 28.40°W). The station is typically subjected to free tropospheric air masses that are long-range transported from North America. Recently, we deployed a set of four high-volume samplers for the chemical analysis of aerosol, a 3-wavelength nephelometer to measure aerosol light scattering and backscattering fraction, a two channels particle optical counter (for particles larger than 300 nm), and a sequential sampler to collect aerosols on nucleopore membranes and lacy carbon grids for electron microscopy analysis. Black carbon mass equivalent concentrations have been measured at the station since 2001 with a 7-wavelength aethalometer. Summertime daily concentrations of free tropospheric organic carbon, elemental carbon, water-soluble organic carbon (WSOC), anions and cations were measured from high-volume filter samples. Selected WSOC samples were further analysed using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Molecular formulas were assigned to accurate masses as described in Mazzoleni et al., 2012. Thousands of monoisotopic compounds containing C, H, O, N, and S were identified from the negative and positive ion ultrahigh resolution FT-ICR mass spectra. The comprehensive composition of free tropospheric WSOC was compared to non-urban aerosol samples collected at the Storm Peak Laboratory in the Rocky Mountains of northwestern Colorado (3220 m asl; 40.455°N, -106.744°W). Considerable differences in the elemental ratios and molecular unsaturation were observed. This presentation will discuss those differences and their relationship to aerosol ageing with respect to long-range transport.

Mazzoleni, L.R., P. Saranjampour, M.M. Dalbec, V. Samburova, B. Zielinska, A.G. Hallar, D. Lowenthal, and S. Kohl, Identification of Water-Soluble Organic Carbon in Nonurban Organic Aerosols using Ultrahigh-Resolution FT-ICR Mass Spectrometry: Organic Anions, Environmental Chemistry, 9(3) 285-297, 2012.

1RA.6

Integrated Analysis of Air Pollution at Antarctic: Past, Present and Future of Monitoring of Brazilian Antarctic Program.RICARDO H. M. GODOI, Heitor Evangelista, Marcio Cataldo, Ana Flavia L. Godoi, Renata C. Charello, Sarah L. Paralovo, René Van Grieken, *Federal University of Parana - Curitiba, PR, Brazil*

Over the past 50 years, the Antarctic continent recorded the largest increase of atmospheric temperature compared to other continents. The range of +2.5 Celsius degrees is contrasted with the global average increase of +0.6 Celsius degrees for the last 140 years. Key mechanisms behind this warmer climate acceleration have been identified as the melting and thinning of the floating ice shelves triggered by warm ocean water. We hypothesize that the West Antarctic warming can be related to the aerosols transported and/or formed in this region. Thus, the analysis of the aerosols composition is essential to clarify the behavior of the aerosols in the atmosphere and its effects on the heating and cooling of this pristine area, since the atmospheric aerosols can influence climate change directly or indirectly.

One of our research proposes is to study the aerosol dispersion from Rio de Janeiro to the Brazilian Antarctic Station at King George Island. Individual Antarctic aerosol particles were analyzed by low-Z EPMA and the bulk of particles by EDXRF, in order to investigate the elemental composition of particles and bulk samples. EPMA results show high contributions of sulphur, sea salts, aluminosilicates, iron rich and a few soot particles. Alongside to the cruise, the elemental concentration results revealed two main groups. The first group is originating mainly from natural sources, and the second group to be related to long-range transport of anthropogenic aerosol. The monitoring of BC showed that the enhanced concentrations from urban origin can be transported to the South–West Atlantic Ocean due to the migration of sub-polar fronts that frequently reach tropical/subtropical regions.

Our actual project (2010-2014) aims to improve the understanding the impact of aerosols in Central West Antarctica, based on the standalone module - Criosfera 1, which started operation during the early 2011/2012 summer period.

1RA.7

Aerosols over the Remote Forest Regions of Amazonia and Siberia Investigated by STXM-NEXAFS. MEINRAT O ANDREAE, Christopher Pöhlker, Paulo Artaxo, Eugene Mikhailov, Alexey Panov, Arthur L. D. Kilcoyne, Ulrich Pöschl, Bärbel Sinha, Kenia T. Wiedemann, *Max Planck Institute for Chemistry*

We investigated the morphology and chemical composition of aerosol samples from remote forest environments in the Amazon Basin and Central Siberia, using Scanning Transmission X-ray Microscopy - Near Edge X-ray Absorption Fine Structure (STXM-NEXAFS) analysis in combination with other microanalytical techniques. The NEXAFS spectra were used to estimate the elemental ratios of C, N and O, as well as the chemical bonding state of these elements. In addition, we characterized the distributions of some other elements, such as K, Ca, and Fe. The aim of this study was to investigate the microphysical and chemical properties of remote background aerosols and their internal mixing state. The samples were collected over several seasons at both sites and represent a range of conditions, from nearly pristine background to anthropogenically polluted.

The Amazonian aerosol during the rainy season was found to be dominated by drop-like organic particles in the fine mode (often in internal mixture with solid particles), and Primary Biological Aerosol Particles (PBAP) in the coarse mode. Liquid organic aerosol coatings were also frequently observed on the PBAPs. Unexpectedly, most SOA particles showed the presence of variable amounts of K, with K mass fractions decreasing with increasing particle size. Furthermore, the spectra exhibit characteristic signal patterns for different functional groups. In most cases, the spectrum near the C-edge is dominated by either the hydroxyl or the carboxylate signal, but prominent peaks for ketone carbonyls, alkanes and alkenes have also been observed. During the dry season, particle number concentrations were 2-3 times higher than in the wet season, and soot particles, often in internal mixture with organics and inorganic ions were frequent. K-rich particles were less abundant than during the rainy season, but (presumably biogenic) SOA still formed a considerable part of the aerosol population.

Over Siberia, large PBAPs were much less frequent than over the Amazon forest, whereas soil dust and combustion-related particles were common constituents of the coarse fraction. In the fine fraction, pollution related particles were always present and usually dominant, as evidenced by the presence of ammonium sulfate and soot carbon. SOA usually occurred as internal mixture with ammonium sulfate. Our results document the pervasive influence of anthropogenic emissions even in the most remote parts of the continental atmosphere.

2AC.1

Aqueous Photooxidation of Fresno, CA and Po Valley, Italy Fogs: Insights into Cloud Processing. JEFFREY R. KIRKLAND, Yong Lim, Stefano Decesari, M. Cristina Facchini, Jeffrey L. Collett, Jr., Barbara Turpin, *Rutgers University*

This work explores aqueous photooxidation of natural fog water to improve our current understanding of secondary organic aerosol formation through gas followed by aqueous chemistry (aqSOA). Fog waters naturally accumulate an ambient matrix of water-soluble gases formed through photochemical oxidation of anthropogenic and biogenic emissions. We expect that further oxidation of these emissions in the aqueous phase will yield low volatility products that remain in the particle phase after droplet evaporation, thus forming SOA. In this work, we examined changes in the composition of fog water samples after the addition of hydroxyl radicals to improve our understanding of aqSOA formation.

Experiments were conducted with winter fog waters collected in Fresno, California and Po Valley, Italy. Batch aqueous photooxidation reactions were conducted in a 33 mL cuvette chamber with fog samples (organic carbon: 50-350 micro-Molar) and OH radicals. OH radicals were continuously formed in situ through H2O2 photolysis. The concentration dynamics were monitored using ion chromatography (IC), positive and negative mode electrospray-ionization mass spectrometry (ESI-MS), and IC/ESI-MS. Insights will be provided regarding precursors and products identified in these experiments and implications to aqSOA formation in fogs.

2AC.2

Measurements of Organic Acids in Eastern U.S. Radiation Fogs. DEREK STRAUB, *Susquehanna University*

Measurements of fog chemical composition have been ongoing at a rural site in central Pennsylvania since 2007. These measurements have focused on the analysis of inorganic ion concentrations and the compilation of a long-term record of fog composition in this region. Starting in 2012, organic acids were added to the analysis protocol. Of the 78 total fog samples collected through the end of 2012, 62 samples have been analyzed for major inorganic ions and 21 samples for organic acids.

Fog samples were collected with an automated Caltech Heated Rod Cloudwater Collector (CHRCC) operated on the campus of Susquehanna University, a setting influenced by local agricultural emissions and transport from the industrial Midwest. The collection system was activated when visibility dropped below 500 m and a single bulk sample was collected during each fog episode. Sample volumes averaged 30 ml and the volume weighted average pH was 4.9.

While ammonium and sulfate were the most abundant ions in the fog samples, organic acids were found to contribute significantly to total ion loading. On average, organic acids accounted for 41% of anions in solution. Formate was the third most abundant ion observed, followed by calcium, nitrate, and acetate. The average formate to acetate ratio was 3.3:1. Propionate and oxalate were also present in the fog samples but at lower concentrations. Seven additional organic acids were measured, but concentrations of these were often, but not always, below detection limits. Results from the fog sampling campaign will be presented along with comparisons to organic acid measurements for dew samples that had higher pH values but lower total ion concentrations.

2AC.3

Chemical Composition, Sources and Processes of Urban Aerosols during Summertime in Northwest China: Insights from a High Resolution Time-of-Flight Aerosol Mass Spectrometer. JIANZHONG XU, Qi Zhang, Min Chen, Jiawen Ren, Dahe Qin,*State Key Laboratory of Cryospheric Sciences, China*

Air pollution has become a serious issue in cities of China due to quick urbanization and industrialization in recent years. Here we report results from a field study conducted in Lanzhou, the capital of Gansu province in northwest China, during July 12th – Aug 7th, 2012. Lanzhou has been regarded as one of the most polluted cities in China mainly due to its unique valley topography. An Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed along with a Scanning Mobility Particle Sizer (SMPS) and an Aethalometer to monitor the chemical variation of sub-micrometer aerosol (PM1) in real time. The average PM1 mass concentration during this study was 15.5 (± 9.5) micro-gram m^{-3}, with mean composition consisting of organics (43%), BC (19%), sulfate (16%), nitrate (9%), ammonium (8%), and chloride (4%). Positive matrix factorization (PMF) was applied to analyzing the organic mass spectra and identified four organic aerosol (OA) factors, representing, respectively, two primary OA (POA) emission sources (traffic and food cooking) and two secondary oxygenated OA (OOA) types – a semi-volatile (SV-OOA) and a low-volatility (LV-OOA) OOA. Black carbon (BC) and HOA displayed distinct diurnal patterns with a morning (~ 6:00-11:00) (Beijing Time) and an evening peak (~ 20:00-23:00) corresponding to the rush hours, while cooking OA (COA) peaked during lunch and dinner periods. The diurnal profiles of sulfate and LV-OOA displayed a broadly peak between ~7:00-15:00, while those of nitrate, ammonium and SV-OOA showed a narrower peak at ~ 8:00-13:00. The later morning and early afternoon peak in secondary aerosol pollution was likely caused by mixing down of pollutants aloft, which were decoupled from the boundary layer during night time. The micropulze lidar data have been used to check the vertical distribution of pollution. In addition, the time variations and their correlations with meteorological parameters have also been evaluated.

2AC.4

Formation and Aerosol Uptake of the Oxidation Products of Isoprene Nitrooxyhydroperoxide (a Product of Isoprene Nighttime Chemistry). REBECCA SCHWANTES, Tran Nguyen, Matthew Coggon, Katherine Schilling, Xuan Zhang, Paul Wennberg, John Seinfeld, *Caltech*

Isoprene (C5H8) reacts with the nitrate radical (NO3) during the night to produce a peroxy nitrate radical. This peroxy nitrate radical can react with nitrogen oxides (NO and NO2) and other peroxy radicals to form isoprene nitrates or with the hydroperoxyl radical (HO2) to form nitrooxyhydroperoxide. Both model [1] and field [2] studies have found that much of the peroxy nitrate radical reacts with HO2. However, chamber studies so far have been run in conditions that optimize the formation of isoprene nitrates rather than the formation of nitrooxyhydroperoxide. In this work, chamber studies designed specifically to study the nighttime HO2 pathway were conducted. The gas phase formation of the isoprene nitrooxyhydroperoxide and subsequent oxidation products were monitored using a chemical ionization mass spectrometer (CIMS). The gas phase oxidation products of the nitrooxyhydroperoxide will be discussed and compared to the products formed during the daytime oxidation of isoprene peroxide. Additionally, the aerosol uptake of the oxidation products of nitrooxyhydroperoxide onto both acidic and neutral seed under dry (RH <3%) and moderate relative humidity (RH ~ 50%) conditions was measured using a time-of-flight aerosol mass spectrometer (ToF-AMS). Off-line analyses of the aerosol produced were also conducted by electrospray ionization mass spectrometry (ESI-MS). The composition of the aerosol produced from the nighttime HO2 pathway will be discussed.

[1] Xie, Y., et al., Understanding the impact of recent advances in isoprene photooxidation on simulations of regional air quality, Atmos. Chem. Phys. Discuss., (In review)
[2] Beaver, M.R., et al., Importance of biogenic precursors to the budget of organic nitrates: observations of multifunctional organic nitrates by CIMS and TD-LIF during Bearpex 2009, Atmos. Chem. Phys., 12, 5773–5785, 2012.

2AC.5

Trends in PM2.5 Strong Acidity Across Canada between 1990 and 2010. JENNIFER MURPHY, Alex Tevlin, *University of Toronto*

Particle acidity plays a role in the gas-particle partitioning of ionisable constituents, and may influence SOA production and particle health impacts. There is no robust technique to directly measure the acidity or pH of ambient particles. In this analysis, we calculate strong acidity based on the difference in equivalents (eq m^{-3}) between the dominant anions and cations ($2*SO_4^{2-} + NO_3^{-} + Cl^{-} - NH_4^{+} + Na^{+}$) measured in 24-h integrated $PM_{2.5}$ samples collected daily between 1990 and 2010. At the majority of sites, especially those in central Ontario and Quebec, we find significant decreases in the inferred strong acidity over the time period. Significant seasonal and geographic differences in strong acidity trends exist among the sites. By combining inferred strong acidities with liquid water content calculated by the Extended Aerosol Inorganics Model (E-AIM), we can estimate particle pH for deliquesced particles. However, as acidity values decrease, the propagated uncertainties in the measurement of each analyte lead to strong acidities that are less frequently statistically distinguishable from zero.

2AC.6

The Effect of Particle Size on Iron Solubility in Atmospheric Aerosols. AURELIE MARCOTTE, Brian Majestic, Ariel Anbar, Pierre Herckes, *Arizona State University*

The long range transport of mineral dust aerosols, which contain approximately 3% iron by mass, results in an estimated 14-16 Tg of iron deposited into the oceans annually; however, only a small percentage of the deposited iron is soluble. In high-nutrient, low chlorophyll ocean regions iron solubility may limit phytoplankton primary productivity. Although the atmospheric transport processes of mineral dust aerosols have been studied, the role of particle size has been given little attention. In this work, the effect of particle size on iron solubility in atmospheric aerosols is examined. Iron-containing minerals (illite, kaolinite, magnetite, goethite, red hematite, black hematite, and quartz) were separated into five size fractions (10-2.5, 2.5-1, 1-0.5, 0.5-0.25, and <0.25 micro-meter) and extracted into buffer solutions simulating environments in the transport of aerosol particles. Preliminary results show that differences in solution composition are more important than differences in size. When extracted into acetate and cloudwater buffers (pH 4.25-4.3), < 0.3% of the Fe in iron oxides (hematite, magnetite, and goethite) is transferred to solution as compared to ~0.1-35% for clays (kaolinite and illite). When extracted into a marine aerosol solution (pH 1.7), the percentage of Fe of the iron oxides and clays transferred to solution increases to approximately 0.5-3% and 5-70%, respectively. However, there is a trend of increased %Fe in the minerals transferred to solution in the largest and smallest size fractions, and decreased %Fe in the minerals transferred to solution in the mid-range size fraction when extracted into the acetate and cloudwater buffers. When extracted into the marine aerosol solution the %Fe in the minerals transferred to solution increases with decreasing particle size. By examining the role of particle size, this work will provide a more complete understanding of iron dissolution during atmospheric transport of mineral dust aerosols.

2AC.7

Mineral Dust Produces Visible Laser Induced Incandescence. TINGTING CAO, Lulu Ma, Jonathan E. Thompson, *Texas Tech University*

Laser-induced incandescence (LII) is a real-time measurement technique for in-situ measurement of black carbon particles (a.k.a. soot). When using LII, the soot within the laser beam is rapidly heated to several thousand Kelvin yielding an incandescence signal. Here, we demonstrate that two types of light-absorbing mineral dusts also emit visible light when illuminated by a 1064 nano-meter Nd:YAG laser beam. The emission presents itself as incandescence, featuring a broad emission spectrum similar to a blackbody at about 4300 K. The emission also exhibited microsecond lifetimes typical of incandescence. Lasing the mineral dust was found to produce alteration of the particle size distributions observed.

2AC.8

TPD Aerosol-CIMS – Investigating the Volatility of Organic Salts. SILJA HÄKKINEN, Joseph Woo, Greg Drozd, V. Faye McNeill, *Columbia University*

Understanding aerosol volatility, i.e. aerosol partitioning between gaseous and particulate phases, is important in order to accurately determine total atmospheric aerosol loadings and furthermore assess the climatic effect of aerosols. It is known that atmospheric organics have a significant contribution to the mass of aerosol particles. The lower the volatility, the more likely it is that an organic species will partition to aerosols, including the very smallest particles. We demonstrate here the use of TPD Aerosol-CIMS (Temperature Programmed Desorption Aerosol-Chemical Ionization Mass Spectrometry) to investigate the volatility properties of the aerosols under laboratory conditions. We generated low-volatility oxalate salt aerosols via the reactive uptake of oxalic acid to $CaCl_2$ particles in an aerosol flow tube reactor as well as by atomizing a solution of sodium oxalate. The TPD Aerosol-CIMS was used to demonstrate the depressed volatility of these particles compared to pure oxalic acid aerosols. As in the Aerosol-CIMS technique, aerosols are passed through a heated flow tube inlet and the volatilized organic compounds are ionized chemically and detected using a quadrupole mass spectrometer. In the TPD Aerosol-CIMS, the inlet temperature is varied between room temperature and 180 degrees Celsius while tracking the evaporation of the organic species of interest. TPD Aerosol-CIMS measurements yield information about the gas-particle partitioning of individual compounds in the studied aerosol, including their effective heat of vaporization.

2AC.9

The Effects of Particle Size, Relative Humidity, and Sulfur Dioxide on Iron Solubility in Atmospheric Particulate Matter.

BENTON CARTLEDGE, Brian Majestic, Aurelie Marcotte, Pierre Herckes, Ariel Anbar, *University of Denver*

Iron is the most abundant transition metal in atmospheric particulate matter (PM). Iron also plays a critical role in the atmospheric sulfur and carbon cycles; however, the extent of that role is believed to be dependent on iron solubility. Changes in iron solubility can also affect numerous other processes such as ocean fertilization and the redox activity of inhaled $PM_{2.5}$. Increased redox activity of iron in inhaled $PM_{2.5}$ has been linked to increased occurrences of cancers, asthma, and other cardiovascular/pulmonary diseases. Particulate iron can be transported thousands of kilometers from its source interacting with other atmospheric species such as short chain organic acids, ammonium nitrate, and anthropogenic species such as SO_2. During transport and interactions with these species in an aqueous environment, the probability of chemical reaction increases which could contribute to iron solubilization. The current study focuses on studying the effects of particle size, relative humidity, and exposure to SO_2 on iron solubility. To mimic oceanic particles, iron minerals were resuspended with sodium chloride and size-segregated on Teflon filters using a Sioutas personal cascade impactor sampler (PCIS). These samplers were then exposed to SO_2 at marine environment humidity (>80%) and arid environment humidity (24%). Soluble iron was determined by extracting the samples in a buffer and then analyzing the extracts via inductively-coupled plasma mass spectrometry (ICP-MS). Total iron was measured by digesting the samples in strong acid using a microwave digestion system and analysis via ICP-MS. As particle size decreased, percent solubility was shown to increase. Additionally, increased iron solubility was linked to increased relative humidity and exposure to SO_2. Since a large amount of atmospheric dust originates in desert regions, gas-particle phase interactions with urban gasses (SO_2) appear to be an important factor in increasing iron solubility especially as the particle is transported into a more aqueous environment.

2AC.10

Quantification of the Catalytic Effect of Nitric Acid on Dehydration of Particulate Cyclic Hemiacetals.

APRIL RANNEY, Paul Ziemann, *UC Riverside*

Dehydration of cyclic hemiacetals in particles formed by OH radical-initiated reactions of alkanes and alkenes has been shown to be catalyzed by nitric acid (HNO^3). This reaction forms unsaturated dihydrofurans, which can evaporate from particles and react with OH radicals, O^3, or NO^3 radicals to form a variety of multifunctional products that can potentially form secondary organic aerosol (SOA). In order to quantify the effects of HNO^3 on the rate of dehydration of cyclic hemiacetals, a series of environmental chamber experiments were conducted in which particulate cyclic hemiacetals were formed from the OH radical-initiated reaction of n-pentadecane in the absence of NOx and exposed to a range of concentrations of HNO^3. n-Pentadecane, dioctyl sebacate (DOS) seed particles, various gas phase concentrations of HNO^3, and O^3 were added to the chamber and then the reaction was initiated by adding tetramethylethene (TME), which reacted with O^3 in 2–3 minutes to form OH radicals with approximately unit yield. A particle beam mass spectrometer was used to monitor the rapid formation and much slower decay of cyclic hemiacetals in real-time, with wall loss accounted for using the decay of DOS signal. HNO^3 was measured using ion chromatography to analyze water extracts of particles sampled onto filters and gas sampled through an impinger. Dehydration rate constants increased linearly with HNO^3 concentration, as expected for an acid-catalyzed reaction, and the amount of HNO^3 measured in SOA particles was proportional to the gas-phase concentration of HNO^3 and the SOA mass concentration, which allowed for an estimate of the Henry's law constant for HNO^3 in SOA particles. These two quantities can be used to model the behavior of cyclic hemiacetals in dry SOA particles as well as concentrations of HNO^3.

2AC.11

Uptake of Organic Compounds from Ultra-Low Sulfur Diesel (ULSD) Exhaust onto Laboratory Generated Inorganic Seed Particles. ZAMIN KANJI, John Liggio, Katherine Hayden, Tak Chan, Marie-Josee Poitras, Shao-Meng Li, *Environment Canada*

Airborne particulate matter is can pose serious health risks and have a large influence on the Earth's climate. Knowledge of the composition of atmospheric particles is crucial to be able to predict air quality as well as the composition of the troposphere. In particular, atmospheric particles can play an important role in re-distributing semi-volatile organic compounds at source through either condensational or reactive uptake. In this work we seek to study the interactions of ULSD exhaust on pre-existing acidic sulfate, ammonium nitrate and ammonium sulfate seed particles using high resolution aerosol mass spectrometry. Primary particles emitted from the exhaust were filtered out so as to observe the partitioning of gas phase species onto the seed particles as a function of dilution and reaction time. Atomized and size selected seed particles with a diameter of approximately 300 nm were mixed with particle-free diesel exhaust and introduced into a flow tube with the option of 6 sampling ports along the length of the flow tube representing an exposure time of approximately 1 – 10 minutes. Preliminary aerosol mass spectrometry results indicate that a significant amount of organic mass is taken up by the acidic seed when sampled at shorter or longer residence times in the flow tube downstream of the engine. Similar ratios of organics to sulfate obtained at both residence times are indicative of a fast reaction time. The organic mass partitioning to the condensed phase scaled with sulfate mass detected indicating diffusion into the particle rather than pure surface condensation. Additionally, for the neutral aerosol particles, a negligible amount of organic uptake was observed. Results from the effect of dilution on partitioning will also be presented. The results suggest that acidic particles will play a role in the partitioning of volatile and semi-volatile organic compounds in the atmosphere.

2AC.12

Heterogeneous Reaction of SOA-Coated Ammonium Bisulfate Aerosol with Gas-phase Ammonia: Impact of SOA Diffusivity. SHOUMING ZHOU, Alex Tevlin, Jennifer Murphy, Jonathan Abbatt, *University of Toronto*

Recent studies have displayed evidence that both laboratory generated and ambient secondary organic aerosols (SOA) behave as highly viscous solid or semi-solid particles rather than well mixed, low viscosity liquids. Since aerosol physical properties, such as phase, morphology and viscosity/diffusivity affect their atmospheric behavior in a number of ways, such as particle formation, evaporation, hygroscopic growth and oxidative aging, there is the need to investigate fundamental properties of SOA.

In this work we will report a study on the diffusivity of SOA formed from reaction of α-pinene with ozone. In particular, we investigate the effect on the rate of the heterogeneous reaction of particulate-phase ammonium bisulfate (ABS) with excess gas-phase ammonia when the particles are coated with SOA. ABS particles are coated with α-pinene SOA in a 1 m3 Teflon chamber and introduced into an aerosol flow tube where the kinetics studies are performed. An Aerodyne Aerosol Mass Spectrometer (AMS) and a quantum cascade tunable infrared laser differential absorption spectroscopy (QC-TILDAS) are used to measure particulate-phase ammonium mass loading and gas-phase ammonia mixing ratios, respectively. Reactive uptake coefficients of ammonia on SOA-coated and uncoated ABS particles under room temperature (296±3K) will be measured. Indications of the SOA bulk diffusivity can be estimated by the constraints of the SOA coating on the heterogeneous reactivity of ABS towards gas-phase ammonia. In addition, the effect of temperature and relative humidity (RH) on the SOA diffusivity will also be presented.

2AC.13

The Effect of Relative Humidity (RH) on Sulfate Aerosol Optical Properties Using Cavity Ring-Down Spectroscopy. XIJING ZHU, Dean Atkinson, *Portland State University*

Inorganic nitrate and sulfate compose a major fraction of the ambient aerosol and there is a strong correlation between visibility degradation and sulfate mass concentration. Inorganic salts are hygroscopic by nature and can grow rapidly in size with increasing relative humidity (RH); the optical properties depend strongly on particle size. In contrast with some other salts, sulfate undergoes 2 ionization steps generating sulfate, bisulfate and sulfuric acid; all of which display quite different hygroscopic behavior. While the pure salts have been studied extensively, the hygroscopicity of bisulfate/ sulfate mixtures is more uncertain. The chemical composition of the aerosol will determine the refractive indices of dry particles and water uptake, thus it is necessary to understand the chemical effect combined with the RH effect for sulfate aerosol and how sulfate aerosol behaves absent the complications of ambient aerosol. Laboratory-generated mixed composition aerosol systems are studied using a Humidity-Controlled Cavity Ring-Down extinction instrument. The extinction coefficients of varying composition salt mixtures of NH_4HSO_4, $(NH_4)_2SO_4$, $NaHSO_4$ and Na_2SO_4 are measured simultaneously at three widely spaced wavelengths (355,532 and 1064nanometer) and three RH conditions (~25%, ~45% and ~80%). Using three wavelengths, the effective radius of the particle size distribution can be derived using the approach derived by O’Neill for Aeronet data[Atkinson et al., 2010]. The RH-dependent radii can then be used to determine the particle hygroscopicity parameter. These experimental results are compared to existing hygroscopic aerosol models with an ultimate goal of better understanding of the behavior of sulfate aerosols in the ambient atmosphere.

2AC.14

Effects of Acidity on the Chemical Composition of Secondary Aerosol from the Isoprene/NOx Photooxidation: Measurements Using an Aerosol Mass Spectrometer. KEI SATO, Akinori Takami, Takashi Imamura, Hong Li, Xuezhong Wang,*National Institute for Environmental Studies*

In order to study the effects of acidity on the chemical composition of isoprene secondary organic aerosol (SOA), we conducted a series of laboratory chamber experiments. In a typical experiment, we injected gaseous SO2 into a laboratory chamber after a substantial amount of SOA is produced by the isoprene/NOx photooxidation. The initial concentrations of isoprene and NO were 2 ppm and 0.5 ppm, respectively. The concentration of SO2 added was 0.2 ppm. When SO2 was injected into the chamber, the concentrations of organic aerosol (OA), nitrate aerosol (NO3), and sulfate aerosol (SO4), measured using an Aerodyne high-resolution aerosol mass spectrometer (AMS), were 38 μg/m3, 4.7 μg/m3, and 0.19 μg/m3, respectively. In one hour after the SO2 addition, the concentrations of OA, NO3, and SO4 increased up to 282 μg/m3, 23 μg/m3, and 47 μg/m3, respectively. Increase in OA concentration would result from acid-catalyzed oligomerization of organic compounds. The OA oxygen-to-carbon (O/C) ratio decreased from 0.58 to 0.49 after the SO2 injection. NO3 observed in this study is predominantly attributed to organonitrates formed from the gas-phase oxidation of isoprene in the presence of NOx. SO4 observed in this study is attributed to a mixture of organosulfates and sulfuric acid. Sulfuric acid is formed from the oxidation of SO2. Organosulfates will then be produced by the acid-catalyzed decomposition of organonitrates. The NO3/OA ratio decreased from 0.13 to 0.08 after the SO2 injection. In contrast, the concentration of gaseous nitric acid, measured using FT-IR, increased from 11 ppb to 16 ppb after the SO2 injection. Sulfuric acid aerosol will catalyze the decomposition of organonitrates on the surface of particles or in the condensed phase to form gaseous nitric acid.

2AC.15

Secondary Organic Aerosol Production from Pinanediol. PENGLIN YE, Neil Donahue, *Carnegie Mellon University*

We have investigated the production of secondary organic aerosol (SOA) from pinanediol (PD) a precursor chosen as a surrogate for first-generation oxidation products of monoterpenes. Monoterpenes have substantial emissions from vegitation, and when they are oxidized some products have very low vapor pressure and thus contribute to SOA formation. Experiments at the CLOUD facility at CERN are focusing on chemistry that can drive formation of new particles in the atmosphere (nucleation), and further oxidation of products such as PD has been proposed as an important contributor to nucleation. Smog-chamber studies allow us to analyze the chemical change and SOA production from PD. We have constrained the SOA mass yield, defined as the mass of SOA formed divided by the precursor consumed. We hypothesize that oxidation products participating in new-particle formation are a subset of those products forming SOA; SOA mass yields are 10-30%, whereas only a few percent of the oxidation products participate in new-particle formation. An objective of this study was to compare the properties of PD oxidation products observed during new-particle formation experiments at CLOUD and properties of SOA derived from PD in smog-chamber experiments to test this hypothesis.

We measured the elemental composition of SOA formed from PD. The average oxidation state of carbon of formed SOA was calculated based on the elemental composition. The value is around -0.6, which is comparable to the most oxidized SOA observed from the direct oxidation of α-pinene. In contrast, composition data from CLOUD show an oxidation state of -0.2 for the smallest molecular clusters, dropping to -0.8 for clusters containing 4 or more oxidized organic molecules. This is consistent with the initial organic molecules in new-particle formation consisting of a highly-oxidized subset of the PD oxidation products, with the subsequent growth of those clusters being driven by compounds that resemble those comprising the bulk SOA formed from PD.

In order to describe organic aerosol chemical evolution, we plot the volatility and average oxidation state of carbon of the oxidized organic products from PD in the two-dimensional volatility-oxidation space (2-D VBS).

2AC.16

SimpleGAMMA: Reduced Mechanism for Aqueous Aerosol SOA Modeling. Joseph Woo, V. FAYE MCNEILL, *Columbia University*

Recently, the McNeill Group developed the Gas-Aerosol Model for Mechanism Analysis (GAMMA), a zero-dimensional kinetic model that couples gas- and aqueous aerosol-phase chemistry for speciated prediction of SOA and organosulfate formation in the aqueous aerosol phase under ambient or laboratory conditions. Results from GAMMA simulations (McNeill et al. ES&T 2012) indicate that, under low-NOx conditions, organosulfate and aqueous-phase SOA formation is dominated by IEPOX ring-opening chemistry. In urban (high-NOx) environments, aaSOA is primarily formed via reversible glyoxal uptake. This suggests that it is possible to model the great majority of aqueous aerosol phase SOA mass using a highly simplified reaction scheme which is computationally efficient and suitable for coupling with larger-scale atmospheric chemistry models. We have therefore developed an abridged version of GAMMA, simpleGAMMA.m, which reduces the total number of tracked aqueous species from ~75 to 5 and the number of species partitioning between the gas and aqueous aerosol phases to 2 (glyoxal and IEPOX). Agreement (to within 40% of predicted SOA mass) between simpleGAMMA and the full version of GAMMA is observed under all conditions tested (between pH 1-4 and RH 40-80%), after 12 hours of simulation.

2AC.17

Gas and Particle Phase Chemical Composition of Marine Emissions from Mediterranean Seawaters: Primary Aerosol Particles and Formation of Secondary Organic Components. J. PEY, H. Langley DeWitt, Brice Temime-Roussel, A. Même, E. Sarrasin, C. Rose, E. Freney, M. Hervo, B. Charriere, R. Sempere, K. Sellegri, B. D'Anna, Nicolas Marchand, *Aix-Marseille Université-CNRS, LCE FRE 3416*

Marine emissions are among the largest source of secondary organic aerosols (SOA) at a global scale. Whereas physical processes control the primary production of marine aerosols, the biological activity is responsible of most of the organic components released from marine sources, potentially transformed into SOA when exposed to atmospheric oxidants. The Mediterranean atmosphere displays important concentrations of SOA (El Haddad et al. 2011), especially in summer, when atmospheric oxidants and photochemical activity are at their maximum. Such elevated concentrations of SOA are unclear in origin but they are mainly from contemporary sources (Minguillon et al. 2011, El Haddad et al, 2011).

In view of this, the fingerprint of marine emissions in terms of gas and particle phase chemical composition is desirable. To this end, a number of smog chamber experiments were conducted on marine aerosols produced from bubble bursting processes. Different aging conditions were tested. The experiments were carried out in Lyon (France) in November-December 2012, in the context of the SAM (Source of marine Aerosol particles in the Mediterranean atmosphere) project. The marine emissions and their transformations inside the chamber were registered by a multi-instrumental high-time resolution set-up. Thus, aerosol concentrations and their physical characteristics were controlled by means of Scanning Mobility Particle Sizers; gas-phase composition of volatile organic compounds was determined by using Proton Transfer Reaction Time-of-Flight Mass Spectrometers (H3O+ and O2+modes); and aerosol chemical composition was obtained from High Resolution Time-of-Flight Aerosol Mass Spectrometers.

The preliminary results display a high abundance of halogenated volatile organic species such as methylcloride, ethylcloride and vinylcloride, as well as different (with low molecular weights) volatile organic compounds.

References

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2AP.1

Predicting Porosity of Dust Cakes under General Conditions Via Brownian Simulation. GUSTAF LINDQUIST, Christopher Hogan Jr., David Y. H. Pui, *University of Minnesota*

The capture efficiency and pressure drop resulting from dust cake accumulation is strongly dependent on that dust cake's porosity. Many papers have been published describing this dependence, but limited work has been done to predict the porosity in generalized circumstances. Porosity can be a function of many parameters, such as fluid temperature, fluid viscosity, particle size, particle density, and fluid face velocity. These parameters can be reduced to two dimensionless quantities: the diffusive Knudsen number, and the "thermal energy ratio", which is the ratio of the kinetic energy with thermal energy of a particle. Using a Brownian Dynamics simulation with these two numbers as input parameters, it is possible to create virtual dust cakes and model the resulting porosity and structure. By running such a simulation over a grid of these input parameters, a model can be constructed predicting the porosity as a function of said parameters.

2AP.2

Observing Water Microdroplet Freezing below "Homogenous Nucleation Temperature Limit" with Ultrafast X-ray Laser at LCLS. HARTAWAN LAKSMONO, Trevor A. McQueen, Jonas A. Sellberg, Congcong Huang, N. Duane Loh, Raymond G. Sierra, Dmitri Starodub, Dennis Norlund, Martin Beye, Daniel P. DePonte, Andrew Martin, Anton Barty, Jan Feldkamp, Sebastien Boutet, Garth J. Williams, Michael J. Bogan, Anders Nilsson, *SLAC National Accelerator Laboratory*

Water is arguably the most important substance in our life, environment, and industry. In addition, water is also fascinating due to many anomalous physical properties, and many phases of solid it forms. Although many have performed experiments to understand water and its phase transition, there is still a region, below "homogenous nucleation temperature limit", ~232K, where it is not well understood due to rapid crystallization complicating experimental studies. In addition, understanding phase transition within this region is important to predict cloud properties and phases of water in the interstellar space. Our knowledge of water freezing within this region is limited because there are only a few experiments performed. With a recent development in an ultrafast and ultrabright X-ray Free Electron Laser at the Linac Coherent Light Source (LCLS), many researchers have been able to probe matter in high resolution by taking snapshots using femtoseconds long X-ray pulses. Here we will present our ongoing effort to understand phase transition below the "homogenous nucleation temperature limit" from our recent wide angle X-ray scattering experiment using a specialized setup to take advantage of the X-ray laser at LCLS.

2AP.3

Investigation of Poissonian Sampling Behavior for Nanometer-Sized Aerosols. BRIAN DAMIT, Chang-Yu Wu, Meng-Dawn Cheng, *University of Florida*

The Poisson distribution is traditionally believed to describe how aerosols are sampled. Given a constant aerosol concentration, it is assumed that a Poisson process describes the fluctuation in the measured concentration because aerosols are stochastically distributed in space. Practically, the Poisson distribution relays confidence in a concentration measurement. Recent studies, however, have demonstrated that sampling of micrometer-sized aerosols has non-Poissonian behavior with positive correlations. The validity of the Poisson assumption for nanometer-sized aerosols has not been examined and thus was tested in this study. Four particle sizes - 10 nm, 25 nm, 50 nm and 100 nm - were first sampled from indoor air with a DMA-CPC setup to obtain a time series of particle counts. Truncated time series which showed constant underlying concentration were found and five metrics were calculated from the data: pair-correlation function (PCF), time-averaged PCF, coefficient of variation, probability of measuring a concentration at least 25% greater than average, and posterior distributions from Bayesian inference. To identify departures from Poissonian behavior, these metrics were also calculated for 1,000 computer-generated Poisson time series with the same mean as the experimental data and then compared with the experimental metrics.

For nearly all comparisons, the experimental data fell within the range of 80% of the Poisson-simulation values. Essentially, the metrics for the experimental data were indistinguishable from a simulated Poisson process thus supporting the validity of the Poisson assumption for nanometer-sized aerosol sampling. Brownian motion, which is more influential for nanometer-sized aerosols, may explain the Poissonian behavior observed here and not for larger aerosols. Although the Poisson assumption was confirmed to be valid in this study, it must be carefully applied as the results here do not definitively prove its use in all aerosol sampling situations.

2AP.4

Q-Space Analysis of Scattering by Particles of Arbitrary Shape. CHRIS SORENSEN, William Heinson, Amit Chakrabarti, Evgenij Zubko, *Kansas State University*

Q-space analysis of light scattering by particles involves plotting the scattered intensity versus the scattering wave vector q on a double log plot. The analysis uncovers power law descriptions of the scattering for a wide range of particle morphologies including dielectric spheres of arbitrary size and refractive index (Mie scattering), fractal aggregates and irregularly shaped particles such as dusts. Conventional plotting versus the scattering angle yields non-descript and indistinguishable curves. Here we demonstrate the efficacy of the Q-space method for four different types of randomly and strongly perturbed spheres. DDA was used to calculate the scattered intensity as a function of the scattering angle for these perturbed spheres at three different refractive indices. Q-space analyses uncovered power laws and the powers were different than the Porod value of -4 obtained for the structure factor of the particles.

2AP.5

A Computationally Efficient Multi-particle Sintering Model. VIVEK SHAH, Pratim Biswas, *Washington University in St. Louis*

In high temperature aerosol processes, sintering determines the physical characteristics, and hence the final application of the synthesized aggregate. A better estimate of the properties of the synthesized material can be obtained by simulating the final properties of sintered aggregate. Although there are various models for sintering of multiple particles, the models are either too simplistic such as Koch and Friedlander model (Koch and Friedlander 1990) or are computationally intensive such as molecular dynamics model.

In this work a multi-particle geometric sintering (MPGS) model is developed which is computationally efficient and hence can be used to simulate the sintering of large number of particles. The MPGS models extends neck radius based model (Cho and Biswas 2006; Xie 2008) whose application has been limited because of the lack of a suitable model for multiple particles. The MPGS model is compared to the Koch and Friedlander model for predicting the normalized surface area. The MPGS model is then applied to test cases of linear agglomerates and fractal agglomerates to study the effect of number of particles in the cluster. The surface area decrease has been shown to be dependent on the number particles in the agglomerate in contrast to Koch and Friedlander model. Finally the model is applied to a film of particles to study the effect of sintering on the morphology. A good estimate of the morphology of the film which consists of 10000 particles or more is easily obtained because of the computational simplicity of the model.

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2AP.6

Theoretical and Experimental Investigation of Particle Formation from Evaporating Microdroplets. Mohammed Boraey, Alberto Baldelli, REINHARD VEHRING, *University of Alberta, Canada*

Diffusion controlled particle formation from evaporating microdroplets was described using a numerical model which is based on a newly developed normalization of the diffusion equation in one-dimensional spherical coordinates. Radial concentration profiles as a function of time were calculated for isothermally evaporating multicomponent solution and suspension microdroplets. The model results were expressed in terms of non-dimensional process parameters such as Péclet number, normalized drying time, and normalized concentration. The numerical results were fitted with analytical expressions so that the results can be applied without programming. Final dry particle properties such as particle diameter, particle density, and aerodynamic diameter were predicted. For hollow particles, which are formed under conditions characterized by a high Péclet number, the shell thickness was approximated successfully. The model results were found to be in good agreement with published results, and were compared to experimental results generated using a novel monodisperse droplet chain setup. Monodisperse aqueous microdroplets were generated in a diameter range of 10 – 50 micro-meter, using a piezo-ceramic droplet-on-demand dispenser at frequencies < 100 Hz. The droplets were injected into a laminar gas flow with controlled temperature and relative humidity, creating an evaporating, widely spaced droplet chain. The droplet chain was illuminated by a pulsed diode laser and an argon ion laser to determine microdroplets diameter, spacing, and velocity. Dried microparticles were sampled from the flow onto membrane filters and subsequently analyzed by ultramicroscopy. The dry particles were found to be monodisperse, possessing nearly identical morphology. Geometric particle diameter and particle density as a function of process conditions were determined.

2AP.7

Aggregation during the Crossover from Ballistic to Diffusive Motion. William Heinson, Chris Sorensen, AMIT CHAKRABARTI,*Kansas State University*

We investigate, through simulation, a system of aggregating particles in the free molecular regime that undergoes a crossover from ballistic to diffusive motion. As the aggregates grow, the aggregate mean free path becomes smaller and the motion between collisions becomes more diffusive. From growth kinetics we find that when the ratio of the mean free path to the aggregate nearest neighbor separation reaches of the order of unity , a crossover to diffusive motion occurs. This ratio, called the nearest neighbor Knudsen number, becomes an important parameter in understanding aerosol aggregation in the free molecular regime.

2AP.8

The Optical Behavior of Soot as a Function of Relative Humidity.

YIYI WEI, Qing Zhang, Jonathan E. Thompson, *Texas Tech University*

Black carbon contributes significantly in absorbing visible solar radiation in the atmosphere and leads to atmospheric warming. Yet, the extent to which this occurs depends on particle morphology and mixing state. In this work, we have explored the optical properties of kerosene soot under different humidity conditions ranging from 10% RH to 95% RH. Optical parameters were measured via photoacoustic spectroscopy and the albedometer that has previously been developed in our laboratory. In addition, the effect of soot particle aging was considered.

2AP.9

Numerical Evaluation of Fuch's Bipolar Charging Theory Using Stochastic Ion Mass and Mobility in a Non-Equilibrium Neutralizer.

JEAN DE LA VERPILLIERE, Jacob Swanson, Adam M Boies, *University of Cambridge*

The need for portable, non-hazardous, bipolar aerosol chargers has led to the recent development and commercialization of soft x-ray and AC corona neutralizers. In past work we have demonstrated that x-ray and AC corona neutralizers led to different charging characteristics relative to radioactive charging. Measurement of ions from different neutralizers indicated that each approach produces ions with different electrical mobility distributions, but the standard Fuchs charging theory failed to explain the observed charge distribution discrepancies between the neutralizers. The objective of this work is to investigate two modifications to the existing theory in order to improve the understanding of the mechanisms responsible for charging inside three commercially-available neutralizers.

The first modification considers that steady state is not reached within the neutralizer due to ion diffusion losses to the neutralizer wall. Transport equations for particles of each polarity and for ions are derived from charge conservation equations, and solved using a forward numerical method. An existing model developed by Alonso and Alguacil (2003) is extended to neutralizers of more complex geometries, relying on different ionizing sources.

The second modification incorporates a stochastic modeling approach to reflect the variety of ion mobilities and masses that are known to exist in any bipolar charging environment. Distributions of ion mass and mobility are incorporated from past experimental measurements and the Fuchs charging theory is numerically solved for multiple iterations using a Monte Carlo approach. The ion-aerosol attachment coefficients are derived stochastically and the effect of multiple ion species is evaluated relative to standard deterministic charging models.

Results of the numerical simulations are compared to the experimental trends to determine whether the physical explanations used to justify the theoretical modifications reduce the discrepancies observed between neutralizers.

2AP.10

Identification of Airborne Particles by Forward Light Scattering. PAUL LANE, Matthew Hart, Brian Saar, Jay Eversole, *Naval Research Laboratory*

Environmental, health and security concerns are driving our interest in techniques to characterize airborne particles in real time. The primary cause of attenuation of incident radiation in aerosols is scattering, which is a function of the complex refractive index and the size and shape of particles. Light scattering varies significantly over wavelengths near an absorption maxima, because the complex refractive index is changing rapidly over this interval. This feature can be exploited to determine the absorption peak(s) of a particle, and hence, indicate its composition. Using silica particles as a test case, we show that we can differentiate bare particles from those thinly coated by an organic dye with an absorption maxima using three incident lasers selected with wavelengths slightly above and below this peak. Experimental results on spherical and nonspherical particles will be presented and compared to scattering theory.

2AP.11

Spectro-microscopic Characterization of Physical Properties and Phase Separations in Individual Atmospheric Particles.RACHEL O'BRIEN, Bingbing Wang, Steven Kelly, Nils Lundt, Scott A. Epstein, Amanda MacMillan, Yuan You, Alexander Laskin, Sergey Nizkorodov, Allan Bertram, Ryan Moffet, Mary Gilles, *LBNL and University of the Pacific*

The phase state and liquid-liquid phase separations of ambient and laboratory generated aerosol particles were investigated using (1) scanning transmission x-ray microscopy/near-edge x-ray absorption fine structure spectroscopy (STXM/NEXAFS) coupled to a relative humidity (RH) controlled in-situ chamber and (2) environmental scanning electron microscopy (ESEM). The phase states of the particles were determined from measurements of their size and optical density. A comparison is made between the observed phase states of ambient samples and of laboratory generated aerosols to determine how well laboratory samples represent the phase of ambient samples. In addition, liquid-liquid phase separations in laboratory generated particles were investigated. Preliminary results showing that liquid-liquid phase separations occur at RH’s between the deliquescence and efflorescence points and that the organic phase surrounds the inorganic phase will be presented. The STXM/NEXAFS technique provides insight into the degree of mixing at the deliquescence point and the degree of phase separation for particles of atmospherically relevant sizes.

2AP.12

Molecular Dynamics Simulations of the Mass Accommodation of Dicarboxylic Acids and Other Organic Compounds.

Jan Julin, ILONA RIIPINEN, *Stockholm University*

The condensational growth of atmospheric aerosol particles is limited by their ability to accommodate incoming molecules of the various condensing vapor species. This ability is quantified by the mass accommodation coefficient, which gives the fraction of incoming molecules that will remain in the condensed phase. Molecular dynamics (MD) simulations provide a straightforward method to determine the mass accommodation coefficient, since in MD the trajectories of individual molecules can be followed as a function of time.

We will present MD mass accommodation simulation results of several organic species on surfaces consisting of the same species as the incoming vapor molecule. The species studied include two dicarboxylic acids, namely adipic and succinic acid, and a simple polycyclic aromatic hydrocarbon, naphthalene. The interaction potential used was the OPLS-AA force field, and the simulations were performed at a constant temperature of T=313.15 K. The studied surfaces include both planar surfaces and nanosized droplets. As the simulation temperature is below the melting points of the studied species, we also studied separately cases where the condensed phase was either a subcooled liquid or a solid.

The following simulation setup was used: at the beginning of a simulation an incoming molecule is generated at roughly 2 nm above the target surface, and the simulation is then run for 80 ps. By simulating one hundred of such incoming molecules for each studied surface, the value of the mass accommodation coefficient can be determined by studying the fates of the incoming molecules at the surface. The simulations resulted in mass accommodation coefficients close to unity.

2AP.13

Composition and Mixing Timescale Measurements of Biomass-burning Aerosol and Secondary Organic Aerosol from alpha-pinene Using Two Particle Mass Spectrometers.

ADAM AHERN, Ellis Shipley Robinson, Daniel S. Tkacik, Rawad Saleh, Robert J. Yokelson, Albert A. Presto, Allen Robinson, Neil Donahue, Ryan Sullivan, *Carnegie Mellon University*

The composition of atmospheric aerosol can change significantly as freshly emitted aerosol is processed in the atmosphere. The mixing of secondary compounds with the existing aerosol cores can lead to changes in the aerosol’s properties, such as its hygroscopicity and volatility. The insoluble core can also provide important information for source apportionment, and affect the optical properties of these internally-mixed aerosols.

During the fourth Fire Lab at Missoula Experiments (FLAME IV), we investigated the mixing timescales of biomass smoke with biogenic SOA. Smoke from biomass burning was used to fill two environmental chambers. alpha-pinene-derived secondary organic aerosol (SOA) formed via ozonolysis in a separate Teflon bag was introduced to the larger smoke-filled environmental chamber and allowed to mix while being simultaneously monitored by two particle mass spectrometers.

We probed the mixing timescale using a Light-Scattering Aerosol Mass Spectrometer (LS-AMS), and a new Single-Particle Mass Spectrometer (SP-MS). These instruments use thermal desorption/electron ionization, and laser ablation, respectively, for aerosol compositional analysis. Particle clustering algorithms were used to identify homogeneously nucleated SOA particles from the single-particle mass spectrometry data, to observe their mixing dynamics with the primary smoke aerosol. Although the size distribution from the AMS was inconclusive with respect to mixing, tracer ions K^+ and $C_2H_3O^+$ were used to identify some smoke particles and SOA, respectively. The ensemble aerosol mass spectrum measured by the AMS changed rapidly to reflect the addition of the nucleated SOA and the SP-MS measured particles that contained both K^+ and $C_2H_3O^+$ soon after mixing, suggesting rapid mixing. However, particles containing the SOA tracer and devoid of K^+ persisted for several hours.

2BA.1

Evaluation of an Ion Capture Device for Determination of Aerosolized Venezuelan Equine Encaphailitis Virus and a Novel Method for Absolute Particle Count Determination. JULIAN GORDON, Prasanthi Gandhi, Tiffany Sutton, Karen Pongrance, Jerold Bottiger, *Inspirotec LLC, Chicago, IL*

Ionic capture devices have had widespread use for air cleaning. We are exploring the use of a miniature device (cICD) for capture and detection of allergens, bacteria and viruses. Here we present data for its use in detection of gamma-irradiated inactivated Venezuelan Equine Encephalitis Virus. Samples are collected on removable silk envelopes covering the entire electrode. As references, data was obtained by extraction from the electrodes directly, and with a sampling filter run in parallel. Capture was quantitated by q-RT-PCR. Controlled aerosols were released into an environmental chamber and particle size and concentration were held constant during 30 minutes. There is a possibility that irradiation damage to the viral RNA rendered it un-amplifiable. An alternative method of evaluation was devised based on limiting dilution conditions where amplification occurred in some, but not all, PCR reactions. The occurrence of amplification is a stochastic event determined by Poisson distribution. We make the approximation that, when the proportion of reactions giving amplification was less than 50%, there was either 0 or 1 amplifiable particle per reaction. From that, the average number of amplifiable molecules may be calculated. Using this metric, the LOD for the sampler is 0.06 amplifiable particles per liter and for the reference filter it is 1.4. The higher LOD for the reference filter is simply accounted for by the fact that the extraction is done in 10 times the volume compared with the electrodes. Capture efficiencies and LOD's from the disposable and the entire electrode were equivalent. The number of amplifiable particles is considerably lower than the number calculated from the calibration based on the original PFU. The method provides a method for determining an absolute amplifiable particle count, independent of any calibration. The cICD offers a simple, low cost, silent method of efficiently determining airborne viruses.

2BA.2

Evaluating Bioaerosol Transport Using Unique DNA-Barcoded Aerosol Test Particles and Passive Sampling. Ruth N. Udey, Elizabeth K. Wheeler, A. Daniel Jones, GEORGE R. FARQUAR, *Lawrence Livermore National Laboratory*

Aerosol transport monitoring is important for detecting the presence of airborne contaminants and tracking their fate in populated environments where they may adversely affect human health. We have developed novel aerosol test particles containing DNA barcodes for evaluating aerosol transport that are customizable and safe for human exposure. The generation methods enabled size tuning of the particles to accurately mimic bioaerosols. The addition of different DNA molecules as unique particle identifiers created distinctive particle types for detection of simultaneous or sequential aerosol releases in the same test environment. These customizable aerosol test particles will provide vital experimental feedback for evaluating atmospheric and particle transport models in populated environments.

Saccharide food additives approved by the FDA for human exposure (e.g. maltodextrin) were the bulk materials for these novel test particles. The non-coding DNA barcodes were also safe for human contact and yielded customized test particles specifically detected using quantitative real-time polymerase chain reaction (QRT-PCR) assays. A commercial spray dryer was used to generate the test particles in gram-scale quantities, and the resulting particle size-distributions were tunable between 1 and 10 micrometers by varying solution concentrations and production parameters.

These aerosol test particles were successfully aerosolized, collected, and detected using QRT-PCR during several atmospheric release tests. Particles were collected actively on filters using dry filter unit aerosol samplers, as well as passively on common materials, including glass slides, paper, and cotton t-shirts. Passive sampling provided alternate aerosol collection methods that prevented building airflow alteration, which was observed when active sampling methods were employed.

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2BA.3

Fluorescence of Bioaerosols: Concentrations and Optical Properties of Relevant Molecules Needed for Modeling Emission from Bacteria. STEVEN HILL, Yong-Le Pan, Chatt Williamson, Joshua Santarpia, Hanna Hill, *US Army Research Laboratory*

Fluorescence is useful for detection and partial classification of bioaerosols, especially in flow-through single-particle systems. A problem in modeling the fluorescence of bioaerosols is in estimating/finding the concentrations and optical properties of the fluorescent and other absorbing molecules in bioaerosols. We have extracted/estimated from the microbiology and biochemistry literature the concentrations, absorption and fluorescence spectra, and fluorescence quantum yields of the main absorbing and fluorescing primary metabolites and macromolecules in bacteria. Included are amino acids and nucleic acids (and polymers of these: proteins, DNA, RNA); coenzymes (nicotinamide adenine dinucleotides, flavins, vitamers of B6); quinols; and calcium dipicolinate. Secondary metabolites are not included. The uncertainties in the numbers extracted range from less than 10% (e.g., for the molar absorptivity of DNA) to 20 fold or more (e.g., for the concentrations of several metabolites in bacteria when the growth conditions are unknown). We also describe a simple model that uses these concentrations and optical properties to simulate the emission from particles composed of bacteria, viruses or proteins. The bioparticles are modeled as homogeneous spheres. Calculated total fluorescence cross sections for particles excited at 266, 280, and 355 nm are compared with measured values from the literature for several bacteria, bacterial spores and albumins. The calculated 266-nm and 280-nm excited fluorescence is within a factor of 3.5 of the measurements for the vegetative cells and proteins. However, the measured fluorescence of spores is overestimated by a factor of 10 or more, suggesting that in spores the fluorescence of tryptophan is significantly quenched.

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2BA.4

Performance of Cascade Impactors for Sampling Aerosolized Viruses. MICHAEL SCHUIT, Jamie Kline, Kristin Bower, Paul Dabisch, *NBACC*

INTRODUCTION: Many studies have been published on the effects of infection with aerosolized filoviruses in animal models to support medical countermeasure evaluation. In inhalation studies, knowledge of the particle size distribution (PSD) of an inhaled aerosol is critical since it is known to affect regional deposition in the respiratory system and potentially disease presentation. However, the PSDs of the aerosols generated in previous inhalation studies with filoviruses were not routinely measured and reported, and no studies were identified which characterized the performance of different particle sizing instruments with airborne filoviruses. Therefore, the aim of the present study was to assess the accuracy of two different cascade impactors for estimating the PSD of airborne filoviruses.

METHODS: Ebola virus stocks diluted in media and containing 100-nm fluorescent polystyrene latex beads as a non-viable tracer were aerosolized in a small test system and sampled with two different impactors – a Mercer cascade impactor and a micro orifice uniform deposit impactor (MOUDI). Viral titers were determined by microtitration and tracer concentrations determined with a fluorescence reader. The fluorescence values and virus titers for each stage were used to estimate the particle size distribution of the sampled aerosols, and the ratio of fluorescence to the viral titer was used as a measure of the relative losses in viral infectivity from stage to stage.

RESULTS AND CONCLUSIONS: For either impactor, no significant difference was observed in the particle size distribution calculated from the viral titers and fluorescence measurements and the ratio of fluorescence to viral titer did not change significantly from stage to stage, suggesting that viral infectivity was not affected by the changes in impaction velocity that occur from stage to stage. These results demonstrate the validity of the Mercer cascade impactor and the MOUDI for estimating the PSD of airborne Ebola virus in animal inhalation studies to support countermeasures development.

2BA.5

A Multiparameter Bioaerosol Spectrometer (MBS). Paul Kaye, Warren Stanley, Edwin Hirst, MARTIN GALLAGHER, Niall Robinson, Ian Crawford, *University of Hertfordshire*

The real-time in situ detection of airborne biological particles is required in wide range of fields from military and counter-terrorism agent detection through to atmospheric cloud microphysical research and air quality monitoring. To help meet this requirement, the authors had previously developed the WIBS (Wideband Integrated Bioaerosol Sensor) instrument that has been increasingly used in atmospheric and environmental research studies and is now available commercially from Droplet Measurement Technologies Inc. (Boulder, CO, USA). Here, we report on a new instrument, the Multiparameter Bioaerosol Spectrometer (MBS), that has been developed from the WIBS technology to help maximise the potential of combining particle fluorescence spectroscopy with high-resolution light scattering analysis in the detection and classification of airborne biological particles.

Whereas the WIBS instrument records intrinsic particle fluorescence over just two wavebands, 310-400nm and 420-650nm (corresponding to the peak emissions from bio-fluorophores tryptophan and NADH), MBS records the fluorescence over eight channels from approximately 310 to 640nm. This improves discrimination of biological particles from ‘interferent’ non-biological particles that may exhibit similar fluorescence properties. Similarly, while WIBS uses a simple quadrant detector to assess light scattering asymmetry and hence particle shape, the MBS uses two 512-pixel CMOS detector arrays to record high-resolution sections through the particle’s spatial light scattering pattern, potentially yielding data on both the macroscopic shape and surface characteristics of the particle. Again, this can enhance the prospects of particle classification and reduce false-positive bio-particle detection.

The MBS records the size, 8-channel fluorescence spectrum, and high-resolution particle scattering data from up to 100 particles/s, with additional particles counted only. Development of clustering algorithms to process these multiparameter data are continuing, but examples of raw MSB data from a variety of biological and non-biological particles will be given together with initial examples of how this data may be processed to yield particle classification.

2BA.6

Investigation of ATP-based Bioluminescence Effectiveness for Bioaerosol Quantification. TAEWON HAN, Ting Cai, Kelsey DuBois, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

There has been continuous interest in the development of methods for rapid quantification of biological agents sampled from ambient environments. In addition to numerous existing methods for analyzing bioaerosol samples, including impedimetry, piezoelectric biosensors, immunological methods, and nucleic acid based assays, an adenosine tri-phosphate (ATP)-based bioluminescence method could add another useful tool for rapid monitoring of microbial contamination. Here, the amount of bioluminescence is proportional to bioaerosol concentration. In our previous studies, we found a time window when the bioluminescence signal is consistent and is not affected by reagent decay. However, there is no information available on how the intensity of ATP-based bioluminescence reactions is affected by bioaerosol sampling methods, e.g., filtration, impingement or electrostatic precipitation. Thus, to further investigate the applicability of this method for bioaerosol applications, we analyzed the ratio of the relative luminescence units (RLU) of the reaction indicative of the total ATP content to cell counts by microscopy for different sampling methods: (1) Button Aerosol Sampler used with polycarbonate, PTFE, and cellulose nitrate filters, (2) BioSampler with 5 mL and 20 mL of collection liquid, and (3) our newly developed Electrostatic Precipitator with Superhydrophobic Surface (EPSS).

The results show that microorganism species commonly used as test particles in bioaerosol research, such as Escherichia coli, Bacillus subtilis, and Pseudomonas fluorescens, may sustain a varying degree of stress and damage depending on the sampling method. All three samplers were tested at three different sampling periods (5, 15 and 60 minutes), respectively. Our findings also showed that extraction efficiency for each filter was crucially important and needs to be investigated separately for each filter type. The results of this study encourage the application of ATP-based bioluminescence in bioaerosol research and provide guidance for achieving maximum sensitivity when using different sampling techniques.

2BA.7

Real-Time Characterization of Fungal Aerosol. Sampo Saari, Jacob Mensah-Attipoe, Anniina Hellsten, Pertti Pasanen, TIINA REPONEN, Jorma Keskinen, *Tampere University of Technology*

Airborne fungal material can cause various health effects for humans and animals both in indoor and outdoor environments. Typically airborne fungal material consists of large spores, but sometimes there are also smaller particles, called fragments. Sub-micrometre fungal fragments may have stronger adverse effects than fungal spores because they can penetrate and deposit deeper into the respiratory tract. Fungal emission can be dynamic and depends on several factors, including air velocity, relative humidity, temperature, growth medium, fungal species, ventilation, human activity and the age of mould growth. Laser induced fluorescence (LIF) is a potential real-time method to detect bioaerosols and distinguish them from non-biological particles. The LIF is an effective technique for detecting biological molecules such as tryptophan, NADH and flavins that are present in microbial cells. In our previous study, we demonstrated that bacterial and fungal spores may be distinguished through the dissimilar fluorescence spectra. The results indicate also that NADH concentration is low both in bacterial and fungal spores. In this study, we used two LIF based real-time instruments BioScout (Environics Oy) and UV-APS (TSI, Inc.) to observe the release of fungal spore and to study their fluorescence properties. We used a dry generation device called the Fungal Spore Source Strength Tester (FSSST) to release fungal particles. We studied effects of flow rate, fungal species, growth medium and age of the culture on the release process and the size distribution of fungal particles. The results show that release of both fungal spores and fragments increased with higher air velocity. There were significant variations in the concentrations and size distributions of released fungal particles between the species and the age of the culture. The LIF based real-time instrument may be a potential tool to analyse fungal spore emission sources in both indoor and outdoor environments.

2BA.8

A New Concept for Single Bioaerosol Particle Material Characterization. MATTHEW BERG, *Mississippi State Univeristy*

This work will present the development of a new photothermal technique to gather information related to a particle's composition simultaneously with an image of it. Here, particles flowing in a sample stream are illuminated by a pulsed ultraviolet (UV) laser. This light combines across a detector with the light forward scattered by the particle. The resulting interference pattern constitutes a digital hologram, from which an image of the particle is reconstructed computationally. To obtain composition information, the particle is illuminated by the UV light twice in rapid succession while also being exposed to light from a pulsed infrared (IR) laser. Two holograms are thus formed on the detector. Performing the computational reconstruction on this double-exposed hologram yields an image of the particle superimposed with interference fringes. The fringes originate from any change in the particle's physical state that occurs between the two UV pulses. Absorption of the IR light by the particle may cause photothermal expansion, and thus register as fringes in the reconstructed image. Since the degree of expansion depends on the light absorbed, the fringes indirectly convey information related to the particle material.

2BA.11

Use of Air-Sampling-Culturing, Free Settling and Filtration Revealed Strikingly Different Bacterial Aerosol Species through High Throughput Gene Sequence. MINGZHEN LI, Kai Wei, Yunhao Zheng, Jing Li, Zhuanglei Zou, Maosheng Yao, Xu Zhencheng, *Peking University*

Bacterial types in the air are important in many aspects including health and climate. In this work, we employed Andersen impactor-sampling-culturing, free settling and filtration to study the bacterial aerosol species in both indoor and outdoor environments with different climatic conditions. The experiments were conducted in 4 outdoor and 2 indoor environments in Guangzhou and Haikou, China. High throughput gene sequence was performed for CFU samples pooled together from culturing and free settling, respectively, over one week and for one filter sample (24 hours at a flow rate of 100 L/min) collected on a particular day during the week.

Our preliminary data showed that regardless of environments use of high volume filtration only obtained about half bacterial species types as compared to those obtained by culturing and free settling methods. For outdoor environments, it seems that culturing and free settling performed equally well in most cases with respect to the bacterial species profiling, while culturing turned to perform better than free settling in indoor environments. Our statistical analysis at 97% confidence level also indicated that use of culturing and free settling also resulted in higher values of Shannon index (bacterial diversity) and Ace (bacterial richness). In this work, we have detected more than 1000 bacterial species in both indoor and outdoor environments, and these two environments were found to exhibit different distribution patterns in addition to different species present in respective environments. Contrary to traditional belief, this study showed that filtration sample would yield less bacterial species than culturing methods employed here through high throughput gene sequence. In addition, our data also suggest that indoor and outdoor environments have their different bacterial emission sources.

Key words: Bacterial species, Culturing, Filtration, Indoor, Outdoor and High throughput gene sequence

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2BA.12

Enhancing Bioaerosol Collection by Andersen Impactors Using Mineral-Oil-Spread Agar Plate. Maosheng Yao, Zhenqiang Xu, KAI WEI, Mingzhen Li, Fangxia Shen, *Peking University*

As a bioaerosol sampling standard, Andersen type impactor is widely used since its invention in 1950s, including the investigation of the anthrax attacks in the United States in 2001. However, its related problems such as impaction and desiccation stress as well as particle bounce have not been solved. Here, we improved its biological collection efficiencies by plating a mineral oil layer (100 µL) onto the agar plate. An Andersen six-stage sampler and a BioStage impactor were tested with mineral-oil-spread agar plates in collecting indoor and outdoor bacterial and fungal aerosols. The effects of sampling times (5, 10 and 20 min) were also studied using the BioStage impactor when sampling environmental bioaerosols as well as aerosolized Bacillus subtilis (G+) and Escherichia coli (G-). In addition, particle bounce reduction by mineral-oil-plate was also investigated using an optical particle counter (OPC). Experimental results revealed that use of mineral-oil-spread agar plate can substantially enhance culturable bioaerosol recoveries by Andersen type impactors (p-values<0.05). The recovery enhancement was shown to depend on bioaerosol size, type, sampling time and environment. In general, more enhancements (extra 20%) were observed for last stage of the Andersen six-stage samplers compared to the BioStage impactor for 10 min sampling. When sampling aerosolized B. subtilis, E. coli and environmental aerosols, the enhancement was shown to increase with increasing sampling time, ranging from 50% increase at 5 min to ~100% at 20 min. OPC results indicated that use of mineral oil can effectively reduce the particle bounce with an average of 66% for 10 min sampling. Our work suggests that enhancements for fungal aerosols were primarily attributed to the reduced impaction stress, while for bacterial aerosols reduced impaction, desiccation and particle bounce played major roles. The developed technology can readily enhance the agar-based techniques including those high volume portable samplers for bioaerosol monitoring.

Key words: Impactor, Bioaerosol, Collection, Mineral oil

2BA.13

Non-Human Primate Animal Model Development Using Aerosolized Cowpox Virus.

Matthew Lackemeyer, KYLE BOHANNON, Reed Johnson, Peter Jahrling, *NIAID*

Poxviruses remain a threat to public health due to zoonotic infections with cowpox and monkeypox viruses occurring naturally within Europe and Africa and the potential for an intentional release pertaining to a bioterror event. In order to improve public health preparedness and medical countermeasure development for poxviruses, a well characterized nonhuman primate (NHP) model is. Aerosolization represents the most natural route of infection for poxviruses and the United States Food & Drug Administration (FDA) requires all progression of animal model development to mimic the natural course of the disease. Particle size and deposition play a key role in disease course, presentation and time to death. In general, aerosol generation of small particles (<3 um) penetrate deep within the alveolar region, whereas aerosolization of large particles (7-10 um) move within the nasopharyngeal region, depositing within the nose, mouth, pharynx and larynx. Particles that are intermediate in size (3-6 um) will deposit within the tracheobronchial region. Controlling and evaluating the site of infection will further refine the NHP model and thus facilitate countermeasure development. The disease course following inoculation with two nebulizers generating variable particle sizes containing cowpox virus within rhesus monkeys will be discussed and evaluated for its relevance for accurately reflecting human smallpox.

2CA.1

In-situ Measurements of Particle Size and Volatility in a Traffic Tunnel.

ALBERT A. PRESTO, Xiang Li, *Carnegie Mellon University*

Motor vehicles are an important source of gas- and particle-phase pollutants to the atmosphere. Emissions from motor vehicles include CO, NOx, volatile organic compounds (VOCs), and particulate matter (PM). Direct PM emissions from vehicles are dominated by the carbonaceous fraction in the form of organic aerosol (OA) and carbon soot (EC/BC). These PM emissions are dominated by ultrafine particles (diameters smaller than 100 nm).

Emissions from vehicular sources can be measured with dynamometer studies, near-road or on-road measurements, and tunnel studies. Tunnel studies hold the unique advantage that primary emissions are largely captive, with minimal mixing from outside air. This poster presents measurements of particle and gas-phase pollutant concentrations from a traffic tunnel in Pittsburgh, PA. Gas-phase measurements include NOx, CO, and CO2. Particle-phase measurements include OC and EC, as measured with an in situ Sunset OC/EC analyzer, black carbon (single particle soot photometer), and particle size distributions (scanning mobility particle sizer). Particles were also sampled through a thermodenuder operating at 60, 80, and 100o C.

The measurements are used to determine emission factors as a function of season, traffic volume, and vehicle fleet composition. Thermodenuder data are used to assess the volatility of primary PM emissions, particularly the OA fraction. Results will be compared to data collected in a recent series of dynamometer test conducted by this group in conjunction with the CA Air Resources Board.

2CA.2

Source Apportionment of PM10, PM2.5, PM1 Organic Aerosol Using Aerosol Mass Spectrometry. ANDRE PRÉVÔT, Carlo Bozzetti, Imad El Haddad, Robert Wolf, Emily Bruns, Adela Krepelova, Kaspar Daellenbach, Jay Slowik, Urs Baltensperger, *Paul Scherrer Institute*

The Aerodyne aerosol mass spectrometer offers quantitative real-time measurements of the size-resolved chemical composition of bulk non-refractory submicron aerosol (Organic aerosol (OA), nitrate, ammonium, sulphate, chloride). To extend the AMS ability to measure size-fractioned mass spectra, we explored the application of laboratory AMS measurements of aerosol filter samples. Such methodology based on offline sampling offer the separation of particles in discrete size ranges, including supermicron particles (PM10). Moreover the high cost and the complex maintenance of the AMS significantly limit the spatial coverage of this instrument and the collection of long-term data. These restrictions motivated us to investigate the application of AMS analysis to filter samples, which are easy and cheap to collect and store. The approach involves a water extraction of the particulate matter from quartz filters by sonication and subsequent nebulisation of the aerosol extract into the AMS. The OA extraction efficiency has been evaluated by comparison with AMS online measurements performed during the same period, estimated as 80% on average for the PM2.5. Method detection limits are estimated for organic aerosol, NO3-, SO42-, and NH4+ as 410 mgL-1, 210 mgL-1, 260mgL-1, and 200 mg L-1, respectively. Here, we present the application of the offline AMS approach to PM1, PM2.5 and PM10 filter samples collected at a rural site in Switzerland during summer and winter. Differences in aerosol fingerprints across particle sizes are examined and results suggest a significantly different composition of coarse particles with higher contribution from fragments that are most probably related to carbohydrates (e.g. m/z 29 and 60). Size-resolved statistical ME-2 analyses applied to these measurements will be discussed and compared with online AMS measurements to identify the contribution of primary biological particles and other components.

2CA.3

Time-resolved Organic Speciation at the Theodore Roosevelt National Park, North Dakota, USA. ARANTZAZU EIGUREN-FERNANDEZ, Gregory Lewis, Nathan Kreisberg, David Worton, Derek Day, Jeffrey L. Collett, Jr., Allen H. Goldstein, Susanne Hering, *Aerosol Dynamics Inc.*

The water-based condensational growth tube sampler, better known as the “spot sampler” for its ability to collect and deposit ambient PM in 1 mm spots, was deployed at the Theodore Roosevelt National Park (North Dakota) as part of a pilot study. The study, organized by the National Parks Services, aims to evaluate the impact of emissions from the surrounding oil and gas production wells. Emissions from well development and production phases, including hydraulic fracturing “fracking” processes and open flame combustion of the extracted methane gas, are not well characterized and their impact on visibility is unknown.

Three “spot samplers” have been deployed at the park’s north site monitoring station, for the collection of time-resolved dry, concentrated $PM_{2.5}$ samples. Collection was conducted from mid February to beginning of April, 2013. An array of organic and inorganic species will be monitored. Samples collected for 6-hrs on PEEK plates will be analyzed for inorganic anions (IC-ECD); Polycyclic aromatic hydrocarbons (HPLC-FL) will be quantified in samples collected over 24-hrs on PEEK plates; and a more detailed organic speciation will be conducted on 24-hr samples collected on quartz filters ($0.2cm^2$) placed in the collection plate wells using Thermo-desorption GCxGC-HR-TOFMS. This will be the first time samples collected with this instrument have been analyzed using gas chromatography.

Results obtained from this pilot study will improve our understanding of emissions from oil production wells and fracking processes, as well as their impact on the visibility and air quality of the park and surrounding communities.

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2CA.4

Black Carbon Emissions from Prescribed Forest Fires in the Southeast United States. AMARA HOLDER, Gayle Hagler, Gavin McMeeking, William Mitchell, Robert Black, Johanna Aurell, Michael Hays, Amy P. Sullivan, Taehyoung Lee, Shawn P. Urbanski, Robert J. Yokelson, Sonia Kreidenweis, Brian Gullett, *U.S. EPA*

Open biomass burning is one of the largest contributors to atmospheric black carbon (BC), which is an important climate forcer. However, there have only been a few measurements of BC emission factors in the field. The emission factor data previously generated focused on a limited number of fuel types, and did not include temperate forests. To address this knowledge gap, BC emissions were measured from several prescribed forest fires in the Southeastern United States. Black carbon was measured with a Single Particle Soot Photometer (SP2) and a Microaethalometer (AE-51); additionally, aerosol optical properties were measured with a Photoacoustic Soot Spectrometer (PASS-3) and an integrating nephelometer (Aurora 3000). Measurements were made at ground level immediately downwind from the burn zone. For a subset of the prescribed fires, a second SP2 was available for airborne measurements of the plume. Biomass fuel samples from the field study sites were also collected and burned in the laboratory to assess the representativeness of laboratory fire simulations. In general, the emission factors measured in the field corresponded to those from the laboratory. However, our field studies produced considerably larger emission factors than those reported for tropical and Savanna fires. We also found that BC concentrations from the different instruments varied substantially, showing nearly a three-fold difference between the lowest and the highest measurements. These preliminary results suggest laboratory simulations provide reasonable estimates of prescribed fire BC emissions, but different measurement methods continue to contribute to BC measurement uncertainty.

2CA.5

Regional-scale Modeling of Organic Aerosol Composition in Europe: Insights from Comparison with Aerosol Mass Spectrometer Factor Analysis. CHRISTOS FOUNTOUKIS, Athanasios Megaritis, Ksakousti Skyllakou, Panagiotis Charalampidis, Christodoulos Pilinis, Spyros Pandis, *Foundation for Research & Technology, Hellas*

A detailed three-dimensional regional chemical transport model (PMCAMx-2008) was applied over Europe focusing on the formation and chemical transformation of organic matter. Three periods representative of different seasons were simulated, corresponding to intensive measurement campaigns at various sites. An extensive set of AMS measurements (15 datasets in total) was used to evaluate the model and, using PMF analyzed data, gain more insight into the sources and transformation of OA, as well as identify strengths and limitations of our current OA modeling framework. Overall, the agreement between predictions and measurements for total fine OA mass is encouraging with the model reproducing more than 72% of the data within a factor of two. Oxygenated OA (OOA) is predicted to contribute 93% to total OA over Europe during May, 87% during winter and 96% during autumn with the rest comprising fresh POA. Predicted OOA concentrations show much less error compared to HOA for all periods. The errors for HOA concentrations are most likely an indication of errors in the emissions rates of OA and/or errors in their assumed volatility distribution. The measured LV-OOA mass compares well with the sum of the modeled background OA and the OOA from the lower 2 or 3 volatility bins depending on the period simulated. Biomass burning OA is most likely underestimated in the emission inventory especially during the autumn period. Sensitivity of model results to the assumed volatility distribution of emissions and the aging rate will be discussed.

2CA.6
Modeling of Carbonaceous Aerosol in a European Megacity. CHRISTOS FOUNTOUKIS, Athanasios Megaritis, Ksakousti Skyllakou, Panagiotis Charalampidis, Christodoulos Pilinis, Spyros Pandis, *Foundation for Research & Technology, Hellas*

Three dimensional Eulerian Chemical Transport Models (CTMs) are often used for the design and assessment of air pollution mitigation policies. Grid resolution is a critical factor for these models since a large model grid size cannot capture inhomogeneities in emission rates, meteorology and land cover while a very small grid size makes the simulation inefficient due to the large computational cost. The lack of adequate resolution limits also the ability of the model to accurately simulate individual processes and their interactions. In this work, we use the regional CTM PMCAMx in a two-way nesting configuration (36 × 36 km grid resolution over Europe and 4 × 4 km over Paris) to study the impact of different grid resolutions on fine particulate matter predictions and analyze the sources and production of carbonaceous aerosol in a European metropolitan area of more than 10 million inhabitants. High time resolution AMS measurements were used to evaluate the performance of the model while high resolution (1 x 1 km) emissions are used. The differences between the two grid simulation results in the Paris area are, on average, small for all species during the summer period (July 2009). The 4-km grid simulation captures the average winter diurnal concentration of fine primary organic aerosol and black carbon better than the coarse grid. Particulate matter levels in the Paris megacity are strongly influenced by sources outside the city with the carbonaceous aerosol being mostly of non-fossil fuel origin. About 70% of the fine PM mass is transported into the megacity from continental Europe. Black carbon concentrations (both predicted and observed) are on the lower end of values encountered in megacities worldwide.

2CA.7
Seasonal Variation of Organic Compounds in PM10 at Seoul, Korea. Se Pyo Lee, Hyung Bae Lim, Eun Jin Hwang, JIYI LEE, Yong Pyo Kim, *Chosun University*

Seoul, Korea is one of the megacities in Northeast Asia with 10 million inhabitants and 2.5 million vehicles, thus, the large emission of air pollutants from Seoul might be expected. In addition, South Korea is surrounded by China and Japan and might be influenced by transport of air pollutants from these areas in addition to local sources. Organic compounds are a large fraction of atmospheric aerosol and have significant impact on the air quality, climate change and human health. Thus, understanding the characteristics of the organic compounds in atmospheric aerosols and the contribution of the various emission sources to the organic compounds in Seoul is essential in order to assess their impact on climate change and/or health risk in Northeast Asia. In this study, PM10 samples were collected for 24 h at every sixth day with no rain from April 2010 to April 2011 at Seoul, Korea and solvent extrable organic compounds such as PAHs, n-Alkanes, n-Alkanoic acids, Dicarboxylic acids and Sugars were identified and quantified In addition, major emission sources and formation route for the organic compounds were discussed.

2CA.8

The Organic Characteristics of PM2.5 and TSP in Asian Dust Episodes at Urban and Background Sites in Korea. HYUNG BAE LIM, JiYi Lee, Se Pyo Lee, Eun Jin Hwang, Jin Young Kim, Hyoun-Cher Jin, *Chosun University*

Asian dust storm originates from deserts and loess areas in northern China and Mongolia and Southern China, Korea, and Japan are major receptor regions of Asian dust. Asian dust frequently occurs during the spring season and many studies have been reported in the world on the composition and sources of Asian dust. However, information on the organic characteristics of the dust, especially, the solvent-extractable organic compounds is still scarce. In this study, ten samples of each PM2.5 and TSP including two Asian dust episodes were collected in urban and background sites, Korea in spring 2012 and solvent extrableorganic compounds (PAHs, n-Alkanes, n-Alkanoic acids, Dicarboxylic acids and Sugars) in aerosol were analyzed in order to evaluate the organic characteristics in Asian dust. Further, major factor determining the distribution of organic compounds in Asia dust will be discussed based on the results of the backward trajectory analysis and other air pollutants characteristics.

2CA.9

BC Mixing State during CARES 2010: Results from and Limitations of the Single Particle Soot Photometer. R. SUBRAMANIAN, Arthur J. Sedlacek, Rahul Zaveri, Claudio Mazzoleni, Noopur Sharma, *RTI International*

Direct radiative forcing by BC-containing aerosols (BCA) is affected by the relative fraction of non-BC material and the particle morphology – collectively referred to as “mixing state”. In June 2010, as part of the CARES field campaign, DMT single particle soot photometers (SP2) were deployed at two ground sites. T0 was located inside the Sacramento, CA urban area, while T1 was 40 km away in Cool, CA. The SP2 provides BC mass per particle, as well as information on the mixing state at the single-particle-level for a narrow range of aerosol sizes. The SP2s deployed at CARES reported mixing state information for BCA larger than ~170 nm. Preliminary results using Gao et al. (2007)’s Leading Edge Only (LEO) Gaussian fitting technique indicate that at T0, BC cores smaller than 100 nm mass-equivalent diameter are thickly-coated, with a coating thickness between 60-120 nm; a detectable coating was not observed for BC cores larger than 200 nm. The mixing state of BC at T0 was influenced by local sources as well as by a build-up of aged aerosols in the region over June 22-28, when the thickly-coated BCA number fraction reached almost 30% for shell/core diameter ratios over two. For BCA particles with a shell/core diameter ratio over 1.5, the thickly-coated number fraction varied between 40-60%. The effect of SP2 instrument limitations and various optical modeling assumptions will also be explored in this presentation.

2CA.10

Long Range Transport of Biomass Burning Emissions based on Organic Molecular Markers and Carbonaceous Thermal Distribution. MIN-SUK BAE, *Mokpo National University*

Semi-continuous organic carbon (OC), elemental carbon (EC), and organic molecular markers were analyzed with the thermal optical transmittance method at the Gosan supersite (on Jeju Island, Korea), which has been widely used as a regional background site for East Asia. The Carbonaceous Thermal Distribution (CTD), which provides detailed carbon signature characteristics relative to analytical temperature, was used to improve the carbon fractionation of the analytical method. Ground-based measurements were conducted from October 25 to November 5 of 2010. During the sampling period, one high OC concentration event and two characteristic periods were observed. Considering the thermal distribution patterns, the relationship between the EC and black carbon (BC) by optical measurements, the backward trajectories, the aerosol optical thickness, and the organic molecular markers, such as levoglucosan, PAHs, and organic acids, we concluded that the event was influenced by the long-range transport of biomass from burning emissions.

This study discusses the CTD analysis with organic molecular marker concentrations, extracts and interprets additional carbon fractions from a semi-continuous data set, and provides knowledge regarding the origin of carbon sources and their behaviors.

2CA.11

Simultaneous Bulk and Speciated Measurements of Low Volatility Organic Compounds in a Pine Forest during BEACHON-RoMBAS 2011. ARTHUR CHAN, Nathan Kreisberg, Yunliang Zhao, Thorsten Hohaus, Pedro Campuzano-Jost, John Jayne, Douglas Worsnop, Jose-Luis Jimenez, Susanne Hering, Allen H. Goldstein, *University of California, Berkeley*

Organic aerosol (OA) is a major fraction of particulate matter, particularly in remote forested regions. Understanding its composition is essential to identifying the sources and processing, but its chemical complexity often limits such analysis. Here we present simultaneous bulk and speciated measurements of semivolatile and particle-phase organic compounds using a novel combined instrument (TAG-AMS) at Manitou Forest, CO during the BEACHON-RoMBAS 2011 campaign. This campaign is the first field deployment of the newly developed Semivolatile Thermal desorption Aerosol Gas chromatograph (SV-TAG), which provides on-line speciation of semivolatile organic compounds with bihourly time resolution, while the AMS provides bulk aerosol mass spectral analysis. The combined instrument provides quantitative organic and inorganic mass loadings, and elemental and PMF analysis of the bulk OA, simultaneously with detailed organic speciation. The data have been integrated so far to include a 2-week period of >100 compounds. These include both anthropogenic and biogenic compounds, with distinct time series. Highest concentrations of polycyclic aromatic hydrocarbons (PAHs) and alkanes were observed during the day, indicating influences of urban air masses at this field site. Speciated sesquiterpenes with molecular formula $C_{15}H_{24}$ (e.g. beta-caryophyllene and longifolene) were observed mostly at night. In addition, we present ambient measurements of a variety of low-volatility biogenic compounds, such as $C_{15}H_{22}$ sesquiterpenes (cuparene, calamenene) and diterpenoids (abietatrienes, retenes), at tens to hundreds of pg/m3. Many of these compounds have been identified in essential oils, but were observed in ambient air for the first time. They are likely reactive and contribute significantly to ozone loss and SOA formation, but are not included in current emission inventories. Using peak fitting analysis of high mass resolution data, we estimate that the total mass concentration of observed SVOCs (hydrocarbons between 13 and 25 carbons) is 0.1 - 0.3 ug/m3 during this field campaign.

2CA.12

Black Carbon Mixing State in Paris during MEGAPOLI: Connecting Particle-Resolved Observations to Particle-Resolved Modeling. SWARNALI SANYAL, Nicole Riemer, Robert Healy, Valérie Gros, John Wenger, Greg J. Evans, *Univerisity of Illinois at Urbana-Champaign*

The composition and properties of black carbon aerosol particles change continuously after emission during transport in the atmosphere. Coagulation, condensation, and photochemistry are contributing processes, frequently called "aging". Understanding these processes is important for assessing the climate impacts of black carbon aerosol. The use of single particle mass spectrometers has allowed unprecedented insight into black carbon mixing state and associated aging processes, however it is difficult to fully exploit these measurements using traditional modal or sectional models. The particle-resolved aerosol PartMC-MOSAIC, on the other hand, is a suitable interface to connect to these observations from the modeling side. In this work, we present the first PartMC-MOSAIC case study that uses data from an aerosol time-of-flight mass spectrometer (ATOFMS) to constrain the model. The instrument was deployed during the 2010 MEGAPOLI winter campaign in Paris, France.

PartMC-MOSAIC is a Lagrangian box model that resolves the per-particle composition and hence provides a detailed representation of black carbon mixing state and aging processes. The model simulates a representative group of particles distributed in composition space, treating coagulation, condensation and other important processes on individual particle levels. For the initial conditions of the aerosol population and for the particle emissions we use quantitative chemical composition estimates from the ATOFMS measurements collected during MEGAPOLI. We then track the particle population for several hours as it evolves undergoing coagulation, dilution with the background air, and chemical transformations in the aerosol and gas phase. We quantify the contribution of coagulation and condensation to black carbon aging, discuss the implications of black carbon aging for cloud condensation nucleation activity, and present a comparison to ATOFMS mixing state observations.

2CA.13

Chemical Composition Changes in Biomass Burning Organic Aerosol from FLAME-IV Perturbation Experiments. ELLIS SHIPLEY ROBINSON, Daniel S. Tkacik, Rawad Saleh, Adam Ahern, Albert A. Presto, Ryan Sullivan, Robert J. Yokelson, Allen Robinson, Neil Donahue, *Carnegie Mellon University*

Biomass Burning Organic Aerosol (BBOA) is a major contributor to atmospheric primary fine particles, and gas-phase emissions from biomass burning are a significant source of to the global burden of trace gases. Despite their significance, however, the light absorbing properties, downwind chemical evolution, and secondary particulate mass enhancement of these emissions are poorly understood.

We present chemical composition measurements from a High-Resolution Aerosol Mass Spectrometer (HR-AMS) of two-chamber, smog chamber perturbation experiments at the FLAME-IV campaign in Missoula, Montana. In most experiments, we filled two smog chambers with emissions from the same fire, and then perturbed one chamber by adding an atmospheric oxidant (e.g. hydroxyl radical, ozone, HONO, lights). This allowed for a characterization of any changes (e.g. increase in O:C ratio, increase in organonitrates) in the primary emissions, as well as the composition change from the perturbation. Additionally, as burn-to-burn variability can be large, even between burns of the same fuel, the two-chamber method represents a way to control for this and focus on the changes in composition, mass enhancement, and light absorption for a given perturbation. We also present the absorptivity of BBOA as a function of the fraction of primary (fresh) OA to total OA, fraction of organonitrates to total OA, fraction of large molecular weight fragments (Th > 100) to total OA, and the OA-to-BC ratio.

2CA.14

Ambient Aerosol Volatility Measurements during SOAS, 2013:Thermodenuder Measurements to Constrain Equilibrium and Kinetics of Aerosol Phase Partitioning. PROVAT SAHA, Andrey Khlystov, Andrew Grieshop, *North Carolina State University*

Volatility is an important property of atmospheric aerosols that strongly influences their atmospheric lifecycle. Thermodenuder (TD) is a widely used tool to measure aerosol volatility in both lab and field. Since evaporation of aerosol in TD is dictated by a large number of independent parameters (C*, ΔHvap and γe), it is difficult to constrain all of the volatility parameters with only 1-dimensional (e.g. TD temperature) perturbation to the initial equilibrium. Systematically operating TD systems at varying residence times and at different temperature stepping can provide insights about the evaporation kinetics of aerosol and equilibrium partitioning in the TD. Here, the volatility of ambient aerosol in rural southern US was measured during the Southern Oxidant Aerosol Study (SOAS) ground site near Centerville, Alabama in June and July, 2013. In this study, a temperature-stepping TD (TS-TD) with a long residence time (about 40 s), was used to extract equilibrium properties of ambient aerosol over a range of temperatures (40-180 ºC). Parallel to this, a variable residence time TD (VRT-TD) with a moderately heated activated carbon surface at constant temperature of 90 ºC was run to acquire information about the isothermal evaporation kinetics of aerosol. Simultaneous measurements of aerosol size distributions were collected in reference and thermodenuded lines using parallel SMPS systems. In addition, non-refractory aerosol chemical species mass (e.g. Organic, Sulfate, Nitrate, Chloride and Ammonium) were measured using Aerosol Chemical Speciation Monitor (ACSM) alternating between denuded and reference lines. The VRT-TD data suggest that aerosol equilibrated after very short residence time (< 2 s), in contrast to other ambient observations. Preliminary analysis show that approximately 50% and 90% of total aerosol mass evaporated at TD temperatures of 100 ºC and 180 ºC, respectively. Evaporation varied substantially with ambient aerosol loading and composition and meteorology.

2CA.15

Brown Carbon in Fresh and Aged Biomass Burning Emissions. RAWAD SALEH, Ellis Shipley Robinson, Daniel S. Tkacik, Adam Ahern, Shang Liu, Allison Aiken, Albert A. Presto, Ryan Sullivan, Manvendra Dubey, Neil Donahue, Allen Robinson, *Carnegie Mellon University*

To date, most climate forcing calculations treat black carbon (BC) and dust as the only particulate light absorbers. Numerous studies have shown that some organic aerosols (OA), referred to as brown carbon (BrC), also absorb light. BrC has been identified in biomass burning emissions, however, its light absorption properties are poorly constrained. Literature values of the imaginary part of the refractive indices of biomass burning OA (k_{OA}) span two orders of magnitude. This variability, attributed to differences in fuel type and burning conditions, complicates the representation of biomass burning BrC in climate models. Proper accounting for BrC absorption in climate forcing calculations is of great importance, and can enhance the models' performance and agreement with observations.

Here, we show that k_{OA} of biomass burning OA, both fresh and aged, can be estimated as a function of a single property of the emissions, namely the BC-to-OA ratio. Specifically, kOA at wavelength (lambda) of 550 nm increases linearly with the BC-to-OA ratio, while the spectral-dependence, w, where $k_{OA} = k_{OA,550nm}*(550/lambda)^w$, is inversely proportional to the BC-to-OA ratio. These correlations were determined by examining emissions from small scale laboratory burns of six fuels (black spruce, pendorosa pine, hay, rice straw, saw grass, and wire grass). The BC-to-OA ratios in the experiments were between 0.01 and 0.2. Aging of the emissions (photo-oxidation or dark ozonolysis) was performed in a smog chamber. k_{OA} values were retrieved by performing optical closure, which combines Mie theory calculations with measurements of light absorption, and total and BC size distributions.

2CH.1

The Study of the Fibrous Membrane Produced by Electrospinning Technology. Kuo Pei-Chen, JIN-YUAN SYU, Chang Yuan-Yi, Chih-Chieh Chen, Wen-Yinn Lin, *National Taipei University of Technology*

Electrospinning is a simple and cost-effective technique for manufacturing of fibers that diameter in nano-scale. The continuous jet is spun from the capillary needle with a polymer solution to ground under a high electric field. Nanofibers that were produced using this technique offer the potential for a wide variety of applications such as filtration for air or water, tissue engineering scaffolds, protective clothing and biomedical application etc., due to the exceptional properties, for instance, high specific surface area, high aspect ratio and much smaller pore size. Therefore, an electrospinning system was set up in this study. The purposes of this study include: (a) the effects of concentration of PMMA solution, sodium chloride volume, feed rate and distance from needle tip to collector (spinning distance) on electrospun nanofiber characteristic, (b) applied to collection of particles under different conditions that were fiber types, face velocity, fiber diameter and surface voltage of the fibrous membrane. PMMA nanofibers were successfully produced by electrospinning technique in this study. The diameter of electrospun fiber was increased and the beaded count of fiber was decreased if the concentration of polymer becomes higher. However, both the beaded count and average diameter of fiber could be decreased if the sodium chloride was added into PMMA polymer solution. In addition, average diameter of fibers decreased as spinning distance increased. The fiber film was applied to collect particles. The results showed the good penetration in collection of particles. In some specific parameters, the best penetration is about 3.0×10^{-5}.

2CH.2

Filter Testing Using Technetium-99m Labeled Airborne Particles. TSZ YAN LING, Lin Li, Kai Xiao, Shigeru Kimoto, Bradley Humphrey, David Y. H. Pui, Jerry Froelich, *University of Minnesota*

Respirators are considered as an effective protection equipment against airborne particles, including radioactive particles. However, there is a lack of studies relating the performance of respirators against radioactive and non-radioactive particles. In this study, we reported a method to determine a suitable metric, namely number, area or mass, to represent the radiation penetration of filter media. A microfiberglass medim was tested with Technetium-99m (Tc-99m) labeled polydisperse particles with two different size distributions. The radiation penetration, when represented by the number median diameter of the polydisperse particles, was found to correlate better to the penetration obtained with monodisperse sodium chloride (NaCl) particles. This can be explained by the small fraction of the Tc-99m molecules contained in the test particles. The procedure demonstrated in this study will allow one to estimate radiation penetration from the measurements made by non-radioactive surrogate particles.

2CH.3

SO2 and PM Removal Performance of a Packed-Bed Scrubber Combined with Electrostatic Precipitation for Marine Diesel Engines. HAK-JOON KIM, Bangwoo Han, Yong-Jin Kim, Hwang Sung-Chul, *Korea Institute of Machinery and Materials*

Wet scrubbers have been used as a SOx and particulate matter (PM) removal method for marine diesel engines. Even though the scrubbers show high removal efficiency against SOx higher than 95%, their PM removal efficiency is relatively very low because PMs from marine diesel engines are ultrafine particles which are hardly removed by droplet and particle collisions. In this study, we combined a cylinder-edge type electrostatic precipitator to a wet scrubber at its inlet to compensate the low efficiency of the scrubber against ultrafine particles. A 3000 cc diesel engine was operated at various speeds and loads, and 0.8%v/v sulphur marine oil was used to generate SO2 and PMs. The flow rate though the scrubber was varied from 3.6 to 7.5 m3/min, and various packing balls made of stainless and plastic (1, 2, 3.5 inch) were used. A SMPS system and photochemical gas analyzer were used to measure concentrations of ultrafine PMs and SO2 gas. Despite of various engine conditions, the SO2 removal efficiency was linearly proportional to L/G. However, the change in size of the packing balls from 1 to 2 inch did not affect on the removal performance. On the other hand, the pressure drop was decreased twice when the packing size was changed from 1 to 2 inch. Finally, we evaluated PM removal efficiency of the standalone wet scrubber and the combined wet scrubber with electrostatic precipitator at the inlet. The PM removal performance with only spraying sea water of 2.5 L/m3 was nearly ineligible because the PMs from the engine even with 0.8%v/v sulphur were mostly ranged at submicrometer range with the mode diameter of approximately 100 nm. However, the combination system with an applied voltage and current of -8 kV/ 0.5 mA removed 100 nm-particles by 80% based on particle number.

2CH.4

Emissions of NOx, NO, NH3, N2O and BC from a Diesel Engine Equipped with an SCR System Fueled with Diesel and Biodiesel: Dispersion Analysis and Pollutant Risk Assessment in Curitiba, Brazil. RICARDO H. M. GODOI, Yara S. Tadano, Guillherme C. Borillo, Thiago O. B. Silva, Amanda Cichon, Fabio B. Valebona, Carlos I. Yamamoto, Marcelo R. Errera, Lucas Martin, Denis Rempel, Ana Flavia L. Godoi, *Federal University of Parana - Curitiba, PR, Brazil*

The combination of recent changes in the composition of fuel, low-sulfur diesel fuel or biodiesel blends, and selective catalytic reduction (SCR) emission control systems brings new insights concerning the emission of gaseous and particulate pollutants. The major goal of our study was to quantify NO_x, NO, NH_3 and N_2O emissions using a four-cylinder diesel engine operated with diesel and a blend of 20% soybean-biodiesel. The measurements were performed in a dynamometer using a 13-mode heavy-duty diesel engine equipped with an SCR system. The target gases were detected by an FTIR system; the speciation of BC was done using a multi-wavelength aethalometer. As expected, our results showed that NO_x and NO concentrations in all tests using engine with an SCR system decreased, when compared with no exhaust aftertreatment. However, the use of aftertreatment produced significantly higher NH_3 and N_2O concentrations with all fuels tested. NH_3 is a health hazardous gas, while N_2O increases exacerbate the greenhouse effect. BC exhaust emissions indicated no significant optical difference between S10 and B20 emissions. Based on our experimental results we performed an AERMOD dispersion model analysis considering the City of Curitiba bus fleet equipped with diesel and engines using SCR emission control systems. Concerning BC, we expect that biodiesel exhaust has similar properties as fossil diesel exhaust. In this way, we expect that the climate benefits of bio-fuels due to CO_2 might not outweigh the effects of the BC emissions.

2CH.5

Correlation between Number Concentration of Generated Particles and Concentration of Airborne Molecular Contamination at Different Relative Humidity and Residence Time under Soft X-ray Irradiation. CHANG HYUK KIM, Zhili Zuo, Hartmut Finger, Stefan Haep, Heinz Fissan, David Y. H. Pui, *University of Minnesota*

Most of the problems caused by particulate contaminations in semiconductor industry have been solved by the development of filtration systems during the last couple of decades. However, particle generation induced by airborne molecular contamination (AMC) is still an important issue. As the manufacturing technology has been improved to make semiconductor devices with smaller feature sizes, nanoparticles and haze can be generated from AMC at very low concentration levels (several ppb or ppt) under high energy irradiation, which increase manufacturing cost by destroying photo masks and reducing products yields. Therefore, it is important to understand the mechanism for the radiation induced particle formation from AMC to prevent the increase of manufacturing cost.

The objectives of this study were to determine the correlation between number concentration of generated particles and concentration of AMC at different relative humidity (RH) and residence time under irradiation and to evaluate an AMC filter performance by measuring AMC concentration based on this correlation. Two major AMCs, ammonia and sulfuric dioxide were diluted with nitrogen gas to achieve concentrations down to a few ppb levels and then introduced to a reaction chamber at different flow rates and RH, where AMCs were converted into particles. Soft X-ray was used to accelerate the gas-to-particle conversion. The resulting number concentration and size distribution of particles were measured by a condensation particle counter and a scanning mobility particle sizer, respectively. The particle number concentration and AMC concentration showed a power-law relationship at different residence time. Results from tests at different relative humidity suggest that water is one of the important reaction components for particle formation and the amount of water needed to generate particles depends on the AMC concentration. AMC concentrations before and after the filtration were detected and compared to evaluate the filter performance based on these results.

2CH.6

On the Development of Indoor Air Quality Control Using Synthetic Jets. Brett McQuillan, Jean Hertzberg, LUPITA MONTOYA,*University of Colorado, Boulder*

The objective of this experimental flow visualization study was to assess the ability of synthetic jets to be adapted for control of airflows and particulates in an indoor environment. Specifically, flow visualization was used to determine whether small synthetic jet modules installed onto the surface of a supply diffuser could significantly impact the angle at which supply air left the diffuser when mixing into the room air. A synthetic jets module was installed in a lab with a high air exchange rate (7 ACH) to test this methodology. This lab space is representative of occupational indoor environments that may require ventilation strategies beyond typical systems to ensure the safest and most efficient operation of the space. Three synthetic-jet modules were tested including two pairs of small one-inch diameter jets used in a previous small-scale ventilation study and two larger two-inch diameter jet pairs constructed specifically for this study. Statistical methods were used to compare the visualized supply flow with active synthetic jet flow control versus a baseline case (no flow control). Results showed a significant impact on the angle of mixing of the supply air.

2CH.7

Development of a Rotating Drum System for Studying the Effects of Humidity and Ozone on Biological Aerosols. Shanna Ratnesar-Shumate, ELIZABETH CORSON, Jonathan Eshbaugh, Christopher Bare, Sean Kinahan, Joshua Santarpia, *Johns Hopkins University Applied Physics Laboratory*

Biological aerosols may undergo physical and chemical changes in the atmosphere due to many different processes. Chemical modifications via oxidation with ozone, uptake of water, solar irradiation, and interactions with atmospheric pollutants may change the viability as well as the physical properties of these aerosols as a function of time of exposure. The ability to observe these changes during time periods on the order of hours in a laboratory setting is difficult. Physical loss of aerosols suspended in static or stirred (mixed) chambers due to settling, deposition, and inertial forces create difficulty in attempting to recreate exposure on time scales that are representative of real world conditions. A rotating drum system was developed that allows for biological aerosols to be generated into a sealed chamber and exposed to varying concentrations of ozone at different relative humidity settings for 4 hour experiments. An automated control system was developed to maintain stable ozone concentration and RH in the drum. Experiments were performed with Bacillus thuringiensis kurstaki spores, Phosphate Buffer Solution (PBS) aerosols, and Arizona Road Dust in order to characterize the physical losses associated with the drum during a four-hour experiment. RH in the drum can be controlled from 20 to 85% via dry air input and a piezoelectric generator. Ozone concentrations from < 5 to 150 ppb were achieved. A standard operation procedure was developed that allows for input of ozone and water vapor in order to maintain the required levels for experiments while minimizing losses due to sampling. Examples of data sets generated using the system will be presented.

2CH.8

Development of Clutter Aerosol Profiles for Test and Evaluation of Biological Detectors. JONATHAN ESHBAUGH, Shanna Ratnesar-Shumate, Elizabeth Corson, *Johns Hopkins Univeristy Applied Physics Laboratory*

The growing need to rapidly identify a pathogenic biological aerosol to prevent infection of a military force or domestic population has led to the development of a variety of biological aerosol sensors. These sensors have been designed to detect spore, bacterial, viral, and toxin threats. Proper evaluation of these new sensors requires that they be challenged with aerosols encountered in an operationally relevant environment. Ambient aerosols can contain both anthropogenic and natural aerosol particles that may interfere with the ability of the sensor to operate effectively. The size distribution and concentration of two operationally relevant aerosols, diesel exhaust and clay soil, that have the potential to the hinder the ability of a prospective sensor to detect biological organisms are discussed. Additionally, novel techniques are used to generate equivalent aerosols, both in size and concentration, under controlled conditions for use with the Dynamic Concentration Aerosol Generator (DyCAG). A diesel aerosol with a mass concentration of 20-50 micro-gram/m^3 and a number peak of approximately 100 nm as well as a clay aerosol with a mass concentration of 0.25 milli-gram/m^3 and a number peak of approximately 2,500 nm were generated. The results of these experiments demonstrate that this technique can be used to repeatedly test biological aerosol sensors under controlled conditions designed to reproduce operationally relevant aerosol challenges.

2CH.9

Bacillus Spore Filtration Efficiency of HEPA Filters. JACKY ANN ROSATI ROWE, April Corbett, Alfred Eisner, *US EPA*

When anthrax contaminated buildings are decontaminated, air is typically removed from the building with high flow vacuum systems using HEPA filters. There is concern, in the clean up/responder community because of the toxicity of the removed agent, and because of the high flow rates used in these systems, that spore collection efficiency may not be as needed. To this end, we conducted research to investigate the spore breakthrough/bypass of HEPA filters at high flow.

Because of physical similarities, Bacillus thuringiensis Var. kurstaki (Btk) was used as a simulant for Bacillus anthracis. A Dash 5 portable air cleaner was used with Magna 1000 series HEPA filters (rated 99.97% efficiency). Aerosol was generated, using a BGI Three-Jet Collison nebulizer, with varying spore concentration levels. Aerosol size distributions and concentrations were measured both prior and post filtration by an Aerodynamic Particle Sizer 3321. Samples of surfaces upstream and downstream of the HEPA filters were collected using microbial swabs and analyzed.

Duplicate runs were performed at four different experimental conditions: high spore concentration/high flow, high concentration/low flow, low concentration/high flow, low concentration/low flow. Generated aerosol size distributions were bimodal, with peaks at 0.65 and 1.2 micron aerodynamic diameters. These peaks were consistent throughout all experiments, with the lower peak being determined via UV APS to be water droplets, and the higher peak being determined to be biological materials. At all experimental conditions, filtration efficiency was 99.99% + or - 0.29. The lowest filtration efficiency occurred at the high spore concentration/high flow conditions.

2CH.10

Rapid Viral Aerosol Inactivation Using Atmospheric Cold Plasma. Yan Wu, Yongdong Liang, MAOSHENG YAO, Jue Zhang,*Peking University*

Effective control of airborne viruses is of vital importance to public health. Here, we investigated the use of atmospheric cold plasma in inactivating airborne viral aerosols. MS2 viruses were aerosolized into the exposure chamber where they were exposed to the produced plasma using different energy (20, 24, and 28 Watt) and carrier gas (air, Ar+O2 and He+O2) for less than 1 second. Similar experiments with extended exposure (up to 3 min) were performed with water-borne MS2 viruses. The contents of the plasma were analyzed using optical emission spectroscopy (OES) and the exposed viruses were examined by scanning electron microscopy (SEM).

The results revealed that the inactivation of airborne MS2 viruses depended on the plasma generation energy, carrier gas type and exposure time. The inactivation rate was shown up to more than 95% when exposed to the plasma at an energy level of 28 W regardless of carrier gas, and decreased with reduced generation energy. Water-borne virus exposure revealed that the inactivation also depended on exposure time. OES analysis indicated that use of higher generation energy resulted in higher emission level of reactive oxygen species for specific carrier gas. SEM images also revealed that after exposure to the plasma the viral envelope was ruptured. In addition, relevant genes which regulate A protein, capsule protein, lysis protein and replication protein, suffered different degrees of damages when exposed to different level of generation energy. This study provides important information for developing high efficient virus decontamination technology using atmospheric cold plasma.

Key words: MS viruses, Cold Plasma, Carrier gas, Viral protein

2CH.11

In Situ Viral Aerosol Inactivation and Mechanisms by Microwave Irradiation. Yan Wu, MAOSHENG YAO, *Peking University*

Previously, we have studied the bacterial and fungal aerosol inactivation by direct microwave irradiation. Here, we further investigated its inactivation of airborne viruses. MS2 coliphage used as a human model virus were aerosolized and exposed to the direct microwave irradiation for ~ 2 min at three different power levels (700 , 29 385, 119 W). In addition to the survival rate, the viral RNA genes coding for viral envelope surface proteins with and without the microwave irradiation were also examined using PCR and gel electrophoresis.

Direct exposure of airborne MS2 virus to the microwave irradiation at 700 W for less than 2 min was shown to result in more than 90% inactivation efficiency, about 65% at medium power level (385 W), and 50% at the lowest level(199 W). Scanning electron images showed visible damages to the viral envelope after the exposure. Damages were also observed to the viral RNA genes coding for envelope surface proteins such as the A protein, the capsid protein, the lysis protein, and the replicase protein, among which the A protein gene was completely damaged. This study demonstrated that even without the filtration the direct microwave irradiation could also achieve rapid inactivation of viral aerosols.

Key words: MS2 virus, Microwave Irradiation, Protein Genes, Inactivation

2CO.1

Predicting Transient Particle Number Emissions from Different Blends and Feedstocks of Biodiesel Using an Artificial Neural Network. TYLER FERALIO, Britt Holmén, *University of Vermont*

Ultrafine particles (UFP, diameter < 100nm), which dominate diesel engine emissions, are known to cause adverse health effects in humans (aggravated asthma, decreased lung function, irregular heartbeat, and nonfatal heart attacks). Previous studies have shown changes in both particle mass (PM) and particle number (PN) emissions when diesel engines are fueled by different blends of biodiesel and petro-diesel as opposed to neat petro-diesel.

The objective of this research was to model the measured UFP emissions for a single engine running on 9 different fuels. Particle number distributions were measured from a 1.9L Volkswagen diesel engine coupled to an eddy current dynamometer in real-time for neat and blended petro-diesel, soybean oil based biodiesel, and waste cooking oil based biodiesel (B0, B10, B20, B50, and B100) with a TSI Engine Exhaust Particle Sizer (EEPS, 32 channels, 5.6-560nm range). For these experiments the engine was run through a transient drive cycle developed from on-road data collected from a Volkswagen TDi vehicle while it was operated through urban, highway, rural, and suburban driving conditions.

Data collected for modeling included fuel properties, standard onboard diagnostics (OBD-II) parameters, and PN emissions data. Principal component analysis (PCA) was performed on all of the potential model inputs to determine which parameters were the predominant factors in UFP emissions. The parameters ‘selected’ using PCA were used to develop an artificial neural network to model PN emissions from the Volkswagen engine. Preliminary data suggest that PN emissions, specifically in the 10nm range, increase as the amount of biodiesel in the fuel increases. Model results will be presented for both soy and waste cooking oil biodiesel blends.

2CO.2

Organic Chemical Composition of Biodiesel Exhaust Particulate Matter Derived from Two Feedstocks: Soybean and Waste Grease. JOHN KASUMBA, Britt Holmén, *University of Vermont*

Biodiesel use and production has significantly increased in the United States and in other parts of the world in the past decade. This change is driven by energy security and global climate legislation mandating reductions in the use of petroleum-based diesel. Recent air quality research has shown that emission of some pollutants such as CO, particulate matter (PM), SO2, hydrocarbons, and carcinogenic polycyclic aromatic hydrocarbons (PAHs) is greatly reduced with biodiesel. However, studies have also shown that some unregulated emissions, such as gas-phase carbonyls, are increased with biodiesel combustion. Very limited research has been done to investigate the carbonyl emissions in the particle-phase of biodiesel exhaust.

In this study, an Armfield CM-12 automotive diesel engine was used to generate particulate matter from two biodiesel feedstocks (soybean and waste vegetable oil biodiesel). The PM emissions were sampled by a variety of instruments: - engine exhaust particle sizer, EEPS (TSI Inc, Model 3090) for measuring particle size distributions between 5.6 and 560 nm in real-time; Teflon filters for gravimetric mass, and quartz fiber filters (QFF) for chemical analysis of the exhaust PM using gas chromatography mass spectrometry (GCMS). PAHs, carbonyls, and alkanes were quantified in B20 soybean biodiesel (20% soybean biodiesel and 80% petrodiesel, volume/volume) and petrodiesel exhaust PM. Preliminary results show that the total PAHs emissions were reduced by about 2 times with B20 soybean biodiesel, while the particle-phase carbonyl emissions increased by about 2 times with biodiesel. Alkanes were found at 2 – 3 times higher concentrations in petrodiesel exhaust PM than in biodiesel exhaust PM. Biodiesel was also found to have less particle mass than petrodiesel, but the particle number concentrations in biodiesel were higher. Soybean and waste grease biodiesel particle-phase exhaust emissions will be compared.

2CO.3

Characterization of PM Emissions from Aircraft Auxiliary Power Units. PREM LOBO, Donald Hagen, Philip Whitefield, *Missouri University of Science and Technology*

Airport operations have been shown to contribute to increased PM levels in surrounding communities. Aircraft engines and auxiliary power units (APUs) are significant sources of emissions at airports. A number of studies have characterized the PM emissions from different types of aircraft engines; however emissions from APUs are not as well defined. APUs are gas turbine engines which generally operate to provide power and air conditioning, while the aircraft is parked at the gate and sometimes during taxi in/taxi out. They are also used to start the main engine in some cases. This paper summarizes the PM emissions characterization of several APUs performed during three recent measurement campaigns. The following models of APUs were studied: GTCP85-98CK, a re-commissioned Artouste Mk113, GTCP 331-200, and GTCP 36-300. PM size distribution parameters and number- and mass-based emission indices were computed for each APU model at different engine operating loads. For PM number-based emission index, the range of values was 6x10e+13 – 7x10e+15 particles/kg fuel burned. The PM mass-based emission index values were in the range 10-600 mg/kg fuel burned. These ranges of values for APU PM number- and mass-based emission indices are of the same magnitude as those for main engine PM emissions. It was also observed that the more modern technology APU models were found to have the lowest PM number and mass-based emission indices. The data from these studies will assist in developing more accurate emissions inventories at airports and thereby contributing to understanding the potential impacts of airport operations on neighboring communities.

2CO.4

Validation of the Moment Method for Determining Smoke Aerosol Properties in Space. MARIT MEYER, George Mulholland, David Urban, Gary Ruff, Zeng-guang Yuan, Victoria Bryg, Thomas Cleary, Jiann Yang, *NASA Glenn Research Center*

Characterizing smoke aerosols in space is difficult due to limitations on the weight and complexity of instruments that can be deployed. However, advances in spacecraft fire safety depend on identifying likely fire sources and characterizing smoke from these materials. Investigations of these smoke aerosols in low gravity provide important design input for the development of future space fire detectors. The Smoke Aerosol Measurement Experiment (SAME) employed three basic aerosol instruments to measure different moments of the smoke particle size distribution for five common spacecraft materials. The count mean diameter of the smoke particles and the diameter of average mass are calculated from these moment averages. Furthermore, the geometric mean diameter and geometric standard deviations can be calculated if the particle size distribution is assumed to be lognormal. Validation of this characterization method has been performed in a set of experiments using the SAME smoke-generating hardware and the returned flight aerosol instruments. A Scanning Mobility Particle Sizer Spectrometer (SMPS) is too large and complex to include in a space flight experiment, but its use in ground-based testing determined whether the log-normal assumptions were valid, and provided high-resolution particle size distributions of the smoke from each material. SMPS particle size distributions from ground experiments are compared to particle statistics generated by moment calculations and particle size distributions from microscopic analysis of TEM images of particles for both un-aged and aged smoke.

2CO.5

Particle Size Distributions from a Light-Duty Conventional Vehicle and Comparable Hybrid-Electric Vehicle During Real-World Driving. KAREN SENTOFF, Britt Holmén, *University of Vermont*

Exposure to ultrafine particles characteristic of motor vehicle tailpipe emissions has been linked to various adverse health implications in humans. Although hybrid-electric vehicles have an increasing portion of the light-duty vehicle market share, little research to date has quantified the particle number emissions from this new vehicle technology. The Total Onboard Tailpipe Emissions Measurement System (TOTEMS) was employed in a conventional model year 2010 Toyota Camry vehicle and its hybrid counterpart. Each test vehicle was operated by a single driver over a real-world, 32-mile route during an 18-month data collection campaign. An Engine Exhaust Particle Sizer (TSI EEPS) and an Ultrafine Condensation Particle Counter (TSI UCPC) measured the size distributions and total particle number from the tailpipe of each vehicle simultaneous to collection of vehicle operation parameters (i.e. speed, acceleration, engine load) and environmental factors (i.e. road grade, ambient temperature, relative humidity). The vehicle specific power (VSP) and speed were used to define the various modes of operation across the real-world route according to the framework for EPA’s regulatory model – the Motor Vehicle Emission Simulator (MOVES). Particle number emission rates across the size distributions from each vehicle type were compared at differing modes of operation encountered along the real-world route. Although a bimodal particle distribution was characteristic of both vehicles, the hybrid demonstrated inconsistent modal diameters as compared to the conventional across vehicle operating modes. Additionally, mean emission rates were greater for the hybrid across nearly all operating modes, with the exception of operation at high speed (50 mph and above) and high vehicle specific power (30 kW/ton and above). The differences between vehicle types were most pronounced for low speed operation with VSP of 6 kW/ton and above, as well as for speeds greater than 25 mph and VSP of 12 kW/ton and above.

2CO.6

Characterizing the Gaseous Toxic Pollutants, Ultrafine Particle Emissions, Size Distributions, Electrophilic, and Redox Properties of Biodiesel Exhaust from Heavy-Duty Vehicles with and without Aftertreatment Controls.

NICHOLAS GYSEL, Thomas D. Durbin, Debra A. Schmitz, Arthur K. Cho, Georgios Karavalakis, *University of California Riverside*

Fuels derived from biological sources, such as fatty acid methyl esters (FAMEs), have received and continue to receive increasing attention. For this study, we examined the emissions impacts of high biodiesel blends of different origin on the exhaust emissions from two heavy-duty trucks equipped with different aftertreatment configurations. Experiments were conducted on a 2012 Cummins ISX15 engine fitted a diesel particle filter (DPF) and selective catalytic reduction (SCR) control devices and on a 2004 Cummins ISX450 engine without an aftertreatment control device. Each truck was tested on four different fuels including a CARB diesel and three biodiesel blends at 50 percent proportion with the CARB diesel. The biodiesel used were a soy-based biodiesel, an animal fat biodiesel, and a biodiesel obtained from waste cooking oils.

For this study, gaseous toxics were analyzed for aldehydes and ketones and for light aromatic hydrocarbons. Chemical analysis for carbonyl compounds and VOCs was performed using a HPLC and a GC-MC, respectively. Emphasis was placed on the measurement of real-time particle size distributions using an engine exhaust particle sizer (EEPS) spectrometer and on the determination of particle number emissions using a condensation particle counter (CPC). Particulate matter 2.5 micro-meter samples and semi-volatile compounds were collected in Teflon filters and XAD-4 resin, respectively, and subsequently analyzed for redox activity by DTT assay and electrophilic properties by GAPDH assay. Preliminary results showed that biodiesel blends resulted in pronounced reductions in particle number emissions for the newer vehicle, while particle number emissions trended higher with biodiesel for the older technology vehicle. For all fuels and both vehicles, particles showed a consistent nucleation mode. Additionally, the use of biodiesel led to reduced DTT activity compared to diesel fuel. This suggests that addition of biodiesel to diesel may result in less toxic emissions and thus reduce adverse health effects and improve urban air quality.

2CO.7

Comparison of Real-World Tailpipe Emissions to MOVES 2010 Model Predictions as a Function of Road Grade.

BRITT HOLMÉN, Karen Sentoff, Wenchao Zhang, *University of Vermont*

MOVES2010 is the new regulatory model required by EPA for project-level mobile source emissions estimation. This study is the first to compare MOVES2010a emissions output to real-world tailpipe emissions data. The University of Vermont Total On-board Tailpipe Emissions Measurement System (TOTEMS) collected second-by-second real-world exhaust emissions and vehicle operating parameters from two light-duty vehicles – one conventional and one hybrid-electric Toyota Camry – while driving the Chittenden County Vermont road network. Three 400-meter road sections with different road grade (-5.7 to +6.0%) were selected from the downtown Burlington portion of the route to examine road grade effects on tailpipe gas and particle emissions and the ability of MOVES2010a to reproduce the measured real-world emission rates. A methodology was developed to generate second-by-second MOVES2010a emissions based on TOTEMS vehicle activity data (speed and grade) at the project-level for each road segment. Project-level MOVES could effectively model instantaneous emissions of the conventional vehicle for the downhill link, but flat and uphill link 1Hz emissions were overestimated by up to a factor of 35 (uphill link). Aggregating MOVES emissions for the flat and uphill links resulted in MOVES emissions that were 3 to 4 times higher than TOTEMS data. Omitting MOVES emissions for two specific operating modes (OpModes 28 and 29: VSP 18 – 30 kW/t at 25-50 mph) improved agreement between measured and modeled emissions somewhat. The hybrid vehicle results for flat and uphill were surprisingly similar to those for the conventional vehicle, but MOVES could not model the downhill link emissions of the hybrid vehicle that operated in “electric-only” mode. New modeling strategies are needed for hybrid-electric vehicle tailpipe emissions as they become a larger fraction of the on-road fleet.

2CO.8

High-Frequency Size-Resolved Sampling of Aerosols from a Three-Stone Fire and a High-Efficiency Cookstove to Determine the Minimum Sampling Rate to Avoid Aliasing.

DANIEL WILSON, Yungang Wang, Kathleen Lask, Ashok Gadgil,*University of California, Berkeley*

Worldwide, three billion people cook their food using biomass such as wood, charcoal, crop residues, and animal dung. Inhalation of emissions from this practice leads to four million premature deaths annually, mostly of women and children. Previous work to characterize the sized-resolved number concentration of disease-causing aerosol emissions from cooking fires has used slow-scanning instruments such as the scanning mobility particle sizer. In published literature, these instruments are reported to have taken more than two minutes to scan through the range of particle sizes from ~5 nm to ~ 500 nm in diameter. During the scan, these instruments could miss dynamic changes in aerosol emissions that occur on time scales faster than the scan frequency of the instrument. If all transient emissions from a cooking fire are not captured, these instruments and measurement techniques may alias time-resolved particle size distributions. In this study, we analyze wood combustion aerosols from both a three-stone fire and fuel-efficient, naturally-drafted cookstove using a fast mobility particle sizer. We utilize the fast sampling rate and broad size range of the fast mobility particle sizer, 1 Hz and 5.6 nm to 560 nm, respectively, to determine the minimum sampling rate necessary (Nyquist frequency) for aliasing-free analysis of cooking fire aerosol emissions. The Nyquist frequency for cooking smoke aerosol sampling is reported as a function of particle size. The determination of the minimum sampling rate for analyzing cooking fire emissions will inform the community about whether slow-scanning and less-expensive scanning mobility particle sizers are appropriate for analyzing cooking fire emissions, or if a more expensive instrument with a higher sampling rate is necessary to prevent aliasing.

2CO.9

Characterization of Soot Particles from Heat Insulation Foam Combustion.

Jesse Fowler, DE-LING LIU, *The Aerospace Corporation*

Concerns were raised for potential spacecraft contamination inside a launch vehicle payload faring (PLF) from soot particles generated by the thermal decomposition of heat insulation foam during the rocket engine ignition process. Soot particles could be ingested through leak paths in PLF envelope, which in turn poses contamination risk to spacecraft optics, solar cells, and thermal control surfaces as soot particles exhibit strong light absorption properties and could alter thermal properties. To gain insights into the effect of soot contamination to spacecraft, measurements of light transmission attenuation and thermo gravimetric analysis were performed to assist in risk assessment due to soot particle contamination.

Soot particles were generated and collected in a test setup consisting of a diffusion burner, a smoke collection funnel, a condenser, a dryer, an agglomeration chamber, a neutralizer, and filter assemblies. High purity hydrogen and compressed air were used as the fuel and the oxidizer, and were pre-mixed prior to feeding into the diffusion burner. Heat insulation foam was cut to the desired size and placed above the hydrogen flame to generate soot particles. Glass frits served as filters to sample soot particles, which were subsequently subjected to thermal gravimetric analysis (TGA) up to 800 degree C in nitrogen or air. For light transmission measurements, soot particles were collected on fused silica plates via smoke impingement above the burner, and the soot transmission properties were characterized by a Lambda-900 Spectrometer (Perkin-Elmer). The TGA results indicate that the collected soot particles contained approximately 40% semi-volatile organic compounds (SVOC), which were generated in the insulation foam combustion process and subsequently condensed/adsorbed on soot particles as the smoke cooled. In terms of effects of soot contamination, light transmission attenuation was observed to first occur in the UV-visible regime, as attributed to light absorption by SVOC. As more soot particles accumulated on the fused silica plates, light transmission attenuation in UV-visible became more pronounced, and continued to evolve into the infrared (IR) region. The findings suggest that soot may serve as unit density filters thus reducing optical transmission throughput in the IR wavelength range once certain soot area coverage is achieved.

2CO.10

Morphology of Particles Emitted from a GDI Engine Fuelled on Gasoline and Ethanol Blends. Brian Graves, Ramin Dastanpour, Steven Rogak, Phillip Mireault, Manuel Ramos, James S. Wallace, JASON S. OLFERT, *University of Alberta*

Gasoline direct injection (GDI) in combustion engines offers benefits in the realms of both power and efficiency; however, the production of nano-particulate emissions is of concern. It has been demonstrated that the introduction of ethanol into the fuel may reduce these nano-particulate emissions; however, the amount of particulate matter produced may be sensitive to fuel composition and operating conditions. Using a 2.0 litre, direct injection, inline 4 cylinder engine, the particulate emissions were characterized with regard to mass and size, and the effects of ethanol on these properties were examined.

The GDI engine was run at two set points: a simulated highway cruise, and a medium speed, low torque condition. The particle size distribution was measured using a scanning mobility particle sizer (SMPS), and the masses of various particle sizes were examined using a differential mobility analyser (DMA) and a centrifugal particle mass analyser (CPMA) in combination with a condensation particle counter (CPC). Soot samples were also taken on TEM grids using a Thermophoretic Particle Sampler (TPS) and analyzed with TEM. Results were obtained for gasoline blended with 0, 10 and 30 percent ethanol. It was found that although these relatively low concentrations of ethanol do not affect particle effective density, the medium speed condition produces lower-density particles than those resulting from the highway cruise. The mass-mobility exponents for the highway and medium speed conditions were determined to be 2.53±0.02 and 2.51±0.04 respectively. All test conditions produced count median mobility diameters between 60 and 80 nanometres, and the addition of a thermodenuder did not significantly reduce the total mass concentration of the particulate matter; however, traces of organic carbon and particle coating were observed in some samples, even when the thermodenuder was used. Samples taken at cold start and hot start conditions also changed shape under the TEM beam. This is an indication of the presence of non-EC particles.

2CO.11

Evaluation of Dilution System for On-Road Aerosol Emission Measurement from Automobiles. JAI PRAKASH, Akash Sharma, Anil Kumar, Gazala Habib, *IIT Delhi*

Aerosol emission and its composition from sources depend upon the energy use pattern and existing technologies in a region. Previous emission inventories have placed biomass fuel use in domestic sector as a major source of aerosol emission in developing regions like India and other part of South Asia, with considerably growing contribution from fossil fuel. Among fossil fuel based sectors, road transportation is one of the major contributors to aerosol emission in India. Real-time aerosol emissions represent complex mixture of solid particles (like EC), inorganic and organic compounds after exiting the source, cooling, and equilibrating to ambient conditions. Therefore, present study focuses on development of dilution sampler for real time aerosol measurement. The system will be equipped with particle sampling probe, vane probe velocity meter, flue gas analyzer, $PM_{2.5}$ sampler, CO_2 analyzer, temperature and relative humidity sensors. The system will be attached to tail pipe of the vehicle with the help insulated hoses. Emission will entrain into stainless steel duct and a fraction (0.6 LPM) of exhaust will be taken into dilution tunnel through particle sampling probe, where it will be diluted through measured quantity of zero air and sampled within residence time of 3 sec. Velocity and CO_2 of exhaust in the duct will be recorded each minute. Fuel consumption will be recorded at the end of each experiment using fuel consumption flow meter. The particles will be collected on quartz filters and emission factors will be calculated using particle mass collected on filter, exhaust velocity, area of duct, experiment time and fuel consumption. The paper will discuss the evaluation of new system and emission factors of $PM_{2.5}$, OC, EC ions for light duty vehicles. The implication of the results for refinement of emission inventory and regional climate study will also be discussed.

2CO.12

Characterization of Mixed Diesel and Gasoline Exhaust by High-Resolution Aerosol Mass Spectrometry under Varied Engine Load and Dilution Conditions. COURTNEY L. HERRING, Matthew H. Erickson, Mylene Gueneron, Jacob D. McDonald, B. Thomas Jobson, Timothy M. VanReken, *Washington State University*

We present the results of a series of experiments conducted at the Lovelace Respiratory Research Institute (LRRI) to investigate the gas- and particle-phase properties of mixed exhaust from diesel and gasoline engines. Approximately 25 tests were conducted across a range of gas/diesel mixing ratios, engine loads, and particle concentrations to examine how these factors affect chemical composition and phase partitioning of the exhaust. The organic aerosol composition was characterized and measured using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). Gas-phase organics were measured with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) fitted with an IVOC sampler. Supporting measurements include the particle size distribution, black carbon mass, and carbon dioxide mixing ratio.

Analyses of HR-AMS data for the diesel and diesel/gasoline mixtures show several interesting patterns potentially associated with differences in particle mass loadings and engine operating conditions. Strong signals have been identified associated with a wide range of polycyclic-aromatic-hydrocarbons (PAHs), including those that can partition between the gas and particle phases. Additionally, differences in relative abundances at some unit-resolution ion masses suggest significant differences in exhaust chemical processing under varying conditions, some resulting in nitrogen-containing organic species. Further analysis and investigation into the particle phase data along with the gas phase measurements is ongoing with the goal of better understanding the gas/particle partitioning behavior of gas/diesel mixtures and the potential for this partitioning to affect aerosol toxicity.

2CO.13

Analysis of Real-time Emission Data from In-home Use of Cookstoves in Rural Karnataka, India. ANDREW GRIESHOP, Grishma Jain, Karthik Sethuraman, Ther Aung, Julian Marshall, *North Carolina State University*

New cookstove technologies may play a key role in reducing the impacts of primitive biofuel use in developing countries on human mortality and climate change. However, standard lab protocols for cookstove testing have been shown to inadequately represent in-use efficiency or emissions. Spatio-temporal and inter-household variation in activity and other factors may preclude development of a single protocol able to represent all uses for all purposes. However, there is great value in detailed analysis of available stove emission data. A recent field trial built around a carbon-credit financed stove intervention in rural India resulted in an extensive stove usage data set for two stove models during two seasons. This poster presents analysis of real-time gas- and particle-phase emission data collected during 104 individual tests in 33 households. Emission measurements with an autonomous instrument package were conducted during family stove use in homes before and after cookstove replacement. The Stove Emission Measurement System (STEMS) was deployed for 50 pre- and 54 post-intervention cooking periods. STEMS uses an in-plume dilution probe to collect data on real time (1-2 s) CO2, CO, PM light scattering and absorption (at 3-wavelengths). Statistical analysis of data is used to characterize stove activity and time-varying emissions rates and characteristics (e.g. modified combustion efficiency; MCE). Estimates of aerosol optical properties including Absorption Angstrom Exponent and Single Scattering Albedo are determined as a function of stove activity. Inter- and intra-test variability is characterized and it is shown that season, stove technology and fuel attributes have a substantial impact on emission characteristics. Stove use periods are grouped into several types based on the distributions of use intensity and MCE which correlate with aerosol optical properties. Implications for laboratory protocols to represent in-field use are presented.

2CO.14

A Comparative Study on Emission Characteristics of Different Cook Stoves and Modeling of Particle Formation During Cook Stove Operation. SAMEER PATEL, Jiaxi Fang, Anna Leavey, Siqin He, Chang Ki Kang, Kyle O'Malley, Smit Shah, Pratim Biswas, *Washington University in St Louis*

A large fraction of the world's population depends on biomass to cook their food; and due to the inefficient combustion this results in serious public health and climate issues. However, on the other hand, biomass is emerging as a sustainable and carbon-neutral energy resource and is receiving increased attention for energy generation. Biomass combustion in cookstoves typically results in higher PM which deteriorates air quality and adversely impacts health. Although particulate formation during biomass combustion in cookstoves has been studied extensively [1, 2]; there has been a lack of detailed characterization of particle formation and the evolution of aerosol size distributions. Variations among cookstove designs along with the different operating conditions make it difficult to compare different cookstove studies. A better understanding of particulate formation in cook stoves along with detailed characterization of aerosol processes is necessary to overcome this limitation.

The goal of this study is to examine emission characteristics of different types of cookstoves in a controlled environment. Three different representative cookstoves which operate on different principles were examined in this study. Emissions measurements such as $PM_{2.5}$, CO-CO_2 ratio, lung deposited surface area concentration, total organic carbon and particle number size distributions were obtained. The effect of fuel type was studied by measuring emissions from two types of fuels; apple wood and coal.

Results from these measurements were used to compare to predictions from a cookstove aerosol model to elucidate particulate matter formation and growth dynamics. The effects of biomass chemical composition, size and cookstove operating conditions on emissions were studied using the model. Data generated in this study will contribute to a comprehensive understanding of the major parameters affecting overall indoor air pollution and exposure during cookstove operation.

References:
1.Sahu et al. (2011) Env. Sci. Tech, 45(6):2428-34.
2.Leavey et al. (2013) Aerosol Sci. Tech, 47(9):966-978

2HA.1

Some Aspects of Aerosol Production by Modern Flush Toilets of Various Designs. DAVID L. JOHNSON, Robert A. Lynch, Jacob F. Jones, Kenneth R. Mead, Deborah V.L. Hirst, *Dept Occup/Envir Health, Univ OK HSC*

Background. A microbe-contaminated toilet will produce bioaerosol droplets when flushed, some of which will remain airborne. We assessed toilet plume aerosol from dual flush high efficiency (HET), dual flush pressure-assisted high efficiency (PAT), and Flushometer siphonic toilets.

Methods. Both total and droplet nuclei “bioaerosol” production were assessed for the toilets, which had similar bowl water and flush volumes. Monodisperse 0.25 or 0.30 µm fluorescent microspheres served as microbe surrogates. Experiments were conducted in the particle-free environment of a mockup 175 cu ft water closet (WC) purged with HEPA-filtered air. Bowl water was seeded with microspheres before each flush. Airborne particles were sampled onto 0.2µm pore size MCE filters for 30 minutes beginning 15 minutes after the flush, using 4 open-face cassettes mounted 2 and 5 feet high on the WC side walls. Pre- and post-flush bowl water samples were filtered through the same type filter, and all filter particle counts were analyzed via fluorescent microscopy.

Results. Bowl headspace droplet count size distributions were bimodal and similar for all toilet types and flush conditions, with 95% of droplets < 2 µm diameter and over 99% < 5 µm. Up to 145,000 droplets were produced per flush, with the relatively high energy Flushometer producing over 3 times as many as the lower energy PAT and over 12 times as many as the lowest energy HET despite similar flush volumes. However, the mean numbers of fluorescent particles aerosolized and remaining airborne were similar for the three toilets at approximately 1100-1200 per flush.

Conclusions. Toilets produced denser aerosols, but with similar size distributions, with increasing flush energy. However, the number of droplet nuclei “bioaerosols” was similar for similar flush volumes. These findings suggest two concurrent aerosolization mechanisms – splashing for large droplets and bubble bursting for the fine droplets that form droplet nuclei.

2HA.2

Toilet Plume Droplet Nuclei Aerosol Production and Bowl Clearance during Sequential Flushes. DAVID L. JOHNSON, Robert A. Lynch, Jacob F. Jones, Kenneth R. Mead, Deborah V.L. Hirst, *Dept Occup/Envir Health, Univ OK HSC*

Background. Toilets will generate bioaerosols for several flushes following contamination. Bowl water will remain contaminated even after several flushes, possibly due to bowl wall particle adhesion. This study compares droplet nuclei “bioaerosol” generation and bowl water clearance for three modern siphonic toilet types during sequential flushes after an initial seeding.

Methods. Three siphonic toilet types were seeded with 0.25 µm fluorescent polymer microspheres as microbe surrogates. The toilets had similar flush and bowl water volumes but different flush energies. Bowl water was seeded prior to the first flush only and a water sample collected before the first flush. The toilet was flushed and airborne particles sampled onto 0.2µm pore size MCE filters for 30 minutes beginning 15 minutes after the flush, using 4 open-face cassettes mounted 2 and 5 feet high on the water closet side walls. A water sample was collected and cassettes changed between flushes. Water samples were filtered, and air and water filters counted via fluorescent microscopy. Air samples were collected over 4 sequential flushes and water samples over up to 24 flushes.

Results. All toilets exhibited clearances of 3+ log bowl water concentration reductions with the 1st flush, 1-2 logs with the 2nd flush, and less than 1 log thereafter. Post-flush #3 the clearances were extremely gradual. Air concentrations did not decrease in proportion to water concentration, spanning 2 orders of magnitude compared to a span of 6 o.m. in bowl water concentration. These findings were consistent with previous reports for 3-7 flushes using microbes Surfactant addition after 24 flushes boosted the bowl water concentration.

Conclusions. Particle adhesion to and re-release from bowl water surfaces was demonstrated, with substantial bowl contamination remaining for at least 24 flushes.

2HA.3

Characterization of a Vortex Shaking Method for Aerosolizing Fibers. BON KI KU, Gregory Deye, Leonid Turkevich, *Centers for Disease Control and Prevention, NIOSH*

Generation of well-dispersed, well-characterized fibers is important in toxicology studies. A vortex-tube shaking method is investigated using glass fibers to characterize the generated aerosol. Controlling parameters that were studied included initial batch amounts of glass fibers, preparation of the powder (e.g. pre-shaking), humidity, and aerosol flow rate. Total fiber number concentrations and aerodynamic size distributions were typically measured. The aerosol concentration is only stable for short times ($t < 10$ min) and then falls precipitously, with concomitant changes in the aerosol aerodynamic size distribution; the plateau concentration and its duration both increase with batch size. Pre-shaking enhances the initial aerosol concentration and enables the aerosolization of longer fibers. Humidity strongly affects both the number concentration and the particle size distribution, resulting in a higher number concentration but a smaller modal diameter. Running the vortex shaker at higher flow rates ($Q > 0.3$ lpm) yields an aerosol with a particle size distribution representative of the batch powder; running the vortex shaker at a lower aerosol flow rate ($Q \sim 0.1$ lpm) only aerosolizes the shorter fibers. These results have implications for the use of the vortex shaker as a standard aerosol generator for powders of polydisperse or asymmetric particles.

2HA.4

Aerosol Deposition in Nasal Airway Replicas: Infants, Children, and Adults. Mindy Guo, YUE ZHOU, Jinxiang Xi, Hammad Irshad, Yung-Sung Cheng, *Lovelace Respiratory Research Institute*

Understanding aerosol deposition in the human respiratory tract is crucial in assessing health effects of environmental exposure and improving inhalation drug delivery. The nasal airway is the first line of defense for the entire respiratory system's functions and serves as a filter of ambient aerosols during inhalation. However, there is significant variability of particle deposition in nasal airways of infants, children, and adults due to age-related differences in airway geometry and breathing rate. The previously published particle deposition models were based on similar nasal airway geometry. In such cases, one model can only be used in one age group to estimate particle deposition. The estimated particle deposition is crude and the calculation of deposition efficiency requires several models to cover all age groups. In addition, it does not take individual geometric variability into account.

We developed a simple way to investigate nasal aerosol deposition in all age groups in this study. We conducted in vitro testing of micrometer particle deposition in nasal airways for infants, children, and adults by using five nasal replicas (10-day, 7-month, 3-year, 5-year, and 53-year) at similar breathing conditions. Monodisperse oleic acid aerosols ranging in size between 2 and 28 micro-meters were delivered into replicas at the rest condition. The size range covers the deposition efficiency up to 100%. The combined data set of infants, children, and adults demonstrated that the aerosol deposition in the nasal airway is strongly dependent on the particle size and pressure drop. Since the method is pressure drop based, it is not influenced by individual geometric variability. In conclusion, our study proved that the deposition efficiency can be calculated based on a single empirical equation for all age groups.

2HA.5

Modeling Mainstream Cigarette Smoke Inhalation and Deposition in the Human Lung. BAHMAN ASGHARIAN, Owen Price, Caner Yurteri, John McAughey, *Applied Research Associates, Inc.*

Determination of dose to the lung of inhaled mainstream cigarette smoke aids in determining vulnerable sites in the respiratory tract, which experience enhanced deposition. Components of the cigarette smoke that may be responsible for the adverse effects can also be identified; thus providing a roadmap for harm reduction of cigarette smoking. A particle deposition model specific to cigarette smoke particles was developed for in vitro oral cavities and the lung by extending existing models for environmental particles and accounting for cigarette smoke particle size growth by hygroscopicity, phase change, and coagulation. In addition, since the cigarette puff enters the respiratory tract as a dense cloud, the impact of the cloud effect on particle drag and deposition was accounted for in the deposition model. Models of particle losses in the oral cavities were developed during puff drawing and subsequent mouth hold. Cigarette smoke particles were found to grow by hygroscopicity and coagulation, but shrank as a result of evaporation of nicotine and other volatile constituents. Predicted deposition of cigarette smoke particles was smaller than measurements when treated as a collection of non-interacting individual particles. Accounting for cloud movement provided the necessary physical mechanism to explain the greater than expected, experimentally-observed particle deposition. The deposition model for cigarette smoke particles can provide the necessary input to determine the fate of inhaled cigarette smoke particles in the lung and the rest of the body for health assessment, identification and removal of harmful components of cigarette smoke particles. This study was funded by British American Tobacco.

2HA.6

Distinct Reaction of Bacterial Culturability and Viability on Antimicrobial Air Filters Coated with Sophora Flavescens Nanoparticles. GI BYOUNG HWANG, Kyoung Mi Sim, Jae Hee Jung, Gwi Nam Bae, *Korea Institute of Science and Technology*

Most studies evaluated the performance of antimicrobial filters by means of measuring the loss of culturability of bacteria, and some estimated the antimicrobial effect on viability using the plate count method. However, recent studies related have indicated that this method may produce overestimations or partial results because bacterial culturability is susceptible to natural decay and environmental stimuli such as acidic water, low temperature, and etc. Additionally, the plate count method cannot demonstrate bacterial viability and the presence of VBNC bacteria, which have low metabolic activity but may be able to reproduce at favorable conditions. Therefore, to investigate the more precise antimicrobial effect of filters on bacteria, their effects on the culturability and viability of bacteria must be investigated, particularly in terms of the VBNC state. This study was performed to investigate effects of antimicrobial air filter on culturability and viability of E. coli and B. subtilis bacteria. At the antimicrobial test with various exposure time, after 60 min, >80% of both bacteria species lost culturability on control filter due to natural decay whereas >86% kept their viability and the number of VBNC bacteria increased as residence time of bacteria on control filter increased. For antimicrobial filter, culturability reduction trends of both bacterial species were similar, but viability reduction differed with it. E. coli viability reduced gradually from 77% to 66% over 60 min, while that of B. subtilis decreased dramatically from 70% to 22% over the same period. As residence time increased, the proportion of E. coli cells that entered the VBNC state also increased; however, the proportion of B. subtilis cells that entered the VBNC state decreased.

2HA.7

Characterization of Atmospheric Bioaerosols Found in Tijuana, Mexico. LILIA HURTADO, Guillermo Rodriguez, Penelope Quintana, Miguel Zavala, Jonathan Lopez, Mariela Juarez, *Universidad Autonoma de Baja California, Tijuana, Mexico*

The atmosphere is not considered a habitat for microorganisms, but a variety of them that are transported through it during their life cycle. These microorganisms in the atmosphere has great environmental importance by their degree of dispersion that can be achieved by partnering with condensation nuclei, freezing and fog. Microorganisms come from both natural and anthropogenic sources and distribution is regulated by atmospheric chemistry, biological and meteorological factors. In this work, 9 different areas of the city of Tijuana were periodically samples for aerial microbial content during one year period (2012-2013). Overall viable counting afther air collection by an impactation method with Millipore M Air T air analyzer, showed levels of microbial contamination of 2,500 to 50,000 CFU/liter.

The above results were correlated with meteorological variable sampling area and allow noted that variation in microbial concentration is regulated by relative humidity, temperature, wind speed and direction. Also found higher microbial load in the period from June to September and a considerable decrease in November to February. Several potentially pathogen bacteria were detected, such as Staphylococcus aureus, Enterococcus faecalis and Pseudomonas aeruginosa was the must common. The incidence of bacterial showed a different temporal ditribution. This is the first work of evaluation of bioaerosols in the northwest of the country.

2HA.8

Tobacco Smoke Dose at the Air-Liquid Interface In Vitro. Jason Adamson, JOHN MCAUGHEY, *British American Tobacco*

Tobacco smoke is a complex dynamic aerosol. It is a self-selected source of particle inhalation and exposure, despite its documented adverse health effects. It is important to fully characterise absolute particle dose in vivo and in vitro, and to consider dose in terms of particle number, surface area or mass. This approach offers insight into the relationship between dose and subsequent biological effect.

Tobacco smoke exposures (30 minutes) using a Borgwaldt RM20S smoking engine ranging from 0.22–25.75 micrograms per cm^2 for smoke dilutions from 1:400 to 1:5 respectively were measured using a quartz crystal microbalance in a well-based air-liquid interface (ALI) exposure system. Smoke particle diameter by electrical mobility(Cambustion DMS-500, UK) gives a volume-weighted median diameter of 394 nm at 1:60 dilution. Assuming a confluent monolayer of A549 lung epithelial cells of notional 18 micrometer diameter at the ALI, this represents an approximate cell density of 3.93e5 cells per cm^2. Assuming a log-normal distribution and a smoke particle density of 1120 kg per m^3, a 394 nm diameter particle will weigh 35.8 fg. Thus, the measured mass depositions of 0.22–25.75 micrograms per cm^2 for the smoke are equivalent to particle number exposures of 6.14e6-7.18e8 per cm^2 and particle surface area exposures of 7.5e-3-8.8e-1 cm^2 per cm^2 lung surface area. In practice, this suggests each A549 cell is exposed to 16-1830 smoke particles over the measured dilution range. These surface area doses are similar to reported pro-inflammatory threshold values of 1-10 cm^2 particle surface area per cm^2 cell surface area.

The precision and accuracy of the smoke measurement methods and the resulting absolute metrics will be compared with daily in vivo dose estimates and measurements in the airways of smokers.

2HA.9

Aerosol Measurement of E-cigarettes. Ross Cabot, Anna Koc, Caner Yurteri, JOHN MCAUGHEY, *British American Tobacco*

Electronic nicotine delivery systems (e-cigarettes) are a new type of product rapidly gaining popularity with adult cigarette smokers. They are typically cigarette shaped battery-powered devices which produce a condensation aerosol containing nicotine and water with glycerol, propylene glycol or a mixture of each.

Particle size measurements were conducted on a glycerol, water and nicotine based commercial e-cigarette bought from UK retail sources and tested to a puffing regime of a 50 mL puff of 3s duration every 30s. Measurements were conducted by gravimetric filter analysis, electrical mobility using the Model DMS-500 with Smoking Cycle Simulator (Cambustion, UK) and by laser diffraction using the Spraytec (Malvern, UK).

Gravimetric mass per puff was 1.86+/-0.13 mg per puff with the aerosol composition matching the source cartridge composition. Volume weighted median diameters were 252+/-11 nm by electrical mobility and 435+/-39 nm by laser diffraction. Measured geometric standard deviations were 1.55–1.65 and particle number per puff by electrical mobility was 4.99e10+/-2.26e9. Back-calculation of the diameter of average mass from the gravimetric data, number concentration and mixture density (1.216 g/cc) gave a volumetric diameter of average mass of 388 nm supporting the hypothesis of evaporation losses during the electrical mobility measurement. The particle diameter data, in the sub-micron range, are similar to those from tobacco smoke.

In conclusion, the measurement data suggest that the aerosol plume from e-cigarettes can be characterised with good precision, by real-time analytical methods using commercially available equipment.

This work was conducted in-house by British American Tobacco.

2HA.10

Temporal and Spatial Distributions of PAHs in the Atmosphere of Korea and Their Toxicity. HYE JUNG SHIN, JiYi Lee, Soon A Rho, Jong Choon Kim, Seok Jo Lee, *National Institute of Environmental Research*

PAHs have been considered as one of Persistent Organic Pollutants (POPs) in the world because of their toxic, persistent and semi-volatile properties. Therefore, the Ministry of Environment in Korea has monitored PAH compounds in the atmosphere since 2003 in order to evaluate temporal and spatial distributions and to assess the impact of PAHs concentrations to the human health. In this study, we will statistically analyze PAH time trend data from the thirty one sampling sites (Toxic Air Pollutants Monitoring Stations) which consist of various urban and rural sites in Korea and show the characteristics of the temporal and spatial trends of atmospheric concentrations of PAHs in Korea. Also, based on the measured data, toxicity equivalency factors (TEFs) and mutagenic equivalency factors (MEQs) of PAHs will be produced and the major factor determining high TEFs and MEQs values will be discussed.

2HA.11

Contamination Level of Traffic-related Air Pollutants outside of the Children Day-Care Facilities in Seoul. SEUNG-BOK LEE, Kyung Hwan Kim, Dae-Kwang Woo, Sungho Woo, Gwi Nam Bae, *Korea Institute of Science and Technology*

Traffic-related air pollutants have been reported to have adverse effect to public health, in particular to health of children as an environmental hazardous factor of allergic diseases such as asthma and atopic dermatitis, whose annual prevalence is increasing year by year and becoming one of important social issues in urban area of Korea. In order to characterize the environmental effect of air pollutants to allergic diseases in childhood, indoor exposure level of air pollutants have been measured in children day-care facilities.

In this study, the outdoor contamination level of air pollutants, in particular traffic-related pollutants such as ultrafine particles, particle surface area, particle-bound PAHs, black carbon, and NOx were monitored using a mobile laboratory outside of the two selected children day-care facilities whose indoor contamination levels in Seongbuk-gu and Seongdong-gu, Seoul were classified into the highest group and the lowest group, respectively, in the preliminary survey.
The mobile laboratory measurement of outdoor air quality was conducted not only at 3-4 fixed locations nearby the targeted children day-care facilities but also during driving on the surrounding roads with a total length of 5-9 km.

The traffic-related air pollutants as an indicator of vehicle emission such as concentrations of ultrafine particle number, particle surface area, black carbon, particle-bound PAHs were found higher at the major arterial roads with more than 6 lanes nearby the day-care facilities. The average concentration of measured outdoor NO2 concentrations was lower than that of the indoor air quality for the day-care facility in Seongbuk-gu, implying that there might be indoor sources like cooking. The spatial distribution of traffic-related air pollutants will be discussed in order to consider the penetration of outdoor air contamination to indoor environment for the facility located in Seongdong-gu.

2HA.12

Identification of PM Components that Contribute to Oxidative Potential in the Dithiothreitol (DTT) Assay. JESSICA CHARRIER, Kennedy-Kiet Vu, Alam Hasson, Cort Anastasio, *University of California, Davis*

The rate of consumption of dithiothreitol (DTT) is increasingly used to measure the oxidative potential of particulate matter (PM), which has been linked to adverse health effects. It is important to identify which chemical components of PM cause DTT loss in order to better understand the results of this assay, inform in vivo health studies, and identify PM sources that may pose a higher health risk. In past work we have tested DTT loss from laboratory stocks of individual chemicals and found DTT activity from both soluble transition metals and quinones. We calculated that soluble metals should dominate the DTT response from ambient PM because their concentrations are larger than quinones. However, ambient PM is more complex than laboratory stock solutions, especially in regards to metal oxidation state and ligand binding. Extending findings from laboratory stocks to ambient PM is also complicated by the fact that past studies have not measured both soluble metals and quinones in the same PM samples. To better quantify the contributions of quinones and soluble metals to DTT loss from ambient PM, we are measuring DTT loss, and quinone and soluble metal concentrations, from PM2.5 samples collected in Claremont, CA and Fresno, CA. We will estimate the fraction of DTT loss from each quinone and transition metal using previously measured concentration response curves of pure compounds to identify which chemical species are most important for oxidant production and if these species account for the full oxidative potential of the PM. We will evaluate this approach by comparing the calculated DTT loss based on the chemical composition versus the measured DTT loss.

2HA.13

Correlation of Method 5040 with Other Methods for Carbon Nanotube Exposure Assessment. PATRICK O'SHAUGHNESSY, Adrianne Horne, Ralph Altmaier, *University of Iowa*

The study objective was to compare the use of NIOSH Method 5040 (Elemental Carbon) with other methods for the assessment of carbon nanotubes (CNTs) that may occur in workplace settings. Method 5040 has a limit of quantification of the same magnitude, 7 ug/m3 of elemental carbon (EC), as the proposed recommended exposure limit (REL) for CNTs. We therefore compared results obtained using Method 5040 with other metrics including those obtained with a portable aethelometer (model AE51, AethLabs, San Francisco, CA) and a scanning mobility particle counter. CNT aerosols of varying purity, type, and concentration were dispersed via a nebulized suspension of bulk powder into a small (3 L) chamber from which a gravimetric sample was taken, in addition to readings made by the aethelometer and SMPS. SMPS readings were converted to a volumetric concentration. Filter samples were weighed to determine a mass concentration and then sent to a laboratory for EC, organic carbon (OC), and total carbon (TC) analysis. Surprisingly, the laboratory reported EC content ranging from 6 to 19% with the remainder OC. The highest percentage was found in 99% pure single-walled CNTs. This finding resulted in relatively poor associations between EC and the other measurement methods. Correlations were therefore made between those measurements and TC. Aethelometer readings correlated well with TC concentrations ($r2 = 0.94$) but were 2.5x lower in magnitude. This correlation was not affected by CNT type or purity. Volumetric concentration resulting from SMPS measurements was less well correlated to TC ($r2 = 0.65$). Interestingly, TC measurements had a positive bias relative to mass-based concentration with reported results near 80 ug/m3 when filter measurements were at the limit of detection of the filter balance. Based on these results, a portable aethelometer can be used as an accurate surrogate for Method 5040 for TC measurement.

2HA.14

Fiber Transport and Deposition in Human Upper Tracheobronchial Airways -- the Effect of Brownian Dynamics.

Lin Tian, GOODARZ AHMADI, Philip K. Hopke, Yung-Sung Cheng, *Clarkson University*

Transport and deposition of inhaled asbestos fibers has been studied in the past few decades due to its pathological response in living being. Of the earlier study, in vitro and vivo experiments in human and animal subjects were conducted and measurements were made where carcinogenicity of these particles was investigated. In this work, the transport and deposition of elongated ellipsoidal fibers were numerically simulated in a physiological realistic lung bifurcation model. Detailed motion of the inhaled fibers and their interaction with the surrounding environment were reproduced by solving the system of coupled nonlinear equations governing the fibers' translational and rotational motion. Hydrodynamic drag and torque, shear induced lift, turbulence diffusion, gravitational sedimentation, and Brownian drag and torque were accounted. Correlations of these forces with the fiber transport and deposition pattern, fiber characteristics, human breathing condition, and airway morphology were analyzed. The study uncovered the very important role of Brownian dynamics in thin fibers' motion in human tracheobronchial airways. This can help explain many of the earlier experimental findings. The simulation results were compared with the experimental measurements, and carcinogenicity of the fibers was discussed.

2HA.15

Collection of House Dust Aerosols Complemented with Common Allergen Proteins: Comparison of Sampler Efficiencies with MARIA™ Allergen Assay.

DAVID ALBURTY, Pamela Murowchick, *AlburtyLab, Inc.*

The InnovaPrep ACD-200 Bobcat Air Sampler is a lightweight, portable, dry filter air sampler with a unique wet elution system. This system has been developed to address a broad range of air sampling requirements and was recently included in an aerosol comparative challenge testing for the collection of allergens performed by personnel at AlburtyLab, Inc.

The ACD-200 consists of a self-contained medium volume aerosol collector replaceable 52 mm dry electret filter and a simple to operate electret filter biological sample elutor. During this testing, collection was initiated manually and was operated in the "Extended Run" mode (1 min on at 100 Lpm, 5 min off).

The objective of this testing was to compare the performance of ACD-200 to other commercially available aerosol sampling devices: 47 mm polycarbonate reference filters, NIOSH BC-251 two-stage cyclone-based personal bioaerosol sampler, and AGI-30s.

House dust samples that had been complemented with nine common indoor allergen proteins were pulverized using a mortar and pestle and then disseminated into the aerosol test chamber using a dry dissemination system developed at AlburtyLab referred to as a Tapper. Use of this dissemination device resulted in an aerosol with a concentration of 0.2 mg/m3 and a mass mean particle diameter of 5.048 µm AD.

The allergen protein samples were collected from each of the sampling systems and shipped to Indoor Biotechnologies for analysis using the multiplex MARIA™ Allergen Assay kit.

The calculated aspiration and recovery efficiencies were determined for each of the sampling systems based on the average result determined for the reference filters. The ACD-200 and its associated elution system proved effective in collecting and releasing the allergen complemented house dust to the liquid sample. In many cases the determined aerosol concentration exceeded that determined by the reference method.

2HA.16

Commercial Charbroiling Emission Induces Inflammatory Response in Human Bronchial Epithelial Cells: The Role of Oxidative Stress and p38 MAPK. NING LI, Keisha Williams, Nicholas Gysel, Nachamari Rivera-Rios, Georgios Karavalakis,*Michigan State University*

Commercial charbroiling emissions (CCE) are a significant source of ambient particulate matter (PM). Cooking meat on under-fired charbroilers emits significant amount of PM containing almost exclusively organic compounds, including carcinogenic polycyclic aromatic hydrocarbons which have also been associated with the pro-oxidative, pro-inflammatory and toxic effects of diesel exhaust particles. Currently, little is known about the respiratory effects of CCE. To better understand the effect of these emissions on restaurant workers health, as well as neighboring communities, we investigated whether compounds contained in the organic extracts of commercial charbroiling meat-derived emission had the ability to induce an inflammatory response in human airway epithelial cells, and if this effect was mediated through the generation of oxidative stress. PM2.5 samples collected during meat cooking processes on a commercial-grade under-fired charbroiler were sequentially extracted with water followed by methanol to obtain an aqueous PM suspension (AqPM) and organic extract (OE) respectively. Using human bronchial epithelial cell line (BEAS-2B) and primary normal human bronchial epithelial cells (NHBE) we showed that at non-toxic concentrations, OE, but not the AqPM, strongly induced the expression of antioxidant enzyme heme oxygenase-1, a highly sensitive marker of oxidative stress. The production of IL-6 and IL-8 was also significantly up-regulated by OE and this response could be effectively inhibited by the presence of antioxidant (N-acetyl cysteine), nuclear factor (erythroid-derived 2)-like 2 (Nrf2) activator (sulforaphane), and p38 MAPK inhibitor (SB203580). Our results indicate that organic chemicals associated with PM2.5 emitted from commercial charbroiled meat cooking are capable of inducing oxidative stress and inflammatory responses, which involved the activation of Nrf2- and p38 MAPK-mediated signaling pathways. Further research is needed to better characterize the ability of charbroil cooking emissions to generate inflammatory response, and to assess the resulting adverse health effects on workers in the restaurant industry.

2HA.17

Association of Ambient PM2.5 with Pulmonary and Heart Rate Variability Functions among Healthy Individuals of IIT Delhi. GAURAV SINGH, Gazala Habib, Mukesh Khare, *IIT Delhi*

Ambient particulate matter (PM) pollution itself ranked 4th attributing burden of diseases for East Asia. Risk of urban PM pollution has been reported as moderate to high for cardiovascular, circulatory and pulmonary diseases for developed countries. However, such investigation is lacking for densely populated and rapidly growing countries like India were PM concentration level and composition are expected to be different and may be leading to more severe impact on health. Present study focuses on development of statistical relationship of ambient concentration of $PM_{2.5}$ with pulmonary and cardiovascular functions during January 2012 to April 2013. The subjects were recruited based on standard questionnaire survey designed by American thoracic society and modified for present study. A total number of 100 healthy subjects living in IIT Delhi from last 3 years or more were recruited for monitoring. Morning and evening pulmonary functions [i.e. force vital capacity (FVC); force expiratory volume in 1 second (FEV_1); force expiratory flow rate (FEFR); (FEV_1/FVC)] were measured repeatedly among all 100 subjects of average age 23 years (17-62 years). Simultaneously 8 hours ambulatory electrocardiography were conducted to monitor heart rate variability (HRV) functions [i.e. standard deviation of all NN intervals; square root of the mean squared successive NN interval differences; proportion of number of interval differences of successive NN intervals greater than 50 millisecond to total number of NN interval] repeatedly among 37 subjects of average age of 23 years (20-29 years). High $PM_{2.5}$ concentration was observed in January 2013 [168±88 mcg/m^3 (day), 261±158 mcg/m^3 (night)] while day time low was observed in April [71±32 mcg/m^3] and night time low was observed in March [132±71 mcg/m^3]. The multi-variant linear regression for FVC and SDNN perform moderately (R^2=0.5) for lag_3 day and lag_3 night concentrations. This paper will discuss the relationship between $PM_{2.5}$ concentration with pulmonary and HRV functions.

2HA.18

Biodiesel Exhaust Particulate Matter (PM) Pretreatment and Screening for Health Effect Studies. JIM DUNSHEE, Brian C. Palmer, Tyler Feralio, Muyao Li, Naomi K. Fukagawa, Britt Holmén, *University of Vermont*

Effects of biodiesel emissions on public health are not completely understood. Conflicting data in the recent literature highlight the challenges of drawing conclusions from studies utilizing different engine, fuel, and operating conditions that produce variable concentrations of harmful pollutants. The ability to identify the biodiesel fuel and engine technology that pose the lowest health risk will be a key component of biodiesel sustainability. Variation in how PM is sampled and prepared for use in biological studies may have significant effects on experimental outcomes. Oxidative stress as a response to reactive oxygen species (ROS) is believed to be the common mechanism leading to inflammation. However, not all exhaust particles generate ROS to the same degree. Development of a reliable and easy method for screening PM samples produced from a range of experimental conditions (e.g. fuel source, combustion parameters, exhaust filters) for their potential to induce oxidative stress will enable investigators to efficiently define those conditions linked to adverse health outcomes.

The objective of this study was to evaluate PM sampling techniques of biodiesel exhaust to be used in studies to determine biological effects. Emissions from a light-duty diesel Volkswagen engine run on various blends of biodiesel and petrodiesel were collected into ethanol using impingers. Two approaches to concentrate the suspensions were compared followed by determination of the effects of the PM on ROS generation and redox-sensitive inflammatory pathways in cell and animal models. Results from the abiotic dithiothreitol (DTT) consumption assay identified PM suspensions with greater ROS capacity and, consequently, greater potential for inducing inflammatory responses. Data confirmed that suspensions with higher ROS capacity were associated with evidence of cytotoxicity and inflammation.

2HA.19

Characterization of Spray Velocities from a Pressurized Metered-Dose Inhaler. ABUBAKER ALATRASH, Edgar Matida,*Carleton University*

Pressurized metered dose inhalers (pMDIs) are normally used to deliver medication in the treatment of certain lung diseases such as asthma, chronic obstructive pulmonary disease (COPD), and cystic fibrosis among others, and may be used by several patients all over the world in part of their lives.

Phase Doppler Anemometry (PDA) is point-measurement laser technique that can be used to evaluate pMDI aerosol medication velocity and size as function of time. These measurements can be used to help improving the performance of the inhalers concerning medication delivery. Previous reports (Dunbar, 1996, Crosland et al., 2008) indicated that the pMDI spray deflects as much as 7 degrees downwards from its axis, before coming back to its centreline during actuation. In the present investigation, two inhalers from different pharmaceutical companies, using the same medication (salbutamol sulphate) are tested in order to verify previous spray deflection measurements using PDA.

Results of measurement at the pMDI centreline (25, 50, 75, 100, and 125 mm from the inhaler outlet) show that for both pMDI brands, the spray velocities were bimodal in time, with two velocity peaks, the first one occurring as the spray was leaving the mouthpiece, and the second (at the same location) around 60 ms later, with a drop in the velocity occurring in between the two peaks.

References

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2HA.20

Leakages of Bioaerosols through Controlled Gaps in Respirators: Experiments and Computational Fluid Dynamics.SUVAJYOTI GUHA, Prasanna Hariharan, Matthew Myers, *Food and Drug Administration*

The recent explosions during the Boston Marathon clearly showed that terrorism in the U.S. is a continuing threat. One mode of such a threat is from hazardous bio-aerosols which when suspended in air, could be inhaled by the general population (children as well as adults), causing sickness or even death. Respirators, form the first line of defense against such bioaerosols. The effectiveness of respirators has been shown in prior studies to strongly correlate with how well a respirator fits on a person's face, suggesting that proper fit and fit-testing is critical. Thus, in anticipation of a possible bioterrorism event, we need tools to determine how gaps between the mask and face due to improper fit affect the performance of respirators. Such an evaluation would ideally require experimental study on a large number of human subjects, which would be difficult and expensive to implement. Thus, we have begun development of a CFD-based model using commercial software for computing the barrier effectiveness of different respirators. In order to validate the computational model, we have designed an apparatus with a well-controlled gap profile existing between the respirator and a flat surface. Comparisons between the computational model and aerosol leakage experiments in the controlled geometry will be presented, for different particle sizes and aerosol flow rates. Eventually the computational model will be extended to respirators donned by human manikins whose facial profiles are representative of a segment of the U.S. population. We anticipate that the results from our work will be used in the future to predict leakage through respirators, for different size regimes, flow rates and gap sizes, as part of a comprehensive model for evaluating the utility of respirators as medical countermeasures during attacks of bioterrorism.

2HA.21

In vitro Aerosol Delivery to the Lungs during Non-Invasive Ventilation High Flow Nasal Therapy. LALEH GOLSHAHI, Worth Longest, Mandana Azimi, Ross Walenga, Michael Hindle, *Virginia Commonwealth University*

Administration of conventional sized aerosols through a nasal cannula during high flow nasal therapy (HFNT) results in high drug depositional losses in the circuit components and extrathoracic airways. Controlled condensational growth techniques employing submicrometer aerosols are evaluated to minimize aerosol losses and maximize drug delivery to the lungs during HFNT. A mixer-heater and an Aeroneb Lab nebulizer were used to generate submicrometer (MMAD=0.9±0.2 micro-meter) aerosols from a 0.2% albuterol sulfate and 0.2% sodium chloride in water formulation. A streamlined cannula was employed with aerosol delivered at 20LPM for the excipient enhanced growth (EEG) technique. A divided and streamlined cannula was employed for enhanced condensational growth (ECG) with aerosol delivered at 20LPM to one nostril and heated and humidified air to the other nostril at 15LPM. The cannula was placed in an adult nose-mouth-throat (NMT) model with a filter at the exit of the trachea and attached to a breath simulator. Aerosol was delivered continuously or intermittently (1s or 2s) synchronized with peak inspiratory flows of 23, 35 and 44LPM, respectively. Aerosol drug deposition in the NMT model and the HFNT components was determined by HPLC. The drug mass collected on the filter was considered as the in vitro lung dose. Losses in the HFNT components were low (<10.6%), and there were low drug deposition losses in the NMT model (<6.6%). Emitted doses were greater than 74% of the nominal dose. Mean (SD) lung doses of 62.5(1.7)%, 73.1(2.3)%, and 74.5(3.3)% were produced using 1-second intermittent EEG aerosol delivery with peak inspiratory flows of 23, 35, and 44LPM, respectively. These were significantly greater than observed using the continuous delivery method (31.63(0.54)%). Respiratory losses were consistently lower during 1s delivery compared to 2s and decreased with increasing inspiratory flow rate. Efficient aerosol delivery of submicrometer aerosols was feasible using the controlled condensational techniques.

2HA.22

Lung Cancer Inhibitory Effect of PLGA-coated Budesonide and Polyphenon E in A/J Mice. JINGJIE ZHANG, *Virginia Commonwealth Univerisity*

Polymer nanoparticles as drug carriers have potential advantage in drug-delivery and controlled-release. A properly-selected polymer shell not only improves the solubility and stability of drugs in aqueous solutions, but also reduces the drug toxicity. Aerosol delivery is a promising approach for drug delivery, especially for the diseases in the respiratory tract and the lung. Aerosolized drugs in sub- micrometer-sizes can be inhaled and delivered directly into the lung, thus enhancing the local-regional drug level and reducing the exposure to surrounding organs other than the lung. In this study, we evaluated the advantage of delivering encapsulated drugs via aerosol administration. Two anticancer drugs, budesonide (hydrophilic) and polyphenon E (hydrophobic) were chosen in this experiment. These two drugs have been shown to inhibit benzo[a]pyrene (B[a]P) - induced lung tumorigenesis in A/J mice. PLGA and PVP were used as the polymer coating to encapsulate the drugs separately. Coated-drugs were prepared by the emulsion-evaporation technique. Excess solvent was washed out. Resulted drug-loaded particles were collected by the centrifugal separation and stored in a refrigerator. Prior to the use as-prepared particles were dispersed into an aqueous suspension (with pH 2.0) by ultrasonification. The suspension of drug-loaded particles was atomized using a custom-built Collison atomizer. B[a]P-induced A/J mice were treated three times per week, for 20 weeks consecutively before they were euthanized. Their lungs were examined under a dissection microscope. The tumor number and tumor size were scored and recorded. Our result shows that PLGA-coated budesonide and polyphenon E had inhibitory effects on lung tumors. The detail of this work will be presented in this poster.

2IA.1

Commuter Exposure to Particle Matter and Carbon Dioxide inside High-speed Metro Cabins. PENGYI CUI, Bin Xu, *Tongji University*

In-cabin exposure to PM2.5 and CO2 were investigated inside standard high-speed metro cabins under a variety of passenger numbers and ventilation conditions in China. The mean PM2.5 and CO_2 concentrations inside the metro cabins were observed at ~0.07 mg m^{-3} and 1200 ppm. PM2.5 and CO_2 distribution were similar under different conditions (cabin classes, passenger numbers, and ventilation modes). The PM2.5 concentrations at passenger breathing zone and ventilation recirculation vents were found ~20% greater than the ventilation supply air. As passenger number increased from 10 to 80, PM2.5 and CO_2 concentrations increased 10-20% with the greatest increases occurred at passenger breathing zone. It was found that PM2.5 and CO_2 concentrations were inversely proportional to the air exchange rate (AER) inside cabins. ~25% of PM2.5 concentration reduction was observed as the AER increased from 2.7 h^{-1} to 12 h^{-1}. Greatest in-cabin PM2.5 concentration (0.18±0.02 mg m^{-3}) was obtained at dinning cabin, while the PM2.5 concentrations at other cabin classes were found to be similar. In-cabin air distribution posed a negligible effect on the in-cabin PM2.5 and CO_2 concentration.

2IA.3

Nanoparticle Loading and Agglomeration in Charged and Discharged Electret Filter Media. JAMES MONTGOMERY, Steven Rogak, Sheldon Green, *University of British Columbia*

Inhalation of ultrafine particles (UFP) has been linked to detrimental health impacts. There is an interest in the use of fibrous air filters as a means of preventing exposure to UFPs but little is known with regards to the filtration characteristics of fibrous filters challenged with UFPs. The characteristics of particle agglomerate structures have been shown to impact the increase in flow resistance as a function of particle load, but the agglomeration characteristics of UFPs within fibrous filters remains unstudied.

This work provides a comparison of dust accumulation and particle agglomerates from UFPs (mean diameter 100nm) within commercial HVAC electret filter media. Tests were performed on the media for both the charged and discharged conditions. Ongoing work includes investigation of the impact of an upstream nanofiber web on particle structure. Analysis of SEM images and X-ray nanoCT scans of the loaded filters was used to compare particle agglomerates and dust holding properties of the charged and discharged filter media.

Particle agglomerates on electret fiber surfaces grew with a dendritic structure. Agglomerates on the discharged media of the same physical properties displayed a more dense, collapsed structure. The discharged filter media was also found to be proportionally more heavily loaded with particles on the upstream side of the filter, resulting in less dust holding capacity (DHC). After filter loading to a final flow resistance of 5x the original clean filter resistance, the charged media was found to contain approximately 10% more dust than the discharged media. This study shows that the structure of dust deposits within filter media is influenced by filter properties and impacts the DHC of a filter. These microscale changes in agglomerate growth within the filter media produces a macroscale impact on the energy consumption of the filtration system, by changing the flow resistance through the filter life.

2IA.4

Resuspension Fraction Estimations from 20 Homes in Northern New York. Yuanyin Yin, Yan Ma, Lisa Bramwell, ANDREA R. FERRO, *Clarkson University*

Indoor particulate matter (PM) concentration can be elevated by human activities such as dusting, vacuuming and walking. The resuspended particles can greatly increase human exposure to dust pollutants since people are indoors most of the time. However, most previous studies in this area have been conducted in the laboratory or in a single residence. The objectives of this study are 1) to estimate the house dust resuspension fractions (particle fraction resuspended from flooring per footstep) in real homes; 2) to compare the results with previous studies conducted in laboratories and residences; 3) to determine the difference of resuspension fractions for different flooring types. Walking activities were performed in the main living area of 20 homes in northern New York State. A 10-minute slow walking (68 steps per min.) and 10-minute fast walking (103 steps per min.) were each followed by a 50-minute decay period. Air particle concentrations were monitored semi-continuously both indoors and outdoors using a Grimm (Douglasville, GA) Model 1.108 optical particle counter with 6 seconds interval. Dry ice was emitted as a pulse release in the houses so the air exchange rate could be indicated by CO2 concentration. Floor loading samples were collected by a High Volume Small Surface Sampler (HVS3) for particles with aerodynamic diameters >5µm followed by a MOUDI^{TM} (MSP, Shoreline, MN) for particles <5µm. The homes were kept unoccupied except the ten minute walking periods so no other human activities or other particle sources occurred in the houses. Hard floorings were found to have lower floor loadings (mass of particles per floor area) than carpeted floorings. The resuspension fractions were calculated using a two-compartment materials balance model for four size bins: 0.5-1.0µm, 1.0-3.0 µm, 3.0-5.0 µm, 5.0-10.0 µm. It was found that the resuspension fractions ranged widely from 10^{-5} to 10^{-1}, with larger particles having larger resuspension fractions, which matches previous lab studies.

2IA.5

Ultrafine PM Emissions from Hardcopy Devices Measured per RAL UZ 171. ELLIOTT HORNER, Scott Steady, *UL Environment*

Office equipment with printing capabilities (hardcopy devices) is a source of ultrafine particles (UFPs) in the indoor environment. As of 2013, UFP emissions are included in standard RAL-UZ-171 in addition to e.g. ozone, VOC, etc. RAL-UZ-171 requires the UFP emissions rate (PER) over a 10 minute print phase (PER10) to not exceed 3.5E11 particles emitted per 10 minutes. Pooled data from multiple manufacturers are presented to describe the range of initial observations according to test parameters. Measurements were made using a butanol-based condensation particle counter (CPC); data reduction and calculations are as per RAL-UZ-171. Auxiliary variables used in the determination of PER10 include a particle loss coefficient (beta), the difference in particle concentration between beginning the print job and the PER returning to less than 10 percent of PERmax (deltaC(p)) and the total particle (TP) count emitted. The CV of the beta values across initial runs (different devices) was 33 percent, indicating reasonable consistency in the operation of the measurement chamber. The delta C(p) varied according to device from less than 100 to almost 100,000 with one half of the runs in the range of thousands. TP, which due to the controlled conditions, largely determined PER10, covered three orders of magnitude. PER10 values were measured as low as mid 10E8 level and at over 5E11. This standardized manner of operating hardcopy devices in a well-controlled environment provides reliable evaluation criteria to be delivered, which can support further assessment of hardcopy devices.

2IA.6

Person-to-Person Contaminant Transport in a Ventilated Room with Different Ventilation Systems. S.M. Keshavarz, Mazyar Salmanzadeh, GOODARZ AHMADI, *Clarkson University*

It is now well known that the control of airflow pattern in hospital can mitigate the spread of infectious diseases such as measles, tuberculosis and severe acute respiratory syndrome (SARS). There are guidelines to control aerosol dispersion in isolation rooms by the U.S. Centers for Disease Control and Prevention (CDC), in which specific ventilation systems recommended for different circumstances. However, there is still lack of guidelines for public buildings. The person-to-person contaminant transport in public spaces is quite complicated, and is affected by the ventilation airflow, thermal plume around human bodies, human respiration and/or other activities. In addition, earlier studies were focused on limited particle sizes and environmental conditions. In this study, detailed analyses of person-to-person aerosol transport in public spaces with various ventilation systems are performed. An Eulerian-Lagrangian approach were used computational fluid and particle simulation in ventilated room with realistic manikins. The study provided improved understanding of person-to-person contaminant transport.

2IA.7

Chemical Composition of Hookah Smoke Aerosol Measured with an Aerosol Chemical Speciation Monitor.

PHILIP CROTEAU, John Jayne, Douglas Worsnop, Tim Oh, Cindy DeForest Hauser, *Aerodyne Research, Inc.*

Hookah smoking originated in India during the 15th century and has since spread to various Middle Eastern and Mediterranean regions as well as western countries, including the United States where there has recently been a dramatic increase in its prevalence. In a hookah, air is drawn over charcoal which indirectly combusts the tobacco; the mixture of charcoal and tobacco smoke is then drawn through water to the user. While smoke from cigarettes has been relatively well characterized, little is known about the chemical composition of hookah smoke aerosol, which is expected to be different due to the different method of combustion, the water filtration, the added influence of the charcoal, and the presence of sweeteners, such a molasses, in the tobacco.

Here we present on-line aerosol chemical composition measurements of hookah smoke using the recently developed Aerodyne Aerosol Chemical Speciation Monitor (ACSM). The ACSM samples the air through a 100 µm orifice into an aerodynamic focusing lens where particles are focused into a beam which is transmitted through a vacuum system to a tungsten surface that is heated to 600ºC. The particles are vaporized and the resulting gases along with the remaining air are ionized with electron impact and detected with a small quadrupole mass spectrometer. The particle-only mass spectrum is determined by switching an automated 3-way valve between whole air and filtered air and taking the difference of the filtered and unfiltered mass spectra.

Previous studies of the particle phase of hookah smoke aerosol are quite limited and have relied on off-line techniques to examine total particle mass, individual compounds or classes of compounds (such as nicotine, polycyclic aromatic hydrocarbons, or aldehydes), or tar (nicotine-free dry particulate matter) extracted from filters. This study is the first to measure bulk chemical composition of hookah smoke particles using an on-line technique.

2IA.8

Rapid Allergen Reduction By Atmospheric Cold Plasma.

Yan Wu, Yongdong Liang, MAOSHENG YAO, Jue Zhang, *Peking University*

Allergy has become a global problem, and effective control is greatly needed. In this work, we investigated the use of atmospheric cold plasma in controlling allergens. Both aerosolized and water-borne allergens including Der p 1, Der f 1, Asp f 1, Alt a 1, and Can f 1 were exposed to the plasma generated. As a comparison, allergen exposure to the heat up to 100 oC and ultraviolet irradiation for various times were also conducted. Besides, airborne allergens (Der p 1, Der f 1, Alt a 1 and Asp f 1) from both indoor and outdoor environments were also subjected to the plasma treatment. To further confirm the effectiveness of the treatment, the allergenicity of the plasma treated allergen (Asp f 1) was compared against those without the treatment using blood sera from the allergen sensitized subjects.

Results revealed that atmospheric cold plasma is effective in reducing the allergenicity of lab-prepared and natural allergens. The reductions were shown to range from 30% for Der p 1 to 80% for Can f 1 allergen when exposed to the plasma for 0.12 s. Water-borne exposure experiments also revealed the dependence of allergenicity reduction on exposure time. In clear contrast, traditional methods such as heating and ultraviolet irradiation had little effect on the Can f 1 allergens even with extended exposure up to 30 mins. Allergnicity tests with control and plasma treated allergen (Asp f 1) using ELISA showed that treated allergens caused less binding with IgE sensitized to Asp f 1 compared to the control ones. The results here demonstrated a viable method for effectively controlling fungal and mite allergens, and commercialization of this technology would land a great hand in the combat with allergic diseases.

Key words: Fungal allergens, dust mite allergens, cold plasma, allergenicity

2IA.9

Development of a Particle Resuspension Modelling Capability within a Computational Fluid Dynamics Framework. SARAH WILLIAMSON, Sarah Harrison, Jonathan Hill, John Locke, *Defence, Science and Technology Laboratory, UK*

Aerosol particles that settle onto surfaces might later be lifted off or "resuspended" through various means. This resuspension of previously deposited particles is an important area of research as it may produce health consequences and affect decontamination procedures. The first objective of this study was to incorporate a resuspension model into a computational fluid dynamics (CFD) model, an example of which is demonstrated by simulating a helicopter approaching the ground. The second objective was to conduct small scale experiments to validate the resuspension model.

To understand resuspension it is necessary to consider the adhesive forces holding the particle to the surface and those forces which cause the particle to be removed. An algorithm has been developed to predict resuspension based on the work of Biasi et al[1]. This uses the "rock 'n' roll" theory whereby a combination of lift and drag forces overcome the force of adhesion between the particle and the surface, causing the particle to resuspend. The model has been shown to behave qualitatively as expected.

The resuspension model has been incorporated into CFD software ANSYS® Fluent®, for the simulation of a helicopter vertically descending towards the ground. The model predicts that the resulting flow is strong enough to cause a significant proportion of particles to be resuspended. The fraction of material resuspended from each computational cell at each time step is output by the model.

Small scale experiments have been designed to quantitatively validate the resuspension model. A bench top wind tunnel, fitted with a microscope and video camera, allows particles and their resuspension to be monitored. A silicon wafer surface was analysed before and after the experiments to determine the proportion of silica particles removed. The experimentally measured resuspension will be compared to the model output to validate the resuspension model.

[1] Biasi et al. Aerosol Science, 32, 1175-1200, 2001.

2IA.10

PM2.5 and Ultrafine Particles in Green Vs. Non-Green Homes. KANISTHA CHATTERJEE, Patrick Ryan, Sergey A. Grinshpun, Chris Schaffer, Eric Kettleson, Reshmi Indugula, Gary Adamkiewicz, Yang Qiu, Tiina Reponen, *University of Cincinnati*

Environmental concerns for improved energy consumption and reduced carbon emissions are driving a green building/remodeling movement. Energy conservation efforts have resulted in tighter buildings, which have led to a reduction in the air exchange rates between indoor and outdoor environments resulting in poor indoor air quality. Poor air exchange rates could lead to an increase in particles that often originate from indoor sources (tobacco smoke, cooking), but decrease particles from outdoor sources (construction, traffic, combustion). We assessed the concentration of particles alongside relative humidity, temperature and air exchange rates (AER) in 30 non-green and 27 green homes. Temperature and relative humidity were collected using HOBO® continuous data loggers (Onset Computer Corporation). Particles ≤ 2.5 micro-meter (PM2.5) were sampled on 37 mm, 2.0 micro-meter pore-size PTFE membrane filters using single-stage Personal Modular Impactors (SKC, Inc.) and analyzed gravimetrically. In addition, real-time number concentrations of ultrafine particles were assessed using a P-Trak condensation nuclei counter (TSI Inc.). Capillary adsorption tubes (CAT) and sources were placed in different locations of the homes to determine the AER. Information on home characteristics was collected by questionnaires. Preliminary data show that the geometric mean of the number concentration of ultrafine particles was 25,380 cm^{-3} in green homes and 32,524 cm^{-3} in non-green homes ($p=0.2$). The geometric mean of PM2.5 particles was 80 micro-gram m^{-3} in green homes and 56 micro-gram m^{-3} in non-green homes ($p=0.1$). The relative humidity had an arithmetic mean of 44% in green homes and 42% in control homes ($p=0.6$). AER was significantly higher ($p=0.02$) in non-green homes (median=3.1 h^{-1}) as compared to green homes (median=1.1 h^{-1}). The results from examining the fine and ultrafine particle exposure in post-renovated green homes compared to non-green homes, and the relationships between ventilation, mass and number concentrations and green housing characteristics are presented.

2IA.11

Introduction of the Upstate New York Weatherization Project. DENINA HOSPODSKY, Largus Angenent, *Cornell University*

In 2009, the U.S. Department of Energy has instituted the weatherization assistance program (WAP). Up to 30 million U.S. households are eligible for such weatherization services nationwide. One of the main components of weatherization is to minimize leakage flow though the building and results in reduced levels of ventilation.

The goal of this study is to characterize the effects of ventilation reduction from home weatherization on airborne fungal and bacterial concentrations and on airborne radon, VOC, ozone, carbon dioxide, particle number, and particle mass concentrations. In addition, airborne-, surface-, and occupant- associated fungal and bacterial communities are characterized using next generation DNA sequencing technologies. This study examines ten homes (plus 5 control houses) before and after weatherization through a local WAP in Ithaca, NY.

We herein introduce and compare characteristics of the participating homes before weatherization including building types and material, air exchange rates (AER), flooring area, leakage flow from blower door tests, energy consumption, and numbers of occupants and pets. Results on airborne microbial concentrations, AER, radon, particle number, and particle mass concentrations from a corresponding pilot study in the same geographic area are further demonstrated here. This pilot study examines seasonal effects on abovementioned airborne biological and chemical species in one case and one control home once per season while alterations for energy efficiency purposes take place in the case home. Seasonal effects on AER, radon and carbon dioxide were observed, but PM10 and biological aerosol levels were consistent at averaged 15 micrograms per cubic meter (standard deviation: 6) in the control home and 39 microgram per cubic meter (standard deviation: 14) in the case home. Microbial concentrations were 950 and 380 (for bacteria) as well as 350 and 120 (for fungi) genome copies per cubic meter, respectively, in the case and control home.

2IA.12

Optimal Cleaning Strategies for HVAC Heat Exchangers. AMIN ENGARNEVIS, James Montgomery, Sheldon Green, Steven Rogak, *University of British Columbia*

It is well known that the heat exchangers used in building heating, ventilating, and air conditioning (HVAC) systems become fouled by airborne particulate matter. These systems must be cleaned periodically to maintain good performance. However, the optimal cleaning time to save money, energy and maintain good indoor air quality is not known. A model has been developed to predict the energy use and annual operation cost of finned tube air-to-liquid heat exchangers commonly installed in HVAC air handling units. This model accounts for the changing properties of the coil and upstream filter throughout operation and provides a method of determining the optimum filter selection and coil cleaning time to minimize the annual cost of operating the unit. The optimal cleaning strategy has been shown to vary depending on system specifications such as the filtration efficiency, filter and coil bypass rates, coil geometry, and particle concentration. The sensitivity of the results to model parameters showed that the concentration of particles in the air stream, filter selection, and the electricity cost had the largest effect on annual cost of operation. Increasing the concentration of particles and the electricity cost, increase the cost of operating the system and make more frequent coil cleaning more economically attractive. Upstream filter selection can result in either a net savings or an additional operating cost, depending on the type and efficiency of the filter. Selection of high-efficiency filters compared to low-efficiency filters has likely a small effect on net system energy consumption, but increases the operating cost due to higher initial costs. These results imply the need for caution when considering high-efficiency filters to protect finned tube heat exchangers, and suggest that optimal finned-tube heat exchanger operation involves a compromise between an upstream filter that satisfies the indoor air quality requirements and a periodic coil cleaning program.

2IA.13

Assessing Indoor Air Quality Impact of Wildfires with Chemical Signatures. ODESSA GOMEZ, Alina M. Handorean, Jane Turner, Mark T. Hernandez, *University of Colorado Boulder*

Size segregated aerosols (PM_{10} and $PM_{2.5}$), collected during local and regional wildfires in the Rocky Mountain Front Range, were analyzed for their total organic carbon content (OC) and water soluble fractions (WSOC), elemental carbon content (EC), and their fluorescent properties. A large, high-occupancy university building, evacuated during the course of the sampling, served as a model to determine the performance of a modern building envelope against the unique aerosol challenges presented by wildfire. Aerosol was continuously and concurrently collected indoors and immediately outdoors before and during wildfire events. Conventional thermal-optical methods were used for OC and EC quantitation, water-soluble total organic carbon (TOC) analysis for WSOC content, and 3D excitation-emission matrices (EEM) were used to characterize associated fluorescent properties. During regional wildfire days, averaged outdoor PM_{10}, $PM_{2.5}$ and OC levels were in excess of 10 ug/m^3, while EC levels were significantly lower—averaging at least an order of magnitude less (< 0.5 ug/m^3). Between 45% and 39% of averaged outdoor EC levels were found indoors. As judged by the EEM spectra presented by WSOC components, wildfires impacted the HULIS in both fine and coarse aerosol – this HULIS signature was consistently recovered indoors following fires. We have demonstrated that wildfires have unique aerosol signatures, that these signatures can be used to assess the penetration performance of buildings, and that modern HVAC systems may not be able isolate high-occupancy indoor environments from some of the unique air pollution challenges presented by local or regional wildfires.

2IA.14

Real-time, Size-Resolved Particle Concentrations in a Neonatal Intensive Care Unit. SEEMA BHANGAR, Brandon Brooks, Fuqun Vasiknanonte, Xiaochen Tang, Jillian Banfield, William Nazaroff, *University of California, Berkeley*

Infants in neonatal intensive care units (NICU) are particularly vulnerable to environmental stress including air pollution. However, few studies have reported particle levels in the NICU environment. During a four-day investigation in a private-style NICU, we measured size-resolved particle number concentrations at 1-min resolution. The investigation was conducted in an empty patient room in an otherwise normally functioning NICU, to enable the measurement of parameters inside and outside the incubator, and to observe changes in response to simulated human activities. Internal doors between the room and hallway were open to mimic typical conditions. The NICU air handling system included high-efficiency particle filters.

Preliminary results show background PN levels in the room were 1-2 orders of magnitude lower than outdoors. Four-day (87 h) mean concentrations corresponding to the 6 particle size ranges (0.3-0.5, 0.5-1, 1-2, 2-5, 5-10, >10 micro-meter) were 45, 17, 7.7, 9.2, 2.0, and 2.2 L^{-1}, respectively. Levels inside the incubator were further reduced owing to the presence of a filter in the incubator air inlet. Incubator/room PN concentration ratios ranged from 0.7 to 0.1 across the size ranges evaluated, except when the internal humidifier – which was a source of particles – was in operation. The air-exchange rate of the humidifier was approximately 9 h^{-1}.

The presence and activities of occupants were associated with distinct particle peaks across all measured size ranges. The highest levels were observed when fabrics were handled. However, against the low background, even small perturbations – such as from a person entering and sitting in the room for a few minutes – were discernible. The data are being further analyzed to evaluate the fraction of the total particle signal attributable to occupancy. We are also exploring the use of a material-balance model to estimate human emissions as a function of particle size and the type of activity.

2IA.15

Particulate Mass and Lung-Deposited Surface Area Concentrations from Cookstove Emissions in Rural Households in Udaipur, India. Anna Leavey, SAMEER PATEL, Jessica Londeree, Ravi Shrimali, Gautam Yadama, Pratim Biswas, *Washington University in St Louis*

Approximately three billion people around the globe routinely cook and heat their homes by burning biomass in traditional cookstoves. Nearly 2 million people are estimated to die annually from acute respiratory infections and Chronic Obstructive Pulmonary Disease due to indoor air pollution from these cookstoves. Ninety-nine percent of deaths occur in developing countries, and women and children bear the brunt. One of the most affected countries is India, where cookstove-related poor indoor air quality results in 0.5 million excess deaths a year. Quantifying these emissions and understanding the factors that influence them may help improve the quality of life for billions of the most vulnerable people [1,2].

Gas and particulate measurements were collected for a total of 54 households throughout the months of June-August, 2012, in rural villages in and around Udaipur, India. Of the households sampled, 51 operated traditional cookstoves while 3 operated some type of improved cookstove. The fuel burned was mainly a mixture of biomass and dung. Mean concentrations observed whilst the cookstove was operating under steady-state conditions were 4989.6 (421.3 improved)($\mu^{m2}cm^{-3}$) for lung-deposited surface area, 9835.2 (1126.3 improved) (μgm^{-3}) for $PM_{2.5}$, and 18.5 (3.9 improved) (ppm) for carbon monoxide. Certain fuel and household characteristics modified these concentrationsas well as the extinguishing efficiency, although associations were complex. These included the biomass-mix, roof type, the amount of fuel used and the diameter of the fuel, and different sources of ventilation. Some variables may also be indicative of socio-economic status and should be explored more fully.

It is hoped that this work will help to highlight the hazardous and often full-time work that women and children face every day just to provide their family with food; and offer suggestions as to how their working conditions may be improved.

References

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2IM.1

Validation of the CPMA-Electrometer Suspended Mass Standard against Gravimetric Measurements. JONATHAN SYMONDS, Kingsley Reavell, Jason S. Olfert, *Cambustion*

The Centrifugal Particle Mass Analyser (CPMA, Olfert and Collings 2005) classifies particles by their mass to charge ratio, using opposing centrifugal and electric forces.

For singly-charged particles passing through the CPMA of mass m, there may also be doubly-charged particles of mass 2m, etc. It then follows, by counting the number of charges post-CPMA, we count the number of quanta of mass m. Thus by placing an aerosol electrometer downstream of the CPMA, the mass concentration post-CPMA is given by multiplying the measured charge concentration by the single-charge mass of the CPMA (Symonds et al., 2011). This stream of particles of known mass concentration can be split to provide a calibration source for real-time instruments which infer a mass concentration measurement by less traceable means. A correction may be required for any uncharged particles which pass through the CPMA, but this can be made negligible by the use of a unipolar charger to place a high level of charge on the particles.

A silicon oil with low vapour pressure was nebulised, highly charged with a Unipolar Diffusion Aerosol Charger (UDAC, Cambustion), and passed through a CPMA. The flow was then split, one half passing to an aerosol electrometer, the other half collecting on a filter paper, which was weighed before and after loading. Mass flow meters were used downstream of the filter paper and electrometer. By varying the single-charge mass setting of the CPMA, the mass concentration post-CPMA was varied and plotted versus filter mass concentration. In this experiment, the two methods agreed to within 6%.

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2IM.2

Development of a Triggering-LIBS for Determination of Elemental Composition of Single Particles in Real Time.

HEESUNG LEE, Jihyun Kwak, Gibaek Kim, Kihong Park, *Gwangju Institute of Science and Technology*

The Laser Induced Breakdown Spectroscopy (LIBS) with an aerosol focusing system has been developed to detect the elemental composition of single particles in real time. The LIBS uses a powerful laser focused by the focusing lens, which generates a micro-plasma to dissociate sampled particles to the atoms or ions at the atmospheric pressure. When the excited species go back to its ground state, the specific emission lights appeared depending on their elemental constituents. The distinguishable emission lines were then transferred into a broadband spectrometer, and the LIBS spectra are analyzed for the identification of the elements and their quantification.

The LIBS has been utilized to measure the temporal behavior of heavy metals in the period of Asian Dust or specific particle events in our previous studies (Park et al., 2009; Park et al., 2012). The studies showed significant inspiration for the time resolved properties of the particles. Nevertheless, a single particle detection had not yet been fully accomplished because of the low hitting efficiency of particles by the free-firing laser at atmospheric level of concentration.

In this study, we used a continuous wave laser (642nm, 35mW, Excelsior Laser, Spectra Physics Inc., USA) to find the exact transit time for a single particle to arrive at the focal point of the following pulsed laser and to trigger that second Nd:YAG laser (1064nm, 155mJ/pulse, Surelite II-10, Continuum Inc., USA) which produces a micro-plasma, leading to the enhancement of the hitting ratio of particles by the combination of two lasers. By using various particles of size, composition, and number density, the triggering-LIBS was evaluated. Data show that the particle hitting efficiency of the triggering-LIBS can significantly be evaluated, enhanced compared to that of the free-firing LIBS system.

2IM.3

Real-time Elemental Characterization of Polydisperse Aerosol Particles Using a DMA Coupled with an Inductively Coupled Plasma-Mass Spectrometer.

VIVEK RAWAT, Thaseem Thajudeen, Christopher Hogan Jr., *University of Minnesota*

We have interfaced a differential mobility analyzer (DMA) with an Inductively Coupled Plasma- Mass Spectrometer (ICP-MS), and developed a corresponding “Elemental distribution function” inversion routine to determine the elemental composition of aerosol particles in near-real time. The measurement system consists of a Po-210 bipolar ion a source followed by a TSI long DMA operated with an open-loop Argon sheath flow coupled to both a condensation particle counter (CPC), and Perkin-Elmer Elan 6100 ICP-MS. With the ICP-MS calibrated, the ratio of ICP-MS signal to CPC measured number concentration yields the average mass of each element within DMA-selected particles. While this instrument combination has been utilized previously, its application to polydisperse, chemically complex aerosol particles has been hindered by the fact that the influence of multiply charged particles on ICP-MS signal has not been addressed. These effects are considerable, as the mass of a doubly charged particle of the same electrical mobility as a single charged particle, is significantly higher, and the ICP-MS measured signal intensity is proportional to sample particle mass flow rate. Therefore, without correcting for multiply charged particle influences, the average mass of each element within DMA selected particles cannot be linked directly to the chemical composition of particles at the selected “mobility” size. To this end, we utilize an inversion routine with the Twomey-Markowski method to obtain the actual elemental distribution function. The kernel function for the inversion includes the DMA transfer function, the steady-state bipolar charge distribution determined from a recently developed Brownian dynamics approach, the CPC transport efficiency, and the ICP-MS calibration curve. The DMA-ICP-MS and inversion routine have both been tested using atomizer produced cesium and rubidium iodide salt clusters. The extension of this instrument combination to chemically diverse aerosol particles is also discussed here.

2IM.4

Determination of Chemical and Morphological Properties of Size-Segregated Aerosol Particles Using the Electrical Low Pressure Impactor. PATRICIA FRITZ, Shida Tang, David Guerrieri, Brian P. Frank, *New York State Dept. of Environmental Conservation*

While several methods exist for the measurement of particle size distributions in real time, they do not yield information on particle composition or morphology. The composition and morphology of aerosol particles tend to be poorly characterized, especially for particles less than 1 micron, despite their potential impact on phenomena such as health effects and radiative forcing. Using an Electrical Low Pressure Impactor (ELPI, Dekati, Ltd.) instrument that measures particle concentrations over 12 size bins from 17 nm to 6.8 microns by depositing particles on a series of stages, chemical analysis and/or morphological characterization of size-segregated particles on those stages were attempted in this study. Source particles were generated in the laboratory by several different methods including combustion aerosols generated with the Combustion Aerosol Standard (CAST, Jing, Ltd.), and sampled by the ELPI while simultaneously characterized by other means such as the Scanning Mobility Particle Sizer (TSI, Inc.). The effect of various ELPI substrates on the viability of chemical and morphological analysis of particles are evaluated, including factors such as elution and deposition protocols, and trade-offs between the two analytical methods. Their impact on ELPI operation parameters which can affect the viability of the particle size distribution measurements, such as particle bounce and stage loading, are also evaluated. Based on these findings, preliminary recommendations are made for the potential use of the ELPI for simultaneous measurement of particle size distributions, composition, and morphology.

2IM.5

Preparation of Lead (Pb) Reference Materials by Aerosol Deposition for XRF Analysis of Ambient Particulate Matter. Hardik Amin, Sinan Yatkin, Trzepla Krystyna, ANN DILLNER, *University of California, Davis*

Lead (Pb), one of the six criteria pollutants, is a toxic element in atmospheric particulate matter (PM). X-ray Fluorescence (XRF) is commonly used to non destructively quantify elemental concentrations in PM, including Pb. However, a significant difference exists between the mass loading of Pb on commercially available reference materials (RM) used for calibrating XRF and ambient PM. Moreover, the deposition pattern and substrate of deposition for commercial standards (Nucleopore® or Mylar®) is different than the substrate used for collecting PM (Teflon®).

In this work Pb RMs were prepared by aerosolizing aqueous solution of lead acetate trihydrate. The filters were made with Pb mass loadings between 30% and 350% of NAAQS levels (Pb NAAQS = 0.15 µg/m3 or 0.3 µg/cm2). The Pb aerosol is dried using a diffusion dryer, diluted in a mixing chamber and sampled onto 47 mm Teflon filters. Two types of Teflon filters were used, MTL filters (Measurement Technologies Laboratories, 0.2 µm pore size) used by EPA for Pb sampling and Teflo filters (Pall Life Sciences, 3 µm pore size) similar to filters used by IMPROVE. The Pb aerosol is sampled using Thermo Scientific Partisol Plus 2025i Sequential Air Sampler. In initial experiments, multiple MTL filters were prepared with Pb mass loadings of 0.2 µg/cm2 and 0.6 µg/cm2. Six filters at each mass loading were analyzed using two PANalytical Epsilon 5 energy dispersive XRF instruments. Each filter was analyzed three times on each instrument and the standard deviation was <4%. These filters were also analyzed by an independent laboratory using ARL QUANT'X XRF (Thermo Scientific) instrument. Eleven of twelve filters analyzed showed less than 6% difference, with one filter at Pb mass loading of 0.2 µg/cm2 showing 8% difference, when compared to PANalytical results. XRF and ICP/MS data for additional filters with Pb mass loadings over a range will be discussed.

2IM.6

A CAPS-Based Single Scattering Albedo Monitor. Timothy Onasch, Paola Massoli, Paul Kebabian, ANDREW FREEDMAN,*Aerodyne Research, Inc.*

We present data detailing the performance of a particle single scattering albedo (SSA) monitor that incorporates both a CAPS (Cavity Attenuated Phase Shift)-based optical extinction measurement and an inverse nephelometer in the same measurement volume. Since an absolute extinction measurement is provided, the scattering channel can be calibrated with any non-absorbing particle (e.g., a PSL) or gas (other than air). The monitor demonstrates noise levels (1 s sample time) of less than 1 Mm^{-1} in both channels. Measurements of the single scattering albedo of bare and organic coated soot particles using both this monitor (the CAPS PMssa) and another instrument which comprised a cavity ring down-based extinction system coupled to a photoacoustic particle absorption spectrometer (courtesy of C. Cappa, U.C. Davis) showed excellent agreement between the two. The SSA monitor can be operated in any wavelength region compatible with the availability of high reflectivity mirrors, LEDs and photomultiplier tube PMT) photocathodes. At present, the available wavelength band is restricted to the 400-700 nm region.

2IM.7

Black Carbon in Dust and Geological Material: Reconciling Thermal/Optical and Spectral Quantification Methods. L.-W. ANTONY CHEN, Yongming Han, Jerome Robles, Judith Chow, Junji Cao, John Watson, *Desert Research Institute*

Atmospheric black carbon (BC) aerosol affects the Earth’s climate. Through sequestration of carbon and nutrients in the pedosphere, BC plays an important role in the global carbon cycle. BC in sedimentary rocks also keeps long-term records of paleoenvironmental changes. Quantifying BC in samples dominated by geological material (GM), such as fugitive dust, surface soil, and sediment, is however challenging, since GM interferes BC measurement with commonly used thermal/optical methods by changing organic matter charring behaviour and promoting BC evolution at lower temperatures. Pure optical methods that quantify BC based on light absorption can be interfered by iron-rich GM showing substantial light absorption in the visible region. In this study, improvements in BC quantification were made by introducing acid pre-treatment for thermal/optical methods and spectral detection for optical methods. Surface soil samples with relatively low BC contents and street dust samples with relatively high BC contents were collected from central China. The acid pre-treatment reduces most of the GM interference and concentrates BC levels in the samples. Thermal/optical reflectance (TOR) analysis shows that the pre-treatment preserves most BC and improves the measurement precision and detection limit, allowing <0.1 wt% of BC in the samples to be detected. Parts of the samples were resuspended onto Teflon and quartz-fiber filters and examined with an integrating-sphere-based spectrometer. The measured BC after acid pre-treatment correlates better with light absorption at 900 nm, at which absorption by organic matter and GM is expected to be minor. Further validations with standards and reference materials are carried out and will be presented. The light absorption efficiency/absorption Ångström exponent of BC and GM from spectral measurements will also be discussed.

2IM.8

Towards Fast, Accurate Calculation of Particle Hygroscopic Growth Rates: System Modeling of H-TDMA Performance.RAGHAV RAMAN, Suresh Dhaniyala, *Clarkson University*

The response of particles to humidity in the environment directly influences its lifetime, interaction with sunlight, and ability to form clouds. Measurement of change in particle size as a function of humidity is typically made using a hygroscopic tandem differential mobility analyzer (HTDMA). The effectiveness of particle growth measurements with a HTDMA is dependent upon the time response and precision of the instrument. In this study, a HTDMA software emulator is developed to model the instrument response considering scanning diffusional DMA transfer functions, multiple charging of particles, and statistics of the sampled aerosol. The emulator is used to determine the minimum HTDMA measurement time required for accurate growth measurements to determine the nature of the external mixture. The performance of the emulator is tested against HTDMA measurements made under laboratory conditions for different aerosol types. The development of the emulator, HTDMA instrument, and analysis of the experimental results will be presented and implication for fast HTDMA measurements, such as necessary from aircraft platforms, will be discussed.

2IM.9

Semi-automated System for Measuring Oxidative Potential of Ambient Particles Collected on Filters Using Dithiothreitol (DTT) Assay. TING FANG, Vishal Verma, Rodney Weber, *Georgia Institute of Technology*

Aerosol oxidative potential has been considered as a more relevant parameter to elucidate the adverse health effects of particulate matter (PM) than the mass concentration. Consequently, many methods have been developed to measure the oxidative potential of PM. Among these, DTT assay is the most commonly used method, and which has also been found to correlate with several health markers. In this assay, DTT is catalytically oxidized by the PM and the consumption rate of DTT in units of nmol/minute is considered proportional to the concentration of redox-active species in PM. The conventional manual protocol for DTT assay is very labor-intensive and time-consuming. To address these concerns, we developed a semi-automated system using two syringe pumps (Kloehn, Inc., Las Vegas, Nevada, USA) and a liquid wave-guide capillary cell (LWCC-M-100; World Precision Instruments, Inc., Florida, USA) coupled to an online spectrophotometer (Ocean Optics, Inc., Dunedin, Florida, USA). A simplified protocol was developed by conducting the DTT oxidation in a single vial while withdrawing a small aliquot at different time intervals to calculate the rate of DTT consumption. PM samples collected via filters or impactors once extracted in a solvent (typically water) can be analyzed in batches using an auto-sampler for unattended analysis, at roughly 1 sample per hour. The performance of the automated system was evaluated by multiple field blanks (standard deviation = 26 % of mean, N=13) used as the negative control, and standards (9, 10-phenanthraquinone, standard deviation = 8%, N=35) as the positive control. The reproducibility of the system, determined by conducting the assay on seven different equal sections of the same filter extracted and analyzed separately, also yielded consistent results with a minimal standard deviation in DTT activity (<5 % of mean). The limit of detection (LOD) of the system is 0.25 nmol/minute, comparable with that of the manual protocol (0.21 nmol/minute). Additional scaled down versions, where reaction volumes were reduced by 4 to 20 times, allow similarly high analytical precision and sensitivity at PM mass requirements as low as 30 micro-gram. The scaled-down methods have been successfully used to measure filter samples collected in human-exposure CAPS (concentrated air particles) experiments and within vehicles in traffic. These systems are being used to provide an extensive data set on DTT activity as part of the Emory-Georgia Tech EPA Clean Air Research Center, SCAPE (Southeastern Center for Air Pollution & Epidemiology).

2IM.10

PAH Distribution with Particle Size by Hi-Volume Impactor: Positive Artifact Correction.

JAN BENDL, Jan Hovorka, Jan Topinka, *Charles University in Prague*

Comprehensive characterization of winter urban aerosol, conducted in two industrial cities in the Czech Republic – Ostrava (26 days) and Mladá Boleslav (14 days) during smog and non-smog periods, also included polycyclic aromatic hydrocarbons - PAH distributions with aerosol particle size. Size segregated aerosol samples were then used for toxicology and genotoxicology studies. Since those studies claim rather high aerosol masses, high-volume cascade impactor sampler - BGI 900 was employed. The sampler uses polyurethane foam substrates – PUF, which also retain gaseous PAH, i.e. exhibit positive sampling artifact – PSA. To evaluate the PSA, additional PUF target was placed beneath the back-up ultrafilter. Significant amounts of phenanthrene, anthracene, fluoranthene, pyrene and benzo(a)anthracene were captured in the PUF targets after 24 hour air sampling. The extent of the captured gaseous PAHs positively correlated with their individual vapor pressures (ranging from 10^4 to 10^-1 Pa). Other measured PAHs (coronene, benzo(ghi)perylene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene) with vapor pressures from 10^-5 to 10^-10 Pa did not exhibit the PSA. The PSA also depends on ambient air temperature. The deduction for the captured gaseous volatile PAHs ranged from units to tens of percent of measured particle size fractions of PAHs. The general model will be presented for calculating ambient air temperature-dependent ratio between solid and gaseous fractions for individual PAH captured on the PUF substrates in Hi-Vol BGI 900.

This work was supported by the project CENATOX under grant GAČR P503/12/G147.

2IM.11

An Aerosol Detection Technique for Diesel Fuel Contaminants.

KAI XIAO, Chenxing Pei, Jacob Swanson, David Kittelson, David Y. H. Pui, *University of Minnesota*

High Pressure Common Rail injection systems are designed to increase combustion efficiency and to reduce particle emissions for modern Diesel engines. The rising pressure and reduced clearances make the system more sensitive to contaminants which may cause a higher injector leakage and increased emissions. These issues have raised the need of more efficient fuel filters and a fast and reliable monitoring method for small contaminants in the fuel. The most used way to measure the concentration of liquid-borne particles is based on direct optical measurements of particles using a liquid particle counter. A limitation to easily improving this technique is due to the fact that contaminants in the fuel have similar refractive index as the fuel itself.

An aerosol-based detection technique was developed to characterize particle contaminants in Diesel fuel in the size range of 0.5-4µm. By transforming the liquid-borne particles in the fuel to airborne with a constant output atomizer, the background is changed from relatively opaque Diesel fuel to air. With the help of a catalytic stripper, fuel droplets are removed and particles are detected by the aerosol instrument downstream. The size range of aerosol instrument enables a lower size limit as small as 0.5 µm. Filtered Diesel fuel seeded with monodisperse silica particles has been used for calibration purposes. The sizing tests with three different size (0.73, 1.8 and 3.6 µm) seed particles indicate that the system is able to precisely (measured diameter within 5% of manufacturer's value) determine the size of the contaminants in the fuel. In concentration tests, the air-borne and liquid-borne particle concentrations have been found to follow a linear relationship for all three sizes, although different sizes have different slopes. A compensation procedure was proposed to account for this difference. Using this procedure, liquid-borne concentration could be predicted from the measured airborne concentration.

2IM.12

Aerosol Mixing in Concentric Jets. MATTHEW BROWN, Suresh Dhaniyala, *Clarkson University*

A large number of aerosol instruments rely on detailed knowledge of aerosol-flow interaction to accurately count and size particles. In the DMA, the locational distribution of particles at the introduction to sheath flow is one of the critical factors in the accurate sizing of particles. High-resolution sizing in the DMA requires particles to be in a narrow set of streamlines when introduced at the outer cylinder. The mixing of the aerosol and sheath flows in the DMA may, however, spread particles into a broader set of streamlines, limiting the highest possible instrument resolution. In our study, we experimentally investigate the fundamental processes of laminar shear flow interaction using a particle-laden and clean flow in double concentric jets to better understand the flow field and resulting particle dispersion inside the DMA. The experimental results suggest that there is inherent mixing of jets even under highly laminar flow and the extent of mixing is strongly dependent on the ratio of velocities of the two flows. The experimental setup, obtained results, and their implications in limiting the performance of existing aerosol instruments will be discussed.

2IM.13

Aerosol Analysis Using a Thermal-Desorption Mass Spectrometer (TD-MS) Modified from a Conventional Carbon Analyzer. XUFEI YANG, L.-W. Antony Chen, Xiaoliang Wang, Jerome Robles, John Watson, Judith Chow, *Desert Research Institute*

The thermal-desorption/mass spectrometry (TD-MS) analysis can fingerprint the composition of aerosols, thereby offering useful information to better understand the aerosols’ sources, properties and environmental impacts. This presentation describes our recent modification of a thermal/optical carbon analyzer to enable it for TD-MS analysis of aerosol-laden filter samples, in parallel to conventional organic carbon (OC) and elemental carbon (EC) analysis. In this system, a filter punch is heated following a pre-specified temperature program (e.g., IMPROVE_A) in the carrier gas of ultrapure helium. The evolved gas products first pass through an empty quartz tube heated at 650ºC, a typical vaporization temperature of aerosol mass spectrometer (AMS), and then proceed to an electron-impact mass selective detector (EI-MSD) via a heated transfer line (heated at 220ºC). Heating at 650ºC breaks low-volatility, large organic molecules into small fragments, thus reducing the loss of signals due to condensation along the transfer line. Preliminary results show that although the oxidation by trace oxygen (O2) in the carrier gas causes a certain loss of organic signals at higher temperatures (e.g., at > 480ºC), the system is able to generate aerosol mass spectra similar to AMS operated in the electron impaction mode and provide information related to sulfate, nitrate, ammonium, hydrocarbon-like and oxygenated organic matter (OM). A series of model compounds differing in chemical composition and O/C ratios, such as paraffin, oxalic acid, sucrose, levoglucosan, PAHs, proteins/amino acids, humic acids, ammonium nitrate and ammonium sulfate, as well as real-world source (e.g., mobile exhausts and biomass burning smoke) and ambient samples have been tested. The TD/MS spectra will be presented, and the feasibility of using the spectra to estimate the OM/OC ratio and source contributions will be discussed.

2IM.14

Making the Particle Number Concentration Standard Liquid Suspension Using Aerosol Technique. KENJIRO IIDA, Hiromu Sakurai, Junko Nakanishi, Kensei Ehara, *AIST*

A technique for making the particle number concentration standard liquid suspension is being developed at AIST, Japan. The size-standard polystyrene latex (PSL) spheres are first aerosolized by atomizing the liquid suspension. A differential mobility classifier extracts the PSL spheres from the generated aerosol. About a half of the classified aerosol is sampled into a condensation or an optical particle counter to measure the concentration of the PSL spheres, and another half is send to a growth tube collector (GTC). Inside the GTC the PSL spheres become seeds for the condensational growth and become micrometer-sized water droplets. These PSL-seeded water droplets are accelerated by properly designed nozzles and impacted onto a liquid surface contained in a small vial. A liquid-borne particle counter (LOPC) was used to obtain the total number of PSL spheres collected and stably suspended inside the liquid. The total number of PSL-seeded water droplets produced is known from the measurements in the aerosol phase; therefore, we can evaluate what fraction of these particles became stably suspended particles in the liquid phase. Since the LOPC cannot accurately measure the particle number concentration below several hundred nanometer, the proposed method was evaluated by using the PSL spheres between 250-1000 nm. Above 90% of the condensationally grown PSL spheres became stable liquid suspension, and the performance was reproducible and had no significant size dependence. The proposed method was first verified using a miniature GTC which has a sampling flowrate at 0.3 L/min. The method could be successfully scaled up by 10 times by using a 3.0 L/min GTC. Since the previous studies has proven that the activation efficiency and the final droplet size of the GTC is constant over the particle diameter above 10 nm, the proposed method can potentially make a number concentration standard suspension down to this size range.

2IM.15

Comparison of the Organic Composition of Generated and Ambient Marine Aerosol Measured Using Four Complementary Techniques. AMANDA FROSSARD, Lynn Russell, Timothy Bates, Patricia Quinn, *Scripps Institution of Oceanography*

Four complementary techniques were used to measure the organic composition of generated and ambient marine aerosol collected during the Western Atlantic Climate Study (WACS) in August 2012. Particles were generated using a model ocean system, the Sea Sweep, and compared to ambient particles. The four techniques used are: (i) Fourier transform infrared (FTIR) spectroscopy which gives organic functional group composition of particles collected on filters; (ii) high resolution time of flight aerosol mass spectrometry (HR-ToF-AMS) that determines the non-refractory mass spectral composition of particles; (iii) light scattering (LS) module of the HR-ToF-AMS (LS-ToF-AMS) that determines single particle mass spectral composition; and (iv) scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure (STXM-NEXAFS) that measures the morphology and organic functional group composition of single particles. The organic mass of marine particles was split into organics with high ratios of oxygen to carbon (O/C), such as hydroxyl functional groups, and those with low O/C, such as alkane functional groups. Using this, the ambient composition compares well across all four techniques with all showing about 50% of the organic mass could have a high O/C. LS-ToF-AMS was used to determine the apparent collection efficiency (CE) of the AMS by comparing the number of particles that both scattered light and had a significant mass spectrum to those that only scattered light. For ambient, this CE was about 50%, consistent with past values. For the generated particles, less than 10% of those detected by light scattering also had associated mass spectra, suggesting that more than 90% were refractory. This is consistent with the fact that more than 80% of the generated submicron particle mass is attributed to sea salt, which is refractory. STXM-NEXAFS measurements show that Sea Sweep particles contain high O/C organics on sea salt, which are refractory and not vaporized by AMS.

2IM.16

Evaluation of Selective Ion Flow Tube Mass Spectrometry for Controlled Laboratory Studies. ASHLEY VIZENOR, Chia-Li Chen, Derek Price, Mary Kacarab, Xinze Peng, Kelly McCoy, Igor Irianto, Shaokai Gao, David R. Cocker III, Akua Asa-Awuku,*University of California, Riverside*

Selective Ion Flow Tube Mass Spectrometry (SIFT-MS) is a form of direct mass spectrometry that utilizes precisely controlled chemical ionization reactions to detect and quantify trace amounts of volatile organic compounds (VOCs) from whole air in real time, with typical detection limits at the part-per-trillion level (by volume – pptv). Chemical ionization is induced by one of three positively charged reagent ions: hydronium, nitric oxide, or diatomic oxygen. Soft-ionization reactions occur and the larger fragments of product ions are characterized and quantified. The instrument is operated in two modes: SIM (Selected Ion Mode) and mass modes. A mass scan takes a mass spectrum for each reagent ion, and can be used for identifying products from reactions. In a SIM scan, specific compounds are detected and quantified by detection of product ions. In the research presented, emphasis was placed on the SIM scan mode as accuracy and precision of quantification were the main goal of this study. A Syft Technologies Voice200 SIFT-MS was used to compare known amounts of VOCs with detected concentrations to better understand the accuracy and precision of the instrument. The compounds studied were 1-methylnapthalene, alpha-pinene, benzene, isoprene, m-xylene, naphthalene, toluene, beta-caryophyllene, and longifolene. The data show that SIFT-MS is a helpful tool for approximating concentrations of VOCs, as well as identifying products of reactions from the upper part-per-trillion to lower part-per-million range.

2IM.17

Development and Evaluation of a High-Volume Aerosol-Into-Liquid Collector for Fine and Ultrafine Particulate Matter.DONGBIN WANG, Payam Pakbin, Arian Saffari, Martin Shafer, James Schauer, Constantinos Sioutas, *University of Southern California*

This study presents a novel High-Volume Aerosol-Into-Liquid Collector, developed to provide concentrated slurries of fine and/or ultrafine particulate matter (PM) to be used for unattended, in-situ measurements of PM chemistry and toxicity. This system operates at 200 liters per minute (L/min) flow and utilizes the saturation-condensation, particle-to-droplet growth component of the Versatile Aerosol Concentration Enrichment System (VACES), growing fine or ultrafine PM to 3-4 µm droplets, in conjunction with a newly designed impactor, in which grown particles are collected gradually forming highly concentrated slurries. Laboratory evaluation results indicated an excellent overall system collection efficiency (over 90%) for both monodisperse and polydisperse particles in the range of 0.01 to 2 µm. Field evaluations illustrated that overall a very good agreement was obtained for most PM2.5 species between the new aerosol collection system and the VACES/BioSampler tandem as well as filter samplers operating in parallel. Very good agreement between the new system and the VACES/BioSampler was also observed for reactive oxygen species (ROS) in ambient PM2.5 samples, whereas lower ROS values were obtained from the water extracts of the filter, likely due to incomplete extraction of water insoluble redox active species collected on the filter substrate. Moreover, the field tests indicated that the new aerosol collection system could achieve continuous and unattended collection of concentrated suspensions for at least 2 to 3 days without any obvious shortcomings in its operation. Both laboratory and field evaluations of the high-volume aerosol-into-liquid collector suggest that this system is an effective technology for collection and characterization of ambient aerosols.

2IM.18

Improvement of a Particle Trap Laser Desorption Mass Spectrometer (PT-LDMS) for Ambient Measurement.

TAKEDA NAOKI, Ozawa Yuya, Miyakawa Takuma, Koizumi Kazuhiro, Hirayama Noritomo, Takegawa Nobuyuki, *Fuji Electric CO., LTD.*

A particle trap laser desorption mass spectrometer (PT-LDMS) has been developed for online measurements of sulfate, nitrate, and organic carbon. The main components of the instrument include an aerodynamic lens, a particle trap and cell, an electron impact ionization quadrupole mass spectrometer (QMS), and a carbon dioxide (CO2) laser. The first prototype of PT-LDMS successfully demonstrated the proof of concept (Takegawa et al. AST, 2012). The instrument has been redesigned and reconstructed to reduce the size and weight and also to achieve automated measurements (Takeda et al., AAAR meeting, 2012). This study presents further improvement of the second prototype, focusing on the temporal profile of laser irradiation and cooling of the particle trap during particle collection. The improvement of laser profile is critical for the quantification of ammonium sulfate (AS) because thermal decomposition process of AS significantly depends on the desorption temperature and heating rate. We have tested a number of temporal profiles of laser irradiation and found that the yield of m/z 48 signals from AS can be increased by a factor of 5 compare to the first prototype. The improvement of cooling method is critical for the quantification of semi-volatile compounds such as ammonium nitrate (AN) and some organic compounds. We have newly designed a particle trap holder that has a much better thermal conductivity than the previous version. As a result, the time required for cooling the particle trap after laser irradiation has been drastically reduced. Results from laboratory experiments and ambient intercomparison will be presented and discussed.

2IM.19

Results of On-line Measurement of Volatile Organic Compounds Adsorbed on Diesel Exhaust Particles by PTR-TOFMS.

NOBUHIRO YANAGISAWA, Kenji Enya, *ISUZU Advanced Engineering Center, Ltd.*

Emissions from modern diesel engines for automobiles have become very low by progress in combustion technology and adoption of emission aftertreatment devices. Diesel emissions consist of a large number of compounds in gas- and particle-phase. PTR-TOFMS (Proton Transfer Reaction – Time of Flight Mass Spectrometer) is able to analyze gaseous organic compounds (i.e. volatile organic compounds) on-line in real time with high sensitivity. To analyze particle-phase organic compounds by PTR-TOFMS, sampled exhaust was passed through a heating tube to evaporate particle-phase compounds, which were then introduced to PTR-TOFMS. To determine the concentrations of particle-phase compounds, 2 experiments were conducted. At the first experiment, the heating tube was kept at lower temperature (ca. 100 degC) to measure the concentrations of gas-phase organic compounds. At the second experiment, the heating tube was heated at higher temperature (ca. 300 degC) to measure the total concentrations of gas- and particle-phase organic compounds. The concentrations of particle-phase compounds were determined from the difference between the two measured values.

In this work, analysis of particle-phase organic compounds by PTR-TOFMS was conducted using a modern HD diesel engine (displacement 3L with turbo-intercooler) for small trucks. Exhaust was sampled from an exhaust pipe to a partial flow dilution system. In the dilution system the sampled exhaust was mixed with dilution air at a constant dilution ratio. The diluted exhaust was measured by PTR-TOFMS for organic compounds analysis and EEPS (Engine Exhaust Particle Sizer) for particle sizing.

This paper shows results of emissions of particle-phase organic compounds and particle size distributions during a ramped steady state operation of the engine. The results showed that particle-phase compounds include higher m/Z compounds and particle size distribution is also discussed.

2IM.20

Development of Aerosol Mass Spectrometer (AMS) with Two Switchable Ionization Methods for Characterization of Refractory and Non-refractory Components in Particles. HEE-JOO CHO, Heesung Kwak, Kihong Park, *Gwangju Institute of Science and Technology*

Aerosol mass spectrometer (AMS) has been used as a powerful tool for real-time measurement of chemical constituents of atmospheric aerosols. Various types of AMS have been developed. In particular, the Aerodyne AMS (Aerodyne Research Inc., USA) determines the chemical composition (organics, sulfate, nitrate, ammonium, and chloride) of particles by using a particle vaporization and electron impact (EI) ionization method, in which the non-refractory particles are vaporized at 600 °C under high vacuum and the generated vapors are immediately ionized via electron impact with the subsequent ion analyses by a quadruple or time-of-flight mass spectrometer. We are developing AMS with two convertible modes (laser desorption ionization (LDI) and thermal desorption-electron impact ionization (TD-EI)) equipped with a time-of-flight mass spectrometer. By utilizing LDI and TD-EI with a switchable mode, refractory and non-refractory species in submicrometer particles can be determined. The LDI allows us to measure refractory components such as black carbon, mineral dust, and heavy metals, while the TD-EI provides more quantification of non-refractory species (especially organic species). In this research, the AMS with the LDI and TD-EI is constructed and is being evaluated using various laboratory-generated particles.

2IM.21

Field Measurements of Nitrous Acid (HONO) during the SHARP Campaign. Joseph Pinto, Jack Dibb, Ben H. Lee, Bernhard Rappenglueck, Ezra Wood, Misti Levy, Renyi Zhang, Barry Lefer, Jochen Stutz, , Scott Herndon, Michelle Oakes, *US EPA/NCEA*

Because of the importance of HONO as a radical reservoir, consistent and accurate measurements of its concentration are needed. As part of the SHARP (Study of Houston Atmospheric Radical Precursors), time series of HONO were obtained by six different measurement techniques on the roof of the Moody Tower (MT) at the University of Houston. Techniques used were long path differential optical absorption spectroscopy (DOAS), stripping coil- (UVVIS) absorption photometry (SC-AP), long-path absorption photometry (LOPAP), mist chamber/ ion chromatography (MC-IC), quantum cascade-tunable infrared laser differential absorption spectroscopy (QC-TILDAS) and ion drift -chemical ionization mass spectrometry (ID-CIMS). Various combinations of techniques were in operation during the period from 15 April through 31 May 2009. This study comparing methods is unique in that it compares several techniques entirely at ambient conditions in a polluted atmosphere.

All instruments recorded a similar diurnal pattern of HONO concentrations with higher median and mean values during the night and lower values during the day throughout the entire measurement period. Highest values were observed in the final two weeks of the campaign. The MC-IC, SC-AP, and QC-TILDAS, and to a lesser extent the DOAS, tracked each other most closely. Largest differences between pairs of measurements were evident during the day for concentrations < ~100 ppt. Above ~ 200 ppt, concentrations from the SC-AP, MC-IC and QC-TILDAS converged to within about 20%, with slightly larger discrepancies when DOAS was considered. Relations between HONO and aerosol and gas phase species will be considered.

2IM.22

Chemically Specific Online Removal of Submicron Aquadag Aerosol with the Single Particle Soot Photometer. ALLISON AIKEN, Gavin McMeeking, Manvendra Dubey, Paul DeMott, Ezra Levin, *Los Alamos National Lab*

The ability to separate black carbon (BC) from organic carbon (OC) in an online aerosol sample would enable the physical processes and optical properties to be studied by carbon class. We present a method to remove BC from an online aerosol sample, demonstrated with the soot surrogate Aquadag in the laboratory. This method could be applied to ambient and source aerosol samples to isolate the roles that different carbon classes have on climate, e.g. atmospheric warming, cloud formation and lifetime. A study was performed using two Single-Particle Soot Photometers (SP2s) in series, along with a Three-Wavelength Photoacoustic Soot Spectrometer (PASS-3) for measuring optical properties. Polydisperse and monodisperse Aquadag was sampled from 100 nm to 800 nm in diameter. Comparison of number, mass and optical properties of the Aquadag and the particles remaining after laser-induced incandescence (LII) are reported. For all monodisperse samples, the average percent remaining by mass and number of the original size selected are 11.1% ± 18.6% and 12.7% ± 21.9%, respectively. The results of this study are applicable to other instruments employing LII, e.g. the Soot Particle Aerosol Mass Spectrometer (SP-AMS), and could also potentially be used for the study of new and/or altered carbonaceous particles in a controlled environment.

2SA.1

Radiocarbon-Based Source Apportionment of EC and OC in Fine Particulate Matter at a Regional Background Site on Hainan Island, South China. YANLIN ZHANG, Jun Li, Gan Zhang, Jianhui Tang, Peter Zotter, Lukas Wacker, Andre Prévôt, Soenke Szidat, *University of Bern*

Atmospheric aerosol particles are of worldwide concern for their important effects on climate and human health. Both fossil fuel emissions and biomass burning in Southeast Asia have an important impact on regional particles emissions. To study air pollution outflows from mainland China as well as the impact of Southeast Asian biomass-burning emissions, PM2.5 samples were collected during May 2005-August 2006 at a regional background site of Jianfeng on Hainan Island, South China. The concentrations of elemental carbon (EC) and organic carbon (OC) in PM2.5 were characterized by the lowest abundances during the wet summer season and the highest levels in winter. The observations were associated to wet deposition and the prevailing clean maritime air mass origins in summer on the one hand and the anthropogenic air pollutions transport from continental China with the northeast winds on the other hand. To assign fossil and non-fossil contributions of carbonaceous particles, we analyzed radiocarbon (^{14}C) contents in EC, OC and water-insoluble OC (WINSOC) with the newly developed protocol Swiss_4S. On average, the contributions of fossil sources to EC and OC were 40% and 20%, respectively, indicating generally a dominance of non-fossil emissions. Relatively higher contributions from fossil sources to EC and OC were observed, when air masses originated from Southeast China during low fire periods. The increasing of fossil carbon was associated to long-range transport of particles emitted from fossil-fuel combustion and vehicular emissions in highly urbanized regions of China. An increase of non-fossil contribution by 10-20% was observed during periods with enhanced open biomass-burning activity in Southeast Asia or Southeast China. In addition, a modified EC tracer method was used to estimate the fossil-derived SOC formation with measurement of fossil WINSOC and fossil EC determined by ^{14}C. The results indicate that fossil OC at this site was rather from secondary than primary sources.

2SA.2

Source Apportionment and Organic Compound Characterization of Ambient Ultrafine Particulate Matter (PM) in the Los Angeles Basin. SINA HASHEMINASSAB, Nancy Daher, James Schauer, Constantinos Sioutas, *University of Southern California*

In this study, quasi-UFP ($PM_{0.25}$, dp<0.25 micro-meter) were collected for 24 hours once per week from April 2008 to March 2009 at 10 different locations in the Los Angeles Basin. Organic constituents of $PM_{0.25}$ were grouped into polycyclic aromatic hydrocarbon (PAHs), hopanes and steranes, n-alkanes, and levoglucosan, with concentration levels ranging from 0.16-5.5, 0.09-2.2, 9.3-48, and 2.2-106.2 ng m-3 over all sites and seasons, respectively. A molecular marker-based chemical mass balance (MM-CMB) model was applied to estimate the contribution of major sources to $PM_{0.25}$. The sources included in the MM-CMB model were mobile sources (combined gasoline and diesel vehicles), wood smoke combustion, natural gas combustion, vegetative detritus, and ship emissions. Secondary organic aerosol (SOA) tracers were not included in the model; however their contributions were estimated from non-biomass burning water soluble organic carbon ($WSOC_{nb}$) and un-apportioned OC from MM-CMB model (“other OC”). The High correlation (R^2=0.8) between “other OC” and $WSOC_{nb}$ in summer suggests that “other OC” is highly impacted by SOA, however un-apportioned primary sources may contribute to “other OC” as well. Mass apportionment results revealed that mobile sources are expectedly the major primary contributors to total quasi-UFP mass, with seasonal average contributions to $PM_{0.25}$ of 31±12% in summer and 57±17% in winter. “Other organic matter” was the second largest contributor to $PM_{0.25}$ in all seasons, across the basin, with higher contribution during warmer spring and summer seasons (27%), while lowest during cold seasons (13%). Wood smoke was the third major contributor to $PM_{0.25}$ in winter, whereas its contribution was lowest in summer. As expected, ship emissions displayed the highest contribution at the near-harbor HUD site, and their levels continually decreased as a function of distance from coast. Lastly, vegetative detritus and natural gas combustion, collectively contributed to 1.3±0.8% of $PM_{0.25}$ on an annual average basis over all sites.

2SA.3

Receptor Modeling of Ambient PM2.5 Collected at the National Air Pollution Surveillance (NAPS) Speciation Sites in Ontario for the Years 2005 -2010. UWAYEMI SOFOWOTE, Yushan Su, Ewa Dabek-Zlotorzynska, Ankit Rastogi, Jeff Brook,*AQARU, EMRB, Ontario Ministry of the Environment*

The Canadian National Air Pollution Surveillance (NAPS) network operates five fine particulate matter (PM2.5) speciation sites in Ontario all of which are located in the southern part of the province. Data from these speciation sites from 2005 to 2010 were subjected to positive matrix factorization (PMF) to obtain factors of particulate matter pollution. Up to eight factors were found to be common across two or more sites. These factors were identified with sulphate-rich emissions, nitrate-rich emissions, metal works emissions, crustal matter, calcium-rich emissions, arsenic-rich emissions, wood combustion and oil processing and combustion emissions. On average, sulphate and nitrate related emissions contributed 56% of the total PM2.5 mass across these speciation sites and their temporal variations showed summer and wintertime enrichment respectively. The sulphate factor which is largely energy-related has been on a decline since its peak in 2007. A 10 – 35% reduction in average sulphate contribution observed from 2007 to 2008 across four of the 5 speciation sites may be an indicator of the downturn in the global economy in 2008. Simplified quantitative transport bias analysis (sQTBA) was used to reveal potential source regions of contributions of factors that were common to all five speciation sites in the province. Local areas were dominant sources of contributions from the sulphate factor but regional source areas including the US Midwest, east coast as well as areas in southern states were also observed while the nitrate factor had its strongest source areas around the southernmost parts of Lake Erie. This work shows that the hybrid PMF-sQTBA receptor modeling approach is an effective source apportionment tool for regional pollutants affecting multiple sites.

2SA.4

Indication of Aerosol Aging by Optical Absorption Properties.

LUKA DRINOVEC, Grisa Mocnik, Jean-Eudes Petit, Jean Sciare, Olivier Favez, Peter Zotter, Robert Wolf, Andre Prévôt, Anthony D.A. Hansen, *Aerosol d.o.o., Slovenia*

The ability to discriminate between local and regional air pollution is important for aerosol monitoring and control. Aging by atmospheric processing can change the aerosol’s chemical and physical characteristics. Here we present a new method for indicating aerosol age using optical absorption parameters measured by the dual-spot Aethalometer (Magee Scientific, Model AE33).

This instrument provides a real-time determination of a sample-on-filter loading effect, based on the linear model similar to Virkkula (2007) and Park (2010): BC_measured = BC_ambient (1- k*ATN). The compensation parameter k is determined in real-time for each of the operational wavelengths from 370 nm to 950 nm. The wavelength dependence of absorption and the compensation parameter both provide a highly time-resolved specific spectral fingerprint that may be interpreted in terms of aerosol composition in terms of aerosol sources and age.

Optical and chemical properties of aerosols were measured with high time resolution during summer and winter EMEP campaigns in Paris (France) and Payerne (Switzerland). An Aerosol Chemical Speciation Monitor (Aerodyne, ACSM) and an High Resolution Time-of-Flight Aerosol Mass Spectrometer (Aerodyne, AMS) were used to measure quantitative chemical composition for non-refractory aerosol particles. During summer we observed complex temporal variation of k, where k(880 nm) changed from approximately 0.006 for fresh aerosols to near zero for aged aerosols as shown using Potential Source Contribution Function (PSCF) back trajectory analysis method.

We have combined the Aethalometer and ACSM/AMS measurements, and normalized the sum of inorganic secondary and organic aerosol mass to BC. Values of this ratio are expected to be high for air parcels containing aged aerosols. The ratio correlates well with the loading compensation parameter k measured by the Aethalometer at 880 nm. This indicates that the compensation parameter k can be used for discrimination between local (fresh) and regional (aged) air pollution aerosols.

2SA.5

Retrospective Source Attribution for Source-Oriented Sampling and Toxicity.

KEITH BEIN, Yongjing Zhao, Anthony Wexler,*UC Davis*

In previous work, a novel system that uses single particle mass spectrometry to conditionally sample source-oriented particulate matter (PM) from the ambient atmosphere in real-time was designed and successfully implemented in two separate field studies (summer 2008 and winter 2009) conducted in Fresno, CA. The fundamental concept behind this technique is that single particle composition is a metric of particle source and thus sampling particles based on composition should be synonymous with sampling based on source. System operation relies on real-time pattern recognition in mixtures of single particle source signatures to control the actuation of different ChemVol samplers in a bank of samplers, where each ChemVol is associated with a unique composition signature, or combination of signatures. In the current work, a synthesis of data collected during these studies – including single particle composition, particle number distribution and wind direction – is used in retrospect to reconcile the actual source combinations contributing to the particles collected by each ChemVol. Source attribution is based on correlations between ChemVol sampling and wind direction and temporal variations in the actuation of different ChemVols, coupled to knowledge of single particle composition and the geospatial distribution and activity patterns of sources surrounding the site. Residential and commercial cooking, vehicular emissions, residential heating and highly processed regional background PM were identified as the major sources impacting the site. Different sources were observed to dominate in different seasons and the composition signatures of similar sources observed in different seasons were different. Results show that real-time patterns in single particle mixing state correctly identified specific sources and that these sources were successfully separated into different ChemVols for both seasons.

2SA.6

Anthropogenic and Biogenic Contributions to Secondary Organic Aerosols at two Industrial Cities in the Upper Midwest.

ANDREW RUTTER, David Snyder, Elizabeth Stone, Brandon Shelton, Jeff Deminter, James Schauer, *University of Wisconsin-Madison*

Contributions of anthropogenic and biogenic secondary organic carbon (SOC) to total PM2.5 mass are of interest to air quality management agencies required to demonstrate maintenance of the PM2.5 NAAQS. Currently, quantitative tools to understand the SOC source contributions to PM2.5 mass are not well developed, and the spatial variation of different types of SOC is not known.

In this study concentrations of anthropogenic and biogenic SOC mass were determined using PM2.5 measurements made in Cleveland, OH and Mingo Junction, OH. Organic molecular markers for anthropogenic and biogenic SOC were extracted from the PM2.5 and analyzed by GC-MS. Source apportionment calculations were conducted using the EPA CMB (v.8.2) software.

Calculated SOC concentrations from SOC tracers followed the expected seasonal patterns with maximum contributions during the summer and minimum contributions during the winter. Anthropogenic SOC constituted approximately 37% to the apportioned SOC and 6% to the measured OC, on average across both sites. Biogenic SOC contributed the 42% to the apportioned SOC, and 4% to the measured OC. Anthropogenic SOC contributed strongly to organic PM2.5 meaning that SOC may by partially controllable by reductions in VOC emissions from anthropogenic sources.

Similarities in the month-to-month patterns in alpha-pinene markers were observed between Cleveland and Mingo Junction, suggesting a regional character to this type of SOC. However, such patterns were not readily apparent in the isoprene markers. Comparisons between SOC apportionments from the CMB modeling and measurements of non-biomass burning water soluble organic carbon (NB-WSOC) revealed that approximately half of the NB-WSOC during spring, summer and early fall could not be apportioned with the SOC markers available during this study. This suggested that additional sources not included in the CMB model used in this study contributed to SOC, or that models using markers measured in chamber oxidations are not representative of the study sites.

2SA.7

Sources of Ultrafine Particles in the Atmosphere over the Eastern United States.

LAURA POSNER, Spyros Pandis, *Carnegie Mellon University*

Ultrafine particles can grow to become cloud condensation nuclei (CCN), playing a major role in the formation of clouds and climate change. Additionally, exposure to ultrafine particles has been linked to cardiovascular disease. Most chemical transport models (CTMs) explicitly simulate the mass concentrations of particles; ultrafine particles represent a minor fraction of this mass yet dominate number concentration. In this study, updated size distributions were introduced to the 3-D CTM PMCAMx-UF, which simultaneously simulates both mass and number size distributions of particles from 0.8 nanometers to 40 micrometers in diameter. The performance of the model in reproducing observed number concentrations in the Eastern U.S. is encouraging.

Source contribution simulations were completed by zeroing out approximately 90% of number emissions below a cutoff diameter specific to each source, which maintains larger particles and the corresponding surface and mass concentrations. The source contributions of gasoline, on- and off-road diesel, biomass, dust, and other emissions to particle number in the Eastern United States were quantified for a typical summertime period by running and analyzing a separate simulation for each source. Contributions of boundary conditions, initial conditions, and nucleation were also quantified in separate sensitivity tests. For Pittsburgh, PA, approximately 60% of the number of particles less than 50 nanometers in diameter were found to come from nucleation, while other sources contributed 13%, gasoline 12%, off-road diesel 7%, and on-road diesel 4%. Source contribution to particle number concentrations was found to vary greatly in space in time.

2UA.1

Macrophage Reactive Oxygen Species Activity of Water-soluble and Water-insoluble Fractions of Ambient Coarse, PM2.5 and Ultrafine PM in Los Angeles.

DONGBIN WANG, Payam Pakbin, Martin Shafer, James Schauer, Constantinos Sioutas,*University of Southern California*

This study describes an investigation of the relative contributions of water-soluble and water-insoluble portions of ambient PM to the overall PM redox activity. Size-fractionated ambient PM samples (coarse, PM2.5 and ultrafine PM) were collected in August-September of 2012 in an urban site in Los Angeles, using the VACES/BioSampler tandem system. Ambient PM was concentrated and collected directly into an aqueous suspension thereby eliminating solvent extraction required for PM collected on filter substrates, as well as reducing losses of semi-volatile species during sampling. Separation of water-soluble and water-insoluble fractions of PM was achieved by ultra-filtration of the collected suspension slurries. Chemical analysis, including water-soluble and total organic carbon (WSOC/TOC), elements, and inorganic ions, as well as measurement of macrophage reactive oxygen species (ROS) activity were performed on the slurries. Correlation between ROS activity and different chemical components of PM was evaluated to identify the main drivers of PM toxicity. Results from this study illustrate that both water-soluble and water-insoluble portions of PM play important roles in influencing the ability of PM to produce ROS at the cellular level. While the ROS activity per volume of sampled air for soluble species contributes to major portion of total ROS activity, high intrinsic ROS activity (i.e. expressed per PM mass) for insoluble portions is also observed, despite their lower mass fraction. Organic compounds (OC) in both water-soluble and water-insoluble portions of ambient PM, as well as several transition metal species such as Mn, V, Cu and Zn, are highly correlated with ROS activity. Moreover, the observed ROS activity of the PM samples in this study was generally higher than those reported in previous studies using the conventional PM collection by filtration process. Therefore, collecting particles directly into a liquid suspension may be superior to conventional filtration by eliminating extraction and by reducing the losses of semi-volatile organic compounds.

2UA.2

Seasonal and Spatial Variability in Oxidative Potential of Quasi-Ultrafine Particles (PM0.25) and its Relation to Water Soluble Metals in the Los Angeles Metropolitan Area.

ARIAN SAFFARI, Nancy Daher, Martin Shafer, James Schauer, Constantinos Sioutas, *University of Southern California*

Seasonal and spatial variation of redox activity of quasi-ultrafine particles (PM0.25) and its association with water soluble metals was investigated at 9 distinct sampling sites across the Los Angeles metropolitan area, including source, urban and/or near freeway and rural receptor locations. High-resolution inductively coupled plasma sector field mass spectrometry (ICP-SFMS) was used to quantify the concentration of trace elements and metals and redox activity was assessed by macrophage reactive oxygen species (ROS) assay. Seasonally, fall and summer displayed higher ROS activity compared to spring and winter. ROS levels were generally higher at source and background sites compared to rural receptor locations, except for summer when elevated ROS levels were observed at rural receptor sites. Univariate linear regression analysis indicated strong association between ROS activity and water soluble transition metals (including Fe, V, Cr, Cd, Ni, Zn, Co, Mn, Mo, Pb, Cu and As). Multivariate regression method was also applied to three site clusters to identify the major drivers of ROS and also to obtain a model to predict the ROS activity of PM0.25 based on its water soluble metal content. The most important drivers of ROS were identified as Cu and La at source Long Beach, Fe and V at urban Los Angeles and Fe, Ni and Zn at Riverside as the rural receptor location. At Long Beach, the best fitted model was able to reconstruct the ROS activity with a high coefficient of determination (0.82). For Los Angeles and Riverside, however, the outputs of multivariate regression could not explain more than 63% and 66% of the ROS, respectively. The unexplained portion of the measured ROS activity is likely attributed to the effect of organic species and secondary organic aerosols (SOA) which were not included in our model.

2UA.3

Source Apportionment of Carbonaceous Aerosol in Urban Environments through Single Particle Mass Spectrometry. ROBERT HEALY, Jean Sciare, Laurent Poulain, Monica Crippa, Alfred Wiedensohler, Andre Prévôt, Urs Baltensperger, Roland Sarda-Esteve, Maygan McGuire, Cheol-Heon Jeong, Eoin McGillicuddy, Ian O'Connor, John Sodeau, Alex K. Y. Lee, Megan D. Willis, Jonathan Abbatt, Greg J. Evans, John Wenger, *SOCAAR, University of Toronto*

Single particle mass spectrometers are well suited to the identification of local and regional sources of organic aerosol (OA) and elemental carbon (EC) in urban environments. However, obtaining quantitative mixing state data at the single particle level remains a challenge. In this study, the quantitative chemical composition of carbonaceous particles has been estimated using an aerosol time-of-flight mass spectrometer (ATOFMS) as part of the MEGAPOLI 2010 winter campaign in Paris, France. ATOFMS-derived mass concentrations for OA and EC agreed well with those measured by co-located high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and thermal/optical measurements (R2 = 0.75 and 0.72, respectively). Ten discrete mixing states were identified and quantified for carbonaceous particles. These were associated with traffic, domestic wood combustion, aged wood combustion and mid-to-long range transport. The ATOFMS OA mass fractions associated with each source agreed well with those obtained from positive matrix factorization of the HR-ToF-AMS dataset (R2 = 0.60-0.81). The results indicate that hydrocarbon-like OA (HOA) detected in Paris is associated with two EC-rich mixing states which differ in their relative sulphate content, while fresh biomass burning OA (BBOA) is associated with two mixing states which differ significantly in their OA/EC ratios. A single nitrate-rich mixing state was observed for aged biomass burning OA (OOA2-BBOA), while oxidized OA (OOA) was associated with five particle mixing states, each exhibiting different relative secondary inorganic ion content. These findings demonstrate the diversity of OA mixing states in Paris, and demonstrate the suitability of single particle mass spectrometry for OA apportionment. Preliminary findings from the co-deployment of an ATOFMS and soot-particle aerosol mass spectrometer at a near-road site in downtown Toronto will also be discussed.

2UA.4

Intermodal Fraction of Particulate Matter in Indoor and Outdoor Microenvironments. MARTIN BRANIS, Jana Kozakova, *Charles University in Prague, Faculty of Science*

Coarse and fine particles overlap in a particle size interval between 1 and 2.5 micrometers. Since this interval appears between the accumulation and coarse mode it is called an intermodal fraction. Sources of both coarse and fine aerosols contribute to intermodal fraction to a certain extent and the contributions of individual sources may vary under different meteorological and/or spatial conditions. According to several studies, intermodal fraction correlates more with coarse aerosol during higher wind velocities and windstorms in arid regions. In contrast, other studies have shown ambiguous or different results. Concentrations of size-resolved particulate matter were monitored indoors and outdoors by a low volume cascade impactor during various seasons in different urban and rural locations. Multiple regression analysis with intermodal fraction as a dependent variable and coarse and fine aerosol, temperature, humidity, wind velocity as well as number of persons (indoors) as independent variables showed that generally, outdoor and indoor concentrations of the intermodal fraction were associated predominantly with coarse aerosol. Association between the intermodal and fine fraction was also documented, however, it was much lower than the above mentioned coarse-intermodal association. Future analysis will be focussed on chemical, mineralogical and morphological characteristics as well as the microclimatic conditions in order to find the various sources of this interesting fraction and ascertain the conditions which affect its formation.

2UA.5

Characterization of Ultrafine Particles and Other Traffic Related Pollutants near Roadways in Beijing. Nu Yu, YIFANG ZHU, Xiaosen Xie, Caiqing Yan, Mei Zheng, *UCLA*

Developing countries, such as China, are facing serious air pollution issues due to their fast economic development and lack of appropriate regulations. In this study, traffic related air pollutants, such as the number concentrations of ultrafine particles (UFPs, particles with diameter < 100 nm), mass concentrations of PM2.5 and black carbon (BC) were measured near the Peking University (PKU) campus in Beijing from December 10th to 23rd, 2011. Data were collected concurrently at a roadside site and a campus site. The roadside site was located approximately 25 meters from a roadway intersection with heavy daily vehicle traffic, and the campus site was on the roof of a six-story building that was surrounded by restaurants and dining halls on campus. Meteorological data were collected from a weather station located at approximately 9 kilometers Southwest of PKU. The traffic density at the roadside site was determined from recorded video footage. No correlation was found between UFP number concentrations and PM2.5 mass concentrations. A linear correlation between BC and PM2.5 mass concentrations was found with R^2=0.57. No apparent correlation was found between wind speed and UFP number concentrations, although strong log-decay correlations were found between wind speed and PM2.5, as well as BC mass concentrations with R^2s ranging from 0.93 to 0.97. During the measurements, there are three days when both PM2.5 mass concentrations and UFP number concentrations were higher at the campus site than at the roadside site. This suggests there were strong PM local emission sources on campus. Diurnal patterns of PM2.5 mass and UFP number concentrations showed peaks around lunch time suggesting that the emissions may come from the surrounding restaurants and student dining halls that use Chinese-style cooking which has been associated with high UFP emissions.

2UA.6

Traffic-Related Pollutant Emission Factors from Near-Road Measurements for Various Vehicle Types in Downtown Toronto. JON M WANG, Cheol-Heon Jeong, Robert Healy, Greg J. Evans, *SOCAAR, University of Toronto*

Vehicle emissions contribute significantly to urban air pollution and the resulting exposure has been associated with cancer, cardiovascular, and pulmonary diseases. Models can be used to estimate traffic-related pollution exposure, but this is complicated by changing vehicle emission control technologies, unknown vehicle fleet composition, and uncertainties related to emerging unregulated pollutants. Model accuracy is greatly influenced by how well fleet average emission factors are representative of local vehicle emissions. Up-to-date and accurate emission factors relevant to specific cities would help close the gap between measured and modelled pollutant concentrations.

The goal of this study was to develop a simple method to use near-road measurements to calculate emission factors and use this to determine local emission factors for various vehicle types in downtown Toronto. Continuous stationary pollutant concentrations were measured at high time resolution 15 metres away from a major roadway. Emission factors were calculated using a carbon balance method with selected pollutants normalized to carbon dioxide measured from vehicle plumes. The selected pollutants and their respective instruments include ultrafine particles (FMPS3091, TSI), black carbon (PASS-3, DMT), volatile organic compounds (PTR-TOFMS8000, Ionicon Analytik), and gaseous pollutants – NOx, CO, CO2 (42i, 48c, 410i, Thermo Scientific).

Emission factors could be determined for various vehicle types including diesel and gasoline vehicles. Differences between the emission factors allowed inference of the emission control technologies used in some vehicles. Based on these preliminary data, this proposed near-road method may offer a simple approach for determining site specific factors that can be deployed in other sites or cities.

2UA.7

Light-absorbing Organic Aerosol Emissions from Cultural Practices in South Asia: Contribution to Enhanced Regional Warming. Rajan K. Chakrabarty, Shamsh Pervez, HANS MOOSMULLER, Judith Chow, John Watson, *Desert Research Institute*

Atmospheric heating due to carbonaceous aerosols contributes to fourfold uncertainty in climate forcing over south Asia (SA). Black (BC) and organic carbon (OC) aerosols in the atmosphere over this region alter net solar radiative flux to the Earth's surface, the net effect of which may outweigh the regional warming effect of greenhouse gases. BC aerosols absorb sunlight in visible wavelengths, increasing inversely with wavelengths from near-infrared (1 µm) to ultraviolet with a power law of one. OC aerosols absorb sunlight insignificantly in visible wavelengths, with the exception of brown carbon – a recently identified class of OC – which strongly absorbs in the near-UV.

Current view among climate and emission inventory modelers holds that BC – emitted from fossil and biofuel-driven contained combustion sources – constitute the light-absorbing component of regional aerosols over SA. In this talk, we present our results of aerosol emissions from hitherto uninvestigated combustion sources in SA – open-air burning of funeral pyres and incense burning in temples. We found that large amounts (≈ 98% by mass) of light-absorbing OC are emitted per kilogram of feedstock burned. The emitted OC contributed to greater than 40% of visible solar radiation absorbed by the smoke plume. We calculated that these uninventoried combustion sources in SA contributed to approximately 92 gigagrams of light-absorbing OC annually, which is equivalent to ≈10% and 23% of carbonaceous aerosol mass from regional biofuels and fossil fuels, respectively. Our findings underscore the importance of accounting for cultural burning practices as aerosol sources in emission inventories and light-absorbing OC in climate models, as well as for development of mitigation strategies.

2UA.8

Ground-Based Measurements of CCN Concentrations in Singapore. SAMUEL ATWOOD, Sonia Kreidenweis, Jeffrey Reid, Shiguo Jia, Wei Hong Fan, Liya Yu, *Colorado State University*

A size resolved CCN system was deployed in a rooftop laboratory in Singapore in boreal summer/fall 2012 and again in spring 2013 to measure ambient aerosol hygroscopicity and size distributions as part of the on-going Seven SouthEast Asian Studies (7SEAS) field campaign. Potential aerosol sources in the region range from local anthropogenic pollution associated with industry, vehicles, and heavy shipping traffic, to marine sea salt, and long range transport of smoke from seasonal biomass burning in Southeast Asia and the Maritime Continent. However, measurements were limited to dry particle sizes smaller than 500 nm, where the majority of the CCN number concentration resides. Variations in CCN concentrations reflect both changing meteorology and changes in local and regional sources, including transboundary biomass burning smoke in the region. Potential aerosol source regions are considered through use of the HYSPLIT backtrajectory model at several heights both within and above the boundary layer.

2UA.9

Sources of Black Carbon Condensation Nuclei. Shaokai Gao, Michael Giordano, Daniel Short, Diep Vu, AKUA ASA-AWUKU,*University of California, Riverside*

Black Carbonaceous (BC) aerosol is water-insoluble when freshly emitted (~ 1 day) but can add water-soluble materials in surface oxidation and condensation reactions during its atmospheric lifetime. Hence as a BC particle ages, it can modify the overall insoluble fraction, hygroscopic properties, and reduce the critical water-vapor required to initiate heterogeneous nucleation. We review the complex nature of heterogeneous BC nucleation and discuss relevant properties required for droplet formation. BC properties are acquired from ambient measurements, chamber studies, and controlled vehicular studies. A Multi-Angle Absorption Photometer (MAAP) measures BC concentration. Droplet formation potential is characterized with two methods a) with a cloud condensation nuclei counter and b) with the use of a water based condensation particle counter.

2UA.10

Gas/particle Partitioning Measurements of Polar Semi-volatile Organic Compounds. MINGJIE XIE, Michael Hannigan, Kelley C. Barsanti, *University of Colorado-Boulder*

Both gas and particle phase polar semi-volatile organic compounds (SVOCs; e.g., poly acids and polyols) were collected at Palmer elementary school (Denver, CO), one centrally located site used for the Denver Aerosol Sources and Health (DASH) study. The sample collection started on August 22nd 2012, and will be finished by the end of August 2013. Both filter and absorbent samples were collected every six day for 24-h. Preliminary analysis show that levoglucosan does exist in gas phase, suggesting that the gas/particle (G/P) partitioning might affect the quantification of biomass burning emissions in receptor-based source apportionment studies that only use particle phase levoglucosan data. The polyurethane foam (PUF) was found to have high collection efficiency (> 80%) for gas phase levoglucosan through breakthrough tests. Recent chamber and field studies found that the absorptive G/P partitioning theory, which assumed a reversible and equilibrium G/P partitioning, could not apply for all SVOCs (Perraud et al., 2012; Zhao et al., 2013). Our later work will focus on the quantification of gas/particle partitioning of levoglucosan and other polar SVOCs (e.g., 2-methyltetrols) based on all collected samples, so as to understand if the absorptive partitioning theory could explain the G/P partitioning of those polar SVOCs studied in this work.

2UA.11

Azaarenes in Atmospheric Particulate Matter Samples of Three Different Urban Sites in East of France. OLIVIER DELHOMME, Maurice Millet, *University of Strasbourg*

Air samples collected on three different urban sites in East of France (Strasbourg, Besançon and Spicheren), were characterized to measure the concentrations of azaarenes in the particulate phase (PM10). In general, the sources of azaarenes are largely analogous to those of PAHs, namely vehicle exhausts, coal burning, bitumen spreading and tobacco smoking. Azaarenes are found along with the PAHs in respirable particulate matter from ambient air and primary sources. Some members of azaarenes, particularly four- and five-ring compounds, are known carcinogens and mutagens, and also are of particular interest to the environmental analytical community.

In order to compare the seasonal variability, the sampling campaigns have been performed during the four seasons in Strasbourg, and during two opposed seasons (summer and winter) in Besançon and in Spicheren. Moreover, the sampling campaigns have been performed during 6 h time intervals per day to assess the diurnal variations of azaarenes concentrations. Mean total azaarenes concentrations were 2.8 ng m-3 in Strasbourg, 1.6 ng m-3 in Besançon and 1.0 ng m-3 in Spicheren. For all azaarenes, significantly seasonal variability was found in the three sampling sites, with highest concentration in winter period when combustion sources are greatest and when the azaarenes compounds are mainly associated with the particles phase. A diurnal variation of compound concentrations in the three sites, in warm period, has been observed in accordance with the intensity of the vehicle circulation, with highest concentrations during the morning and the evening. In cold period, there is no difference of concentration between these two time intervals of high vehicle circulation in Strasbourg site and in Besançon site. In this way, it seems that the contribution of domestic heating influenced the diurnal variations of some compounds on the three sites.

3AC.1

Secondary Organic Aerosol Oligomerization, Particle Viscosity, and the Trapping of Volatiles in the Aerosol Phase. DAVID DE HAAN, Melissa Galloway, Nahzaneen Sedehi, Jonathan Bartolomucci, *University of San Diego*

Organic aerosol particles were originally thought of as liquid mixtures. However, recent discoveries of the presence of oligomers in organic aerosol, combined with observations of kinetically-limited evaporation processes in these particles, have led to the idea that oligomerized organic aerosol particles can be highly viscous, or “glassy.” We examine aldehyde + ammonium sulfate and aldehyde + amine reactions that are known to produce oligomers in lab aerosol under certain conditions. Vibrating orifice droplet generation studies indicate that many aldehyde + AS reactions can occur during droplet evaporation, and some of these reaction products do not evaporate from the droplets as they dry, even after many minutes. Furthermore, in some cases these aerosol-phase products represent greater than 100% of the starting aldehyde by volume, indicating that significant amounts of water are also trapped in the product mixture. This effect is especially pronounced in experiments done under cloud-like conditions, where initial concentrations of aldehydes in the VOAG droplets are in the low micromolar range. These results can be rationalized if the evaporating droplet becomes viscous due to fast oligomer formation by the aldehyde + AS reactions.

3AC.2

SOA Aging and Oligomer Content and their Effect on Volatility and Viscosity of SOA Particles Generated from Different Precursors. JACQUELINE WILSON, Alla Zelenyuk, Dan Imre, Josef Beranek, *Pacific Northwest National Laboratory*

Formation, properties, transformations and temporal evolution of secondary organic aerosol (SOA) particles strongly depend on particle phase and volatility. Our recent studies indicate that laboratory-generated alpha-pinene SOA particles are highly viscous semi-solids with viscosity characteristic of tars, and their evaporation rates are orders of magnitude slower than previously assumed.

Moreover, numerous recent studies provide evidence that SOA particles contain significant amounts of high molecular weight organic compounds (oligomers), which affect SOA volatility and have the potential to severely retard diffusion, mixing, and thus evaporation of smaller molecules. We have shown that when SOA particles are made in the presence of vapors of semi-volatile hydrophobic compounds, such molecules become incorporated and trapped within the SOA and their subsequent evaporation rates and thus their rates of diffusion through the SOA and SOA viscosity can be obtained.

Here we present the results of recent studies that explore the relationship between SOA oligomer content and SOA volatility and viscosity. These studies include SOA particles generated by oxidation of several different precursors, including alpha-pinene, isoprene, limonene, n-alkenes, and cyclo-alkenes.

We, and others, also find that oligomer content in SOA increases with time, and with it we expect corresponding changes in viscosity and volatility. We will present the results of studies aimed at characterizing evaporation kinetics and viscosity of SOA particles as a function of particle age. We will also present our findings on the effect of hydrophobic organics on SOA oligomer content, its volatility, and viscosity.

3AC.3

Gas-particle Partitioning of Atmospheric Aerosols: Interplay of Physical State, Non-ideal Mixing and Morphology. MANABU SHIRAIWA, Andreas Zuend, Allan Bertram, John Seinfeld, *California Institue of Technology*

Atmospheric aerosols, comprising organic compounds and inorganic salts, play a key role in air quality and climate. Mounting evidence exists that these particles frequently exhibit phase separation into predominantly organic and aqueous electrolyte-rich phases. As well, the presence of amorphous semi-solid or glassy particle phases has been established. Using the canonical system of ammonium sulfate mixed with organics from the ozone oxidation of α-pinene, we illustrate theoretically the interplay of physical state, non-ideality, and particle morphology affecting aerosol mass concentration and the characteristic timescale of gas-particle mass transfer.

The state-of-the-art thermodynamic model AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients; Zuend et al., 2008; 2011) is used to investigate the effect of phase separation on secondary organic aerosol formation. We demonstrate that phase separation can significantly affect hygroscopic growth and gas-particle partitioning (particle mass and chemical composition). In addition, we estimate the equilibration timescale of SOA gas-particle partitioning using a state-of-the-art kinetic flux model (KM-GAP; Shiraiwa et al., 2012). We demonstrate that semi-solid or glassy phases may kinetically inhibit the gas-particle partitioning and hygroscopic growth especially under low relative humidity and temperature. Thus, the interplay of physical state, non-ideal mixing and morphology have significant implications for the interpretation of laboratory data and the development of improved atmospheric air quality and climate models.

3AC.4

Partitioning of Inorganic Gases to Atmospheric Ice: Effects on CMAQ Predictions of Nitrogen and Sulfur Compounds. Brian Marmo, ANNMARIE CARLTON, *Rutgers University*

This work describes the first implementation of gas-to-ice partitioning of three inorganic gases (HNO3, SO2 and H2O2), along with subsequent chemical reactions and changes in gas phase and particle mass concentrations in the Community Multiscale Air Quality (CMAQ) chemical transport model. Adsorbed HNO3 was assumed to condense and partition to the aerosol phase. Adsorbed SO2 and H2O2 reacted to form sulfate on the ice surface. Four different simulations were performed with CMAQv4.7.1 for August 12th-25th of 2005: 1) base case simulation without the addition of lightning-generated NOx, 2) a simulation with the addition of lightning-generated NOx, 3) 100% partitioning case and 4) 25% partitioning case. Simulations 3) and 4) provide an upper and lower bound for the partitioning of adsorbed HNO3 to remain in the aerosol phase. Considerable decreases, greater than 25% in gas phase HNO3, were noted in the 100% partitioning case for 200-600 mb, with the largest changes at 300 mb and 400 mb. Potential effects induced on other gases in the nitrogen budget (NOx and HONO) and oxidant cycling of atmosphere (O3) due to gas-to-ice partitioning of HNO3 were considered. Decreases in NOx and HONO gas mixing ratios were found to be as high 20%, but were generally less than 10%. Changes in O3 concentration were less than 1%. Increases in nitrate aerosol mass concentration were as high as 0.15 µg/m3 for the upper levels of the atmosphere. No changes in H2O2, SO2, or sulfate aerosol concentrations were observed.

3AC.5

Phase Transitions and Phase Miscibility of Mixed Particles of Ammonium Sulfate, Toluene-Derived Secondary Organic Material, and Water. Mackenzie Smith, Yuan You, Mikinori Kuwata, Allan Bertram, SCOT MARTIN, *Harvard University*

The phase transitions and phase miscibility of particles composed of ammonium sulfate, toluene-derived secondary organic material (SOM), and water were studied in two types of experiments, specifically tandem differential mobility analysis and optical microscopy. The SOM was produced in the Harvard Environmental Chamber by photo-oxidation of toluene at chamber relative humidities of < 5% and 40%. The efflorescence and deliquescence relative humidities (ERH and DRH, respectively) of ammonium sulfate decreased as the SOM organic fraction epsilon in the particle increased, dropping from DRH = 80% and ERH = 31% for epsilon = 0.0 to DRH = 58% and ERH = 0% for epsilon = 0.8. The approximately flat response of the DRH and ERH curves for epsilon < 0.2 were consistent with independent behavior by aqueous ammonium sulfate and toluene-derived SOM and therefore suggestive of immiscibility. The optical images confirmed immiscibility between aqueous ammonium sulfate and toluene-derived SOM for epsilon = 0.12 for RH < 85% and complete miscibility for epsilon = 0.79 to RH < 0.5%. Prolonged exposure time of the aerosol from 0.5 s to 30 s in the relative humidity conditioning portion of the apparatus affected within error neither the ERH(epsilon) nor DRH(epsilon) curves, implying an absence of kinetic effects on the observations. For epsilon > 0.6 the DRH values for particles produced at < 5% RH were measurably lower by 0 to 4% RH than for particles produced at 40% RH. The observed miscibility gap for toluene-derived SOM can be compared to previous reports of full miscibility for isoprene-derived SOM and full immiscibility for α-pinene-derived SOM. The differences among the SOMs can be related to their physicochemical properties, for which the oxygen-to-carbon (O:C) ratio is an indicator.

3AC.6

Liquid-liquid Phase Separation in Particles Containing Ammonium Sulfate, Ammonium Bisulfate, Ammonium Nitrate and Sodium Chloride Mixed with Organics. YUAN YOU, Jacqueline Yakobi-Hancock, Allan Bertram, *University of British Columbia*

As the relative humidity cycles in the atmosphere, particles may undergo a range of phase transitions, including liquid-liquid phase separation. Using optical microscopy, we investigated liquid-liquid phase separation in particles containing organics and the following inorganic salts: ammonium sulfate, ammonium bisulfate, ammonium nitrate and sodium chloride. Specifically we investigated the relative humidity at which liquid-liquid phase separation occurred, which we refer to here as the separation relative humidity (SRH). SRH of the different organic-inorganic salt mixtures showed the same qualitative dependence on oxygen to carbon elemental ratio (O:C) of the organic material: liquid-liquid phase separation was never observed for O:C > 0.8, was always observed for O:C < 0.5 and was frequently observed for 0.5 < O:C < 0.8. These results are consistent with the suggestion that liquid-liquid phase separation occurs widely in the atmospheric particles. In addition, the SRH of almost all of the particles followed the same trend in SRH, $SRH((NH_4)_2SO_4) \geq SRH(NH_4HSO_4) \geq SRH(NaCl) \geq SRH(NH_4NO_3)$. The trend in SRH with inorganic salts is consistent with salting out constants for the different salts and the Hofmeister Series.

3BA.1

Biological Ice Nucleation Activity in Cloud Water. Muriel Joly, Pierre Amato, Laurent Deguillaume, Eleonore Attard, Marie Monier, Cindy E. Morris, Martine Sancelme, ANNE-MARIE DELORT, *Clermont Université, Institut de Chimie de Clermont-Ferrand*

Ice nucleation active (INA) biological particles, in particular microorganisms, were studied in cloud water. Twelve cloud samples were collected over a period of 16 months from the puy de Dôme summit (1465 m, France) using sterile cloud droplet impactors. The samples were characterized through biological (cultures, cell counts) and physico-chemical measurements (pH, ion concentrations, carbon content…), and biological ice nuclei were investigated by droplet-freezing assays from -3°C to -13°C. The concentration of total INA particles within this temperature range typically varied from ~1 to ~100 per mL of cloud water; the concentrations of biological IN were several orders of magnitude higher than the values previously reported for precipitations. At -12°C, at least 76% of the IN were biological in origin, i.e. they were inactivated by heating at 95°C, and at temperatures above -8°C only biological material could induce ice. By culture, 44 Pseudomonas-like strains of bacteria were isolated from cloud water samples; 16% of them were found INA at the temperature of -8°C and they were identified as Pseudomonas syringae, Xanthomonas sp. and Pseudoxanthomonas sp.. Two strains induced freezing at as warm as -2°C, positioning them among the most active ice nucleators described so far. We estimated that, in average, 0.18% and more than 1%.of the bacterial cells present in clouds (~104 mL-1) are INA at the temperatures of -8°C and -12°C, respectively.

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3BA.2

Immersion Freezing of Birch Pollen Washing Water. HINRICH GROTHE, Bernhard Pummer, Heidi Bauer, Johannes Bernardi, Philippe Schmitt-Kopplin, Constanze Mueller, Stefanie Augustin, Susan Hartmann, Dennis Niedermeier, Tina Clauss, Jens Voigtländer, Laura Tomsche, Heike Wex, Frank Stratmann, *Vienna University of Technology*

The ice nucleation of bioaerosols (bacteria, pollen, spores, etc.) is a topic of growing interest, since their impact on ice cloud formation and thus on radiative forcing, an important parameter in global climate, is not yet fully understood. Here we show that pollen of different species strongly differ in their ice nucleation behavior. The average freezing temperatures in laboratory experiments range from 240 K to 255 K. As the most efficient nuclei (silver birch, Scots pine and common juniper pollen) have a distribution area up to the Northern timberline, their ice nucleation activity may be a cryo-protective mechanism. Far more intriguingly, it has turned out that water, which has been in contact with pollen and then been separated from the bodies, nucleates as good as the pollen grains themselves. So the ice nuclei have to be easily-suspendable macromolecules located on the pollen surface. Once extracted, they can be distributed further through the atmosphere than the heavy pollen grains and so augment the impact of pollen on ice cloud formation even in the upper Troposphere. These ice nucleating active (INA) macromolecules were investigated at the Leipzig Aerosol Cloud Interaction Simulator (LACIS). For that, washing water of two different birch pollen samples with different regional origin - Northern (N) birch and Southern (S) birch - was used. Main differences between these were between 255 K and 249 K, where the ice fraction increased with decreasing temperature. There, the N-birch pollen washing water featured two different slopes, with one being steeper and one being similar to the slope of the S-birch pollen washing water. As we assume single INA macromolecules being the reason for the ice nucleation. We have tried to separate these macromolecules by chromatography and to analyze by ESI-FTICR mass spectrometry.

3BA.3

The Potential Role of Bacteria Acting as Ice Nuclei - A Numerical Model Study. MAHER SAHYOUN, Ulrik Korsholm, Jens Sørensen, Niels Nielsen, Kai Finster, Ulrich Karlson, Tina Temkiv, Allan Gross, *Danish Meteorological Institute & Aarhus University*

Some species of bacteria, e.g. Pseudomonas syringae, have been found efficient in nucleating ice at high temperatures in laboratory tests. Bacterial residence time in the atmospheric boundary layer is on the order of several days. Hence, ice nucleation active (INA) bacteria may be involved in the formation of ice and precipitation in mixed phase clouds, and could influence the climate and weather. This impact of INA bacteria could be explained by the presence of protein aggregates on their outer surface membranes, which serve as active sites for ice formation. In this way, bacteria can mediate immersion freezing of super cooled water at temperatures as high as -2°C.

However, having a notable effect of the abundance of the INA bacteria on global atmospheric scales is still not well known and needs to be investigated as well as their actual role on cloud formation.

A parameterization of homogeneous and heterogeneous ice nucleation rate based on classical nucleation theory (CNT) has been developed to calculate the probability of ice formation as a function of time. This parameterization is used to make a sensitivity study to test the probability of ice formation using INA bacteria at different sizes. The theoretical study also includes the impact of INA bacteria on the heterogeneous formation of ice in clouds and a comparison of their impact with other types of aerosols, e.g. dust and soot.

The main purpose of this study is to examine the impact of bacteria on cloud ice formation using a 1-d version of the numerical weather forecast model HIRLAM (High Resolution Limited Area Model). This is done by implementing the probability parameterization in the 1-d cloud scheme STRACO (Soft TRAnsition Condensation) to carry out a sensitivity study of the potential impact of INA bacteria on ice and precipitation formation.

3BA.4

Single Particle Mass Spectrometry of Biological Particles – Linking Their Chemical Composition to Ice-Nucleation Activity. BERKO SIERAU, Cédric Chou, Monika Kohn, André Welti, Bernhard Pummer, Caroline Oehm, Isabelle Steinke, Olaf Stetzer, Ottmar Möhler, Ulrike Lohmann, *ETH Zurich, Institute for Atmospheric & Climate Science*

Atmospheric biological particles such as bacteria, fungal spores and pollen are gaining increasing attention in the research field of cloud microphysics. Their ability to act as heterogeneous ice nuclei has been shown in various laboratory and field studies (e.g. Pratt et al., 2009); however, their atmospheric relevance in aerosol-cloud interactions is still a matter of current research. This is partly due to the lack of understanding of the actual processes driving ice nucleation on biological particles, and the challenging identification of these particles in the field. Both aspects are focus of this study: The ice nucleation behavior of aerosols of diverse biological origin will be presented. Emphasis is put on their identification in the atmosphere using "chemical fingerprints" from single particle mass spectrometric analysis.

We present ice nucleation and single particle mass spectrometry data on the chemical composition of the bacterial cells Pseudomonas syringae and Pseudomonas fluorescence and their residues, fragments of birch and pine pollen, and Lycophyte spores. Additionally, we will discuss results from the analysis of "pollen washing water" containing small fragments of pollen and/or washed-off substances. These substances are expected to play a role in the ice nucleation ability of pollen (Pummer et al., 2012).

The presented data on biological particles helps to explain the ice nucleation process from the chemical point of view, but also provides valuable reference spectra for the mass spectrometric community. For this purpose, we will additionally compare the obtained mass spectrometric "fingerprints" from the bioaerosols with mass spectra of different soil dusts that are potentially bacteria-laden or internally mixed with biological material.

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3BA.5

Characterizing the Organic Ice Nuclei in Soils. THOMAS C. HILL, Paul DeMott, Yukata Tobo, Janine Froelich-Nowoisky, William L. Stump, Gary D. Franc, *University of Wyoming*

Organic ice nuclei (IN) are abundant and active at warm temperatures in most soils. However, their identities are not yet known. We characterized the organic IN present in a range of Wyoming and Colorado topsoils. This included soil beneath semi-arid sagebrush shrubland, a plant community widespread across the North American Western Range that can become a major dust source after wildfires; wind erosion events generate strong vertical fluxes of PM_{10} particles and even large plumes visible from space (Wagenbrenner et al. 2012).

Methods used included physical, chemical and enzymatic tests, and quantitative PCR of the ina gene to enumerate ice nucleation active bacteria. All soils contained 10^6 to $>10^7$ IN active at -10°C. Reductions in IN following heating (105°C) or digestion with hydrogen peroxide indicated that organic IN predominated above -15°C. Treatment with lysozyme, which digests bacterial cell walls and hydrolyzes fungal chitin, reduced IN active at -5°C to -8°C by 80-90% in non-forest soils. Ice nuclei active at colder temperatures were resistant to most challenges.

We also isolated individual IN from the sagebrush topsoil. In this soil, 70% of IN active at -7°C were >5 micro-meters in diameter. Ice nuclei active at -7°C were obtained by selective concentration, using repeated cycles of freeze-testing and subdivision of droplets of dilute soil suspensions. The identity of the first IN isolated is not obvious. They were multi-component structures, were seemingly entirely organic and survived repeated freeze-thaw events intact. However, one particle fragmented after several cycles, generating at least two smaller progeny IN. Sagebrush topsoils freeze and thaw almost daily during shoulder seasons. Their organic IN will both nucleate, and be modified by, the repeated freezing events.

Wagenbrenner, N.S., et al. Wind erosion from a sagebrush steppe burned by wildfire: Measurements of PM_{10} and total horizontal sediment flux. Aeolian Research (2012), http://dx.doi.org/10.1016/j.aeolia.2012.10.003.

3BA.6

Distribution of Biological Ice Nuclei in the Precipitation of Eastern China. RUI DU, Zongmin Liang, Yaling Wang, Pengrui Du, Ziming Li, *University of Chinese Academy of Science*

It was well known that the formation of ice in the atmosphere has significant local, regional and global influence, ranging from precipitation to cloud nucleation and thus climate. Ice nucleation is one of the most basic processes that lead to precipitation. Biological ice nucleators function as catalysts for freezing at relatively warm temperatures (warmer than-10°C). The aim of this paper is to investigate the distribution state of the most active ice nuclei of bacteria Pseudomonas syringae-like which can impact water freezing temperature and were suggested that they have important potential roles in the natural upper atmospheric cloud ice nucleation. We have investigated the freezing temperatures of rainwater collected from the different ecosystems of the eastern China, such as urban, clear grassland and forest regions. Our results show that droplets of rainwater samples can freeze mostly between -14 ℃ and -16 ℃ except those from Hailar and UCAS sites. The further studies demonstrate that although there are pseudomonas bacteria present in the rainwater of these sites through species identification by means of 16srDNA sequencing of filter membranes they do not show as expected ice nucleation activity as reported phenomena. We believe that there may be some effective ice nucleis of biological particles in atmospheric rainwater but they can not be belonged to micro-organisms. Our results suggest that in atmospheric ice nucleation processes, the famous bacterial ice nucleation maybe not play the important role especially in precipitation processes.

3CA.1

Effect of Aggregation and Mixing on Optical Properties of Black Carbon. BARBARA SCARNATO, *NASA Ames*

According to recent studies, internal mixing of black carbon (BC) with other aerosol materials in the atmosphere alters its aggregate shape, absorption and scattering of solar radiation, and then radiative forcing. These mixing state effects are not yet fully understood.

Multiple studies have demonstrated a strong variability in the observed mass absorption efficiency of BC, when it becomes internally mixed with non-absorbing organic compounds. Recent modeling studies show that, BC absorption enhancement depends strongly on the BC aggregate compactness and on the resulting mixing with other aerosol compounds.

The impact of morphology and mixing state on aerosol optical properties is a relevant topic, as well, for interpretation of remote sensing measurements. In radiative transfer calculations, that are also used to interpret space or ground-based observations of Earth, it is common to approximate aerosol shape to homogeneous spherical or spheroidal particles, ignoring the effect of realistic morphology and realistic mixing with other aerosol compounds, which can lead to significant errors in retrieved parameters, such as the aerosol type, optical thickness, particle size distributions and composition, and so forth.

This paper describes a sensitivity study on the effects of aggregation and internal mixing on optical properties BC, including absorption, scattering, linear polarization, scattering phase function, and others. A discrete dipole approximation model has been applied to examine these effects for BC particles bare and mixed with ammonium sulfate, sodium chloride, dust and others. Simulations are in accordance with observed morphology and mixing state published in literature.

The discrete dipole approximation model presented captures complexities in particle morphology that other models do not, and thus may be useful in predicting aerosol optical properties in climate modeling and interpreting data remotely measured with satellites.

3CA.2

Mixing of Biogenic Emissions with Urban Plume: A Case Study from CARES. NOOPUR SHARMA, Swarup China, Manvendra Dubey, Kyle Gorkowski, Bradley Flowers, Madhu Gyawali, W. Patrick Arnott, Rahul Zaveri, Arthur J. Sedlacek, R. Subramanian, Claudio Mazzoleni, *Michigan Technological University*

Single particle analysis can provide detailed characterization of morphology and mixing states of atmospheric aerosol particles and facilitate a better understanding of sources, transport and processing in the atmosphere. The Carbonaceous Aerosol and Radiative Effects Study (CARES) took place in the Sacramento urban area, California in June 2010 to study urban aerosols, their transport, aging and mixing with other atmospheric aerosols. Metrological data show that the measurement sites during the field campaign were dominated by South Westerly (SW) winds which were favorable for transporting the plume from the urban site of Sacramento (T0) to the T1 site located in Cool, a small town 40-km East of T0 in a forested area at the foothills of the Sierra Nevada. During such SW transport events, particles emitted in the Sacramento area mixed with local biogenic particles abundant at T1. In contrast, during NW transport events the urban plume was transported to the Southeast without significantly impacting T1.

In this study we investigate the variations in aerosol optical and morphological properties during the SW transport periods versus NW transport periods. Aerosol samples were collected on nuclepore filters during the campaign for electron microscopy analysis of single particles. For the detailed single particle analysis, we selected two days: 1) June 21, 2010 with NW wind patterns, and 2) June 25, 2010 with SW wind patterns. We analyzed morphology and mixing states of using a scanning electron microscopy. A single particle soot photometer was used to study the black carbon mass concentration and mixing state. The aerosol light scattering and absorption at three wavelengths were studied using a photoacoustic spectrometer. We will present the results of the analysis on biogenic aerosol morphology, mixing state and optical properties with and without influence of the urban plume.

3CA.3

Optical and Morphological Properties of Free Tropospheric Aerosol Sampled at the Pico Mountain Observatory, Azores.CLAUDIO MAZZOLENI, Swarup China, Lynn Mazzoleni, Paulo Fialho, Sumit Kumar, Katja Dzepina, Michael Dziobak, Seth Olsen, Robert Owen, Kendra Wright, Louisa Kramer, Detlev Helmig, Jacques Hueber, Judith Perlinger, Bo Zhang, *Michigan Technological University*

Improved characterization of free tropospheric aerosol optical, chemical and morphological properties is essential to further our understanding of the aerosol lifecycle and aerosol-climate interactions. Free tropospheric aerosols were studied at the Pico Mountain Observatory, located on top of the Pico Volcano in the Azores, Portugal (38.47°N, 28.40°W, 2225m asl). The station typically samples free tropospheric air masses that are transported from North America. Since 2012, we have been deploying a 3-wavelength nephelometer to measure the aerosol light scattering and backscattering fraction, a two-channel optical particle counter (for particles larger than 300 nm), a set of four high-volume samplers for the chemical analysis of aerosol, and a sequential sampler to collect aerosols on nucleopore membranes and lacy carbon grids for microscopy analysis. Additionally, black carbon mass equivalent concentrations have been measured at the station since 2001 with a 7-wavelength aethalometer. Supporting data collected at the site include ozone, carbon monoxide, non-methane hydrocarbons, and meteorological parameters.

Grids and membranes were analysed off-line with scanning and transmission electron microscopy coupled with energy dispersive x-ray spectroscopy to study morphological properties and elemental composition. Unique morphologies of the soot particles were observed. We will discuss the optical properties of aerosol, their potential radiative impact in terms of estimated single scatter albedo and asymmetry parameter, and the morphological differences of carbonaceous aerosols sampled at the station in comparison to continental samples.

3CA.4

Morphology and Mixing State of Fresh and Aged Wildfire Aerosols. SWARUP CHINA, Allison Aiken, Rachael Huempfner, Kyle Gorkowski, Manvendra Dubey, Claudio Mazzoleni, *Michigan Technological University*

Biomass burning is the largest contributor of soot and organic aerosols in the atmosphere and significantly affects Earth's radiation budget and climate. We analyzed ~10,000 single particles from two of the largest wildfires in New Mexico's history using electron microscopy coupled with energy dispersive X-ray spectroscopy. The samples include fresh smoke from the Las Conchas fire (2011) and relatively aged (~ 7 hours) smoke from the Whitewater Baldy Complex fire (2012) collected at Los Alamos National Laboratory. Effects of particle coatings were probed by using thermo-denuder before particle collection and making real time measurements of soot mass and mixing state with a single particle soot photometer.

Tar balls were the most abundant particles (~80% in fresh smoke and ~56% in aged smoke). In addition, in the aged smoke we observed 27% of aggregates mostly consist of large, nearly spherical particles, possibly of organic matter and a small fraction of tar balls. Detailed analysis of those aggregates showed that they contain between 2 to 44 individual particles. Relative abundance of soot particles was found to be the same (~8%) for both fresh and aged smoke. However, their mixing states are significantly different. To this end we classified and quantified them into four categories: bare (no visual coating), partly-coated, and soot-inclusions, where soot particles is not uniformly coated, embedded (heavily-coated). We found that the fraction of soot-inclusion particles were 12% and 30% for fresh and aged smoke, respectively, indicating that the residence time in the atmosphere influences these complex mixings. The fractal dimension of ambient soot decreased significantly upon removal of coatings via thermo-denuding. These findings can guide the development of new parameterizations to improve the performances of numerical models for the simulation of aerosol mixing, morphology and optical properties.

3CA.5

Chemical and Optical Changes to Black Carbon during Aging. ELEANOR BROWNE, Jonathan Franklin, Jesse Kroll, *MIT*

Black carbon (BC) is the second most important contributor to global warming. Due to its short atmospheric lifetime (~days), reductions in BC may be the quickest mechanism to reduce warming. Recent field measurements indicate that BC is a chemically and physically dynamic atmospheric constituent, suggesting that radiative forcing effects of BC may evolve quickly (on the timescale of hours) in the atmosphere. The specifics of how (and even if) the radiative forcing potential of BC changes as it ages, however, is currently under debate, thus leading to significant uncertainties on the magnitude of BC contribution to radiative forcing.

We attempt to help constrain this uncertainty using a series of laboratory measurements that systematically study the aging process of BC. These laboratory measurements are carried out using a photo-oxidation chamber and an extensive suite of measurements including an Aerodyne Soot-Particle Aerosol Mass Spectrometer (SP-AMS) and a Cavity Attenuated Phase Shift – Single Scattering Albedo (CAPS-SSA) instrument. The SP-AMS allows us to quantify and chemically characterize both the BC as well as any coatings present and the CAPS-SSA provides measurements of optical properties. Using this instrument suite, we characterize how the chemical and optical properties of BC change as it is aged heterogeneously (by OH and ozone) and as it is coated by organic material.

3CA.6

Black Carbon Aging from Biomass Burning. ALLISON AIKEN, Manvendra Dubey, Kyle Gorkowski, Claudio Mazzoleni, Swarup China, Shang Liu, Caleb Arata, Team FLAME-IV, *Los Alamos National Lab*

Black carbon (BC) is now considered the second most important global warming factor behind CO2 and is underestimated by a factor of two in most global models (Bond et al., 2013). ~50% of BC is from biomass burning (BB), estimated to contribute up to ~0.6 W/m2 warming of the atmosphere. Organic carbon (OC) from fires condenses and/or mixes, lowering the forcing from BB to 0.03 ± 0.12 Wm-2. The reduction depends strongly on the composition and mixing state of OC and BC. Models and laboratory measurements indicate that a BC core coated with a non-absorbing layer can enhance absorption by 2, although it has not been observed to this degree in ambient data (Cappa et al., 2012). Direct on-line measurements of BC are made with the single particle soot photometer (SP2) from "fresh" and "aged" BB. We investigate BC in concentrated BB plumes from the two largest wildfires in New Mexico’s history with different ages and compare them to BC from indoor generation from single-source fuels, e.g. ponderosa pine, sampled during Fire Lab At Missoula Experiments IV (FLAME-IV). FLAME-IV includes direct emissions, well-mixed samples, and aging studies. Las Conchas Fire (July-August, 2011) BC was sampled after only a few hours of aging and exhibits mostly core-shell structure. Whitewater Baldy Fire (May-June, 2012) BC was sampled after an aging period of 10-20 hours and includes partially coated BC in addition to thickly coated core-shell BC. Partially coated BC is not expected to enhance absorption as much as core-shell BC, therefore, determining the morphology of the BC is important to constraining the extent warming due BC on climate. Ambient BC physical and optical properties from the photoacoustic soot spectrometer are compared with direct laboratory emissions to understand BC aging in order to improve model treatment of BC absorption in global climate models.

3IM.1

Design and Characterization of a New Coarse Particle Collector Based on Microtrap Impactor Technology. Erin Lennox, Nathan Kreisberg, LUPITA MONTOYA, *University of Colorado Boulder*

A microtrap inertial impactor was developed and characterized for use as an area or personal sampler. The microtrap utilizes a high-density multi-jet plate to direct airflow and a matched multi-well plate to impact and collect particles for extraction with a reduced pressure drop relative to inertial impactors with fewer jets. This impactor was characterized using a fluidized bed aerosol generator and a small volume nebulizer to generate particles of Arizona Road Dust, potassium chloride and oleic acid. Collection efficiency was determined by measuring particle size distributions with an aerodynamic particle sizer. Two geometries of the microtrap were tested suitable for a two-stage coarse particle sampler, with 1 - 4 micrometer and a 4 - 10 micrometer stages. The 1 micrometer cut-point microtrap stage has a collection efficiency above 97 percent for particles greater than 2 micrometers in diameter (at a 10 liters per minute flow rate and a pressure drop of 0.12 kPa). The collection efficiency of this stage was constant for a period of up to 10 hours under typical ambient conditions without any coating on the impaction surface. The microtrap provides an improvement in area sampling due to its high collection efficiency at a low-pressure drop across the device, and its use of an uncoated impaction surface allowing for the extraction and analysis of biological samples.

3IM.2

Causes and Implications of Large Particle Penetration during PM10 Sampling. WILLIAM FAULKNER, John Haglund, Raleigh Smith, *Texas A&M University*

Researchers involved in sampling of coarse aerosols such as those derived from agricultural and mining sources have reported “oversampling” of PM10 concentrations when using FRM PM10 inlets compared to concentrations of PM10 calculated by applying a theoretical PM10 sampler penetration curve to total suspended particulate samples that were analyzed for particle size distribution (e.g., Buser et al., 2008). Despite these observations, there is not universal agreement whether the results constitute an “oversampling bias” for industries in which generated particulates typically exhibit a significant coarse fraction. The present research employed analysis methods designed to minimize uncertainty in measured penetration efficiencies for large particles through the FRM PM10 pre-collector in hopes of facilitating resolution to issues associated with sampling of large particles. Non-trivial penetration of particles larger than 15µm was observed, and the regulatory and health-based implications of these findings were explored.

3IM.3

The Splitter Bias Measurements for Calibration of Optical Particle Sizer (OPS) Using Wafer Surface Scanner (WSS) Method for 3 µm Particles at Ultra-Low Concentrations.

SHIGERU KIMOTO, Lin Li, George Mulholland, Miles Owen, David Y. H. Pui, *University of Minnesota*

Optical particle counters (OPCs) are widely used to measure aerosol size distribution and number concentration in the size range of approximately 0.1 to 30 µm by means of light scattering from single particles. They are applied to low concentration measurements such as clean room or ambient PM monitoring, and to high concentration industrial aerosols, e.g. industrial filtration. There is interest in the accurate calibration of OPCs at low concentrations (10-1000 particles/L) of particles in the size range of 1-5 µm in terms of their use for measuring the concentration of virulent biological structures. For the U.S. military, there is interest in calibrating an Optical Particle Sizer (OPS) at low concentrations of 3 µm particles with traceability to SI units realized by the National Institute of Standards and Technology (NIST). This is in support of fielded and future biological agent detectors. Particles are collected on a silicon wafer in a deposition chamber via gravity, and counted by a wafer surface scanner (WSS). Methodology and experimental results at ultra-low concentrations of 10-100 particles/L (total deposited concentration is 100-800 particles/L) by OPS and WSS were reported by Li et al. in 2012. However, the splitter bias measurement was not enough. In this study, we carried out the splitter bias measurement and calibration at the same concentrations ranging from 10-100 particles/L. The splitter bias measurements were carried out by test OPS, reference OPS and CPC. Then, test OPS was calibrated by three kinds of instruments (WSS, CPC and a reference OPS). We will report detail for this study.

3IM.4

DMA Size-Selection and Electrostatic Deposition of Particle Size Standards down to 10nm.

BENJAMIN HUNT, William Dick, Zeeshan Syedain, *MSP Corporation*

Particle deposition system (PDS) tools deposit particles of known size and count on substrates encountered in the semiconductor industry including silicon wafers and reticles (photomasks). Typically, particle size standards such as PSL spheres are deposited to create standards for calibrating inspection tools, such as the laser-based scanning surface inspection system (SSIS). Particle size standards are typically classified with a DMA before they are deposited to eliminate residue particles and minimize agglomerates of monomers. The DMA is also used for measuring the peak diameter and width of the size distribution of the particle size standard via mobility scanning. The operator can specify any particle size for selection by the DMA and subsequent electrostatic deposition, but the deposited size may not be accurately known if the selected size is substantially different than the measured peak diameter. With the next generation of PDS tools slated to achieve sizing accuracy of ±0.5nm and repeatability on the order of ±0.1nm for deposited particle size ranging from 10nm to 50nm, the need for accurate prediction of the size distribution entering the deposition chamber is evident. Such a prediction requires knowledge of the particle size distribution immediately after atomization and the DMA transfer function and therefore requires inversion of the mobility scan of the size standard. The methods of Twomey and Markowski are used to invert the mobility scan data. A means of predicting the diameter shift due to off-peak diameter selection is proposed. This allows the operator to determine the DMA voltage that would result in the desired peak diameter being deposited. The method is tested by deposition of particle size standards on silicon wafers and subsequent inspection with a commercial SSIS tool.

3IM.5

Coupling Electrostatic Precipitation with Attenuated Total Reflectance FTIR for Spectral Signature Studies. ZAHRA CHAUDHRY, Timothy Lippa, Thomas Buckley, Clinton Cahall, Rebecca Koslover, *JHU APL*

Spectral studies of aerosol-environmental interactions are needed which capture and interrogate the material without affecting or changing the aerosol or the interaction of interest. This proof-of-concept study set out to design and build an Electrostatic Precipitator (ESP), which would capture aerosolized material onto an optical crystal that could be spectrally analyzed via Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). This technique brings higher spectral resolution and sensitivity to the field of study, as well as a larger spectral library than is currently available with aerosol chemical detectors. The material of interest was nebulized, mixed with dry air and neutralized prior to entering the ESP. Successful deposition was characterized by a downstream particle counter and monitoring the ion current between the ESP wire electrode and the optical crystal. Data is presented comparing the library spectra with the measured ATR-FTIR spectra for polystyrene latex spheres and ethylene glycol. Future applications of this technology would be laboratory characterization of aged or degraded aerosols, investigation of complex surface chemical reactions, or characterization of chemical vapor-aerosol interactions.

3IM.6

Validation of a Personal Sampler's Performance in Sampling Inorganic Acids According to OSHA Guideline. LIN SHOU, Danielle Hall, Yu-Mei Hsu, Alex Theodore, Chang-Yu Wu, Brian Birky, *University of Florida*

A personal sampling device has been developed to measure the true level of inorganic acidic gases and aerosols simultaneously in occupational environment that may have high acid aerosol mist and gas concentrations. It consists of a parallel impactor upstream, a porous membrane denuder (PMD) in the middle and a filter pack downstream. The parallel impactor, which has 4 parallel and separated impactors with different nozzle sizes, was designed to have a collection efficiency curve that approximates the ACGIH respirable curve. Experimental results proved that the prototype samplers followed closely the penetration characteristics for which it was designed. In the second stage, the PMD, which utilizes the high porosity of membrane material and a configuration of multiple parallel flow channels to compact the size, decrease the weight and increase gas collection efficiency, was used to remove gaseous compounds while allowing aerosol to pass through the section. Experimental results showed that the PMD's collection efficiency for 10 ppm sulfur dioxide over 5 hours was higher than 97%. The sampling capacity of the personal sampler was tested by sampling a dynamically generated controlled test atmosphere containing H_2SO_4 at four times of the OSHA standard concentration (4 mg/m^3) and 72% relative humidity at 20 °C. The personal sampler's overall collection efficiency maintained above 93.9% for 10 hours, and the sampler had a capacity larger enough for 4 times of the OSHA standard. 23.2%±2.3%, 4.2%±0.3%, and 72.5%±2.1% of the feed were collected at the impactor, denuder and the filter pack, respectively. The personal sampler's storage stability and its performance under low humidity and low concentration will be further tested according to the validation guidelines for air sampling methods published by OSHA (Occupational Safety and Health Administration), and experimental results will be updated at the conference.

3RA.1

A Study on Submicrometer Particles and Biological Materials in Seawater and Their Contribution to Primary Marine Aerosol Formation.

JIYEON PARK, Hyunji, Kim Kim, Seungyong Lee, Minsoo Kang, Hee-joo Cho, Seunghee Han, Kihong Park,*Gwangju Institute of Science and Technology*

Chemical constituents (organics, sulfate, nitrate, ammonium, chloride, and methanesulfonic acid) of non-refractory submicrometer particles in the ambient atmosphere were measured in real time using a quadruple aerosol mass spectrometer (QAMS) at a coastal site (Boseung, Korea) in the fall (10/29/2012–11/16/2012). Also, chemical constituents of sea spray particles aerosolized from seawater sampled from the coastal site were measured using the AMS, and biological materials (chlorophyll-a (<700 nm), bacteria (200-450 nm and 200 nm-1 µm), and virus (20-200 nm)) in seawater were determined by an UV spectrophotometer and epifluorescence microscopy method to investigate effects of biological materials on marine aerosol formation. The AMS mass spectra (m/z 30 and m/z 42 for amino acid, and m/z 60, m/z 61, and m/z 73 for carbohydrates) were used for determination of biological species in organic particles. The concentrations of chlorophyll-a (~2.25 µg/l) and bacteria (2.8x105 bacteria/ml) in seawater were the highest on 11/9/2012, and the biological fraction (the ratio of a sum of the biological markers in organic spectra to total organic spectra) in the submicrometer particles in the ambient atmosphere was also highest on that day (~41%), suggesting that the biological organic species in seawater significantly contributed to the formation of the marine aerosols. The biological fraction in the ambient particles decreased to ~11% with continental air mass. Further analyses for chemical constituents of bubble bursting particles from seawater and the amount of virus in seawater are in progress, and will be presented.

3RA.2

Ultrafine Sea Spray Aerosol over the South Eastern Pacific: Open-Ocean Contributions to Marine Boundary Layer CCN.

Romain Blot, ANTONY CLARKE, Steffen Freitag, Vladimir Kapustin, Steven Howell, Jensen Jorgen, Lindsey Shank, Cameron McNaughton, Vera Brekhovskikh, *University of Hawaii, Honolulu, HI 96822*

Accurate measurements of size resolved natural aerosol emissions over the ocean are needed for any relative assessment of the anthropogenic impact of aerosol on the environment or climate. However, isolating the Sea Spray Aerosol (SSA) production and removal flux under ambient marine condition down to sizes as small as 40 nm, those that usually contribute to cloud condensation nuclei (CCN) in marine clouds, has proven challenging. Here we report measured SSA concentrations with diameters larger than 40 nm produced by open-ocean breaking waves over the SEP (South Eastern Pacific). Robust statistics were established through repeated airborne flights over 1000 km along 20 S from the coastline of Chile to 85W during the 2008 VOCALS-Rex (VAMOS Ocean-Cloud-Atmosphere-Land-Study Regional Experiment). Non-volatile SSA number concentrations were inferred using a thermally resolved technique constrained for “clean conditions having a scattering Angtrom exponent below 0.5, Black Carbon (BC) mass concentrations less than 15 ngm-3 and Organic aerosols (Org) concentrations below 0.02 µgm-3. We found that number concentrations of SSA active as CCN for cloud supersaturation about 0.25 % varied between 17 cm-3 and 36 cm-3. However, SSA concentrations did not reveal the expected increase with the increasing mean wind speed encountered further offshore along 20S. Increases in precipitation scavenging of SSA for mean offshore precipitation rate in excess of about 1 mm d-1 appeared to exceed increased production for wind speeds increasing from about 8 – 14 ms-1. These observations demonstrate models of marine SSA and CCN concentrations must adequately represent both the SSA source and the critical role of precipitation as a major sink for SSA and CCN over the remote ocean. Finally, we found that under “clean” conditions and for estimated stratus supersaturations between 0.20 % and 0.43 %, SSA represented about 20 % of the total ambient CCN along 20S.

3RA.3

Size-Dependent Changes in Sea Spray Aerosol Composition and Properties with Different Seawater Conditions. ANDREW AULT, Ryan Moffet, Jonas Baltrusaitis, Douglas Collins, Matthew Ruppel, Luis Cuadra-Rodriguez, Defeng Zhao, Timothy Guasco, Carlena Ebben, Franz Geiger, Timothy Bertram, Kimberly Prather, Vicki Grassian, *University of Iowa*

Single particle methods, including transmission electron microscopy with energy dispersive X-ray analysis, Raman microspectroscopy, and scanning transmission X-ray microscopy with near edge X-ray absorption fine structure spectroscopy, were used for detailed characterization of sea spray aerosol (SSA) particles. SSA particles were produced from breaking waves generated from seawater in a sealed wave flume apparatus from seawater, and changes to the SSA after the addition of biological (bacteria and phytoplankton) and organic material (ZoBell growth media) were probed. SSA particles can be characterized within two distinct populations: one with a distinct sea salt core and organic matter coating (SS-OC), and a second consisting of organic species mixed with sulfate (OC) without core/shell morphology. SS-OC particles exhibit a wide range of sizes, compositions, morphologies, and distributions of elements within each particle. After addition of biological and organic material to the seawater, a change occurs in particle morphology and crystallization behavior associated with increasing organic content for SS-OC particles. Functional group analysis of the organic component of SS-OC particles showed long chain aliphatic species, though different modes in the C-H stretching region were enhanced before and after addition of biological and organic material. The fraction of OC particle types, which are mainly present below 300 nm, are dramatically enhanced with increased biological activity. Changes in relative amounts of SS-OC and OC populations as a function of size and seawater chemistry, as well as the variability within SS-OC, have important atmospheric implications for cloud droplet activation and heterogeneous reactivity.

3RA.4

Precipitation Scavenging of Aerosols in the Niigata Plain, Japan, during the Winter Season. SHIN OHARA, Shin-ichi Fujita, Naoto Kihara, Soichiro Sugimoto, Akira Takahashi, *Central Research Institute of Electric Power Industry*

In a coastal area of the Sea of Japan, it has been reported that the concentrations of Na^+ and non-sea-salt SO_4^{2-} (nss-SO_4^{2-}) in precipitation tend to increase during winter. Northwesterly winter winds off the Asian continent bring sea-salt aerosols emitted from the Sea of Japan as well as long-range transported air pollutants to this area. The seasonally high concentrations of Na^+ and nss-SO_4^{2-} in precipitation would be attributed to scavenged sea-salt aerosols and particulate nss-SO_4^{2-}. However, the processes of precipitation scavenging of these aerosols are poorly understood.

In this work, we studied the precipitation scavenging of aerosols in the Niigata Plain, located along the Sea of Japan, during winter. For this purpose, the field sampling of precipitation and ambient aerosols was conducted at three sites in the Niigata Plain, during winters from 2008 to 2011. The distances from the coast to these sites were approximately 1 km, 17 km and 29 km. At each site, a wet-only sampler was installed for the collection of precipitation samples. Aerosol samples were collected on a 47 mm Teflon filter by using a ten-line low-volume sampler. These samples were collected every 6 hours between December and March during the winters of 2008 - 2011. Samples of the precipitation and the filter extract were analyzed for the species: NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}. The electrical conductivity and pH of the precipitation samples were also determined.

In this presentation, we will discuss some of the analysis of the set data of ionic concentrations in the precipitation and the aerosol samples by using the scavenging ratio as well as some preliminary analysis of the relationship between the concentrations and the distance from the coast, focusing on differences in the precipitation scavenging of aerosols between coastal and inland areas.

3RA.5

Saharan Dust in Southern Europe in the Period 2001-2011: Estimation and Geographical Distribution. J. PEY, N. Pérez, Xavier Querol, Andrés Alastuey, F. Forastiere, M. Stafoggia, *Aix-Marseille Université-CNRS, LCE FRE 3416*

African dust outbreaks affecting southern Europe were studied on an 11-year period (2001-2011), in the context of the MED-PARTICLES (LIFE programme, EU) project. The daily influence of African dust was identified in 17 geographical areas. A methodology for the quantification of daily African dust inputs to PM10 concentrations was applied.

African dust outbreaks are more frequent in the most southern European regions, from 30 to 37 % of the annual days, whereas they occur less than 20% of the annual days in northern sites of the Mediterranean basin. A decreasing south to north gradient of African dust contribution to PM10, driven by the latitudinal position of the monitoring sites is patent across the Mediterranean. From 25ºE eastwards, higher annual dust contributions are encountered due to the elevated annual occurrence of severe episodesof dust but also because of inputs from Middle Eastern deserts. Overall, African dust emerges as the largest PM10 source in regional background southern sites of the Mediterranean (35-50% of PM10), with seasonal peak contributions to PM10 up to 80% of the total mass in the eastern side.

The multi-year study of African dust episodes and their contributions to PM10 concentrations displays a consistent decreasing trend in the period 2006/2007 to 2011 in 4 of the 17 studied regions, all of them located in the NW of the Mediterranean. Such decrease is almost parallel to that of NAO (North Atlantic Oscillation) index for the summer period, being progressively more negative since 2006. As a consequence, a sharp change in the atmospheric circulation over the last 5 years (a similar negative NAO period occurred in the 1950 decade) have affected the number of African dust episodes and consequently the annual dust inputs to PM10 observed in the NW part of the Mediterranean.

3RA.6

The Color of Aerosol Deposition and the Browning of the Taj Mahal. J. JAI DEVI, Michael Bergin, S.N. Tripathi, Tarun Gupta, Michael McKenzie, Martin Shafer, James Schauer, K.S. Rana, *Georgia Institute of Technology*

Over the past decades the Taj Mahal, one of the wonders of the world, has taken on a brown hue that is believed to be linked to air pollution. The Taj Mahal is located in Agra, has extremely high aerosol loadings for much of the year. We will present results from a recent field study that focused on the sources of aerosols in Agra, and the impact of aerosol deposition on the color of the marble surfaces of the Taj Mahal.

Ambient filter samples for $PM_{2.5}$ and TSP were collected at the Taj Mahal from Dec. 2011 to May 2012 for analyses of aerosol mass and chemical composition. In addition, small cuboids of pre-cleaned marbles were stuck on the Taj Mahal to study the particle deposition flux to the monument. After several months of exposure, they were analyzed for particle size and chemical composition. The chemically resolved particle size information was used in conjunction with Mie Theory and a radiative transfer model to determine the impact of deposited particles on the spectral reflectance of the marble substrates. The estimated spectral surface reflectance was translated to color using opponent process theory.

The mean annual concentrations of $PM_{2.5}$ and TSP near the Taj Mahal were extremely high at values of 200 and 400 μgm^{-3}, respectively. The deposition of particles on the marble deposition substrates showed a bimodal surface area distribution with modes around 1 and 5.0 micro-meter. Elemental analyses indicated that the surface coverage was dominated by dust particles, with a much smaller contribution from carbonaceous particles. Model estimates of color based on surface concentrations of dust and carbon quantitatively agree with the surface color change observed on the sample substrates as well as the Taj Mahal exposed marble surfaces. We will discuss the relative impact of deposited dust, black carbon, and brown carbon on the color of the Taj Mahal.

3SA.1

Seasonal and Spatial Variation of Trace Elements and Metals in Quasi-Ultrafine (PM0.25) Particles in the Los Angeles Metropolitan Area and Characterization of Their Sources. ARIAN SAFFARI, Nancy Daher, Martin Shafer, James Schauer, Constantinos Sioutas, *University of Southern California*

To investigate the variability and sources of trace elements and metals, year-long sampling campaign of quasi-ultrafine particles (PM0.25) was conducted at 10 distinct locations (including source, urban and/or near freeway, rural receptor and desert-like) across the Los Angeles south coast air basin. Time-integrated (24-hour filter-based) samples of aerosols were collected at each site and concentrations of trace elements and metals were quantified using high-resolution inductively coupled plasma sector field mass spectrometry (ICP-SFMS). In order to identify likely sources using elemental grouping information, principal component analysis (PCA) was applied to the dataset. The major sources were identified as road dust, vehicular abrasion, residual oil combustion, cadmium sources and metal plating. These sources accounted for approximately 85% of the total variance of PM0.25 elemental content. Transition metals (such as manganese, iron and cobalt) along with mineral metals (magnesium, calcium, potassium, and sodium, to name a few) were the most important constituents of the first component, originating from road dust, influenced by vehicular emissions as well as resuspended soil. Copper, barium, antimony and molybdenum were the major elements in the second component identified as vehicular abrasion. Tracers of residual oil combustion, including sulfur and vanadium, displayed high loading factors (above 0.8) in the third component and the fourth component was characterized by cadmium as the major element. Finally, nickel and chromium likely associated with metal plating and other industrial activities distinguished the fifth component. Distinct temporal and spatial variations were observed for the identified elemental groups. The concentrations of elements associated with the source and urban locations generally displayed a decline as we proceeded from the coast to the inland. Occasional concentration peaks in the rural receptor sites were also observed, likely driven by the dominant westerly/southwesterly wind transporting the particles to the receptor areas.

3SA.2

Characteristics and Source Apportionment of Marine Aerosol over Chinese Seas. MEI ZHENG, Huaiyu Fu, Caiqing Yan, Xiaoying Li, *Peking University*

Under appropriate meteorological conditions, urban emissions can be transported to marine environment and deposit into the ocean. This study aims to investigate atmospheric particulate emissions from northern China and the changes of its physical and chemical properties during the transport from land to sea. As part of a major ocean field campaign, online and offline aerosol sampling were performed over Yellow Sea and Bohai Sea over three weeks from November 2 to 21, 2012 using real-time instrument Single Particle Aerosol Mass Spectrometry (SPAMS), Fast Mobility Particle Sizer (FMPS) and high volume sampler. SPAMS can provide online size and chemical composition information for each single particle in the size range of 200 to 2000 nm, while FMPS gives size information of finer particles (5.6-560 nm). With the analysis of quartz filters by the high volume sampler, detailed organic speciation provides information of composition and concentration of various organic compounds such as polycyclic aromatic hydrocarbons (PAHs), fatty acids, alkanes and others. Source apportionment of fine atmospheric particles in marine environment is conducted to estimate the impact of urban anthropogenic emissions from land with SPAMS online and high-volume offline chemical composition data. During the field campaign, about five particle episodes were observed. Based on particle size and composition date provided by FMPS and SPAMS, it revealed that sources and mechanisms of these five episodes might be different. Trajectory analyses were performed to better understand sources of these particles. As moving away from land, particle number decreased with distance and particle size shifted to slightly larger size. The changes of source impacts and inorganic and organic pollutants will be also discussed.

3SA.3

Source Apportionment of Fine Atmospheric Particles in Marseille: A One Year Study. DALIA SALAMEH, Anaïs Detournay, Henri Wortham, Jean Luc Jaffrezo, Christine Piot, Alexandre Armengaud, Damien Piga, Michaël Parra, Magali Deveze, Nicolas Marchand, *Aix Marseille University, Laboratoire Chimie Environnement*

Marseille is the second most populated city in France with more than one million inhabitants. With traffic of about 88 million tons (Mt) in 2011, Marseille is also the most important port of the Mediterranean Sea, and also in the vicinity of the large petrochemical and industrial area of Fos-Berre, located 40 km northwest of the metropolitan area.

For these reasons, Marseille area represents a challenging case study for source apportionment exercises, combining an active photochemistry and multiple emission sources, including fugitive emissions from industrial sources and shipping. In order to develop strategies for controlling and reducing air pollution, there is a need of source apportionment studies in order to better understand the influence of the different sources of aerosol particles.

Within the framework of the EU-MED APICE project (Common Mediterranean strategy and local practical Actions for the mitigation of Port, Industries and Cities Emissions; www.apice-project.eu), sources of atmospheric particles were evaluated for a one-year period by a long monitoring campaign conducted at two sampling sites. PM2.5 were collected continuously on a 24h-basis in an urban background site from July 2011 to July 2012 and on a 48h-basis for the Eastern dock from November 2011 to July 2012 using high volume samplers operating at a flow rate of 30m3/h.

In this work, two receptor models: CMB (Chemical Mass Balance) and PMF (Positive Matrix Factorization) were used to explain the chemical observations, and to investigate the sources of organic aerosol in Marseille. These two models were used with organic molecular markers, metals/trace elements and combined to quantify the contribution of the main aerosol particles sources.

Both approaches are able to identify major sources, the combination of these two commonly used receptor models offers interesting perspective, especially when the factors derived from PMF analysis are injected as source profiles in CMB calculation.

3SA.4

Is Alaska Truly the Great Escape from Air Pollution? – Long Term Source Apportionment of Fine Particulate Matter in Fairbanks, AK. YUNGANG WANG, Philip K. Hopke, *Lawrence Berkeley National Laboratory*

Most people think of Alaska as one of the last great escapes from air pollution. However, they have not spent a winter in Fairbanks or the nearby town of North Pole, where the daily average $PM_{2.5}$ concentration was 170 micro-g/m^3 in December 2012. Prior source apportionment modeling was performed using $PM_{2.5}$ speciation data collected at Fairbanks, Alaska during 2008 to 2011 (Ward et al., 2012). Wood combustion was found to be the largest contributor to PM2.5 throughout the winter months. Huy and Mölders, (2012) investigated effects of exchanging noncertified with certified wood-burning devices on the $PM_{2.5}$ concentrations in Fairbanks, Alaska during the cold season. Changing out 2930 uncertified woodstoves and 90 outdoor wood boilers reduced the daily average $PM_{2.5}$ concentrations by 0.6 micro-g/m^3. In this study, source apportionment using Positive Factorization Matrix (PMF 5.0) has been conducted based on the 2005-2012 $PM_{2.5}$ compositional data including elements, sulfate, nitrate, ammonia, elemental carbon (EC), and organic carbon (OC) from the U.S. Environmental Protection Agency speciation network. The $PM_{2.5}$, EC, and OC concentrations apportioned to wood combustion has been quantified. The temporal variation of wood combustion contributions has been studied as well. In the future, additional source apportionment using other receptor models and tracers will need to be conducted to confirm the results. For example, aethalometer delta-C, a simple, cheap, readily accessible, and of high time resolution marker of wood smoke, could help further apportion the wood stove contributions to $PM_{2.5}$ (Wang et al., 2011).

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3SA.5

PMF*PMF: Towards a Better Link between PMF Outputs from ACSM Measurements and Aerosol Sources - First Application in the Region of Paris (France). JEAN-EUDES PETIT, Jean Sciare, Olivier Favez, Roland Sarda-Esteve, Valérie Gros, Jose B. Nicolas, Philip Croteau, John Jayne, Grisa Mocnik, *INERIS*

Aerosol Mass Spectrometer (AMS) measurements combined with statistical tools (Positive Matrix Factorization, PMF), are nowadays more and more used worldwide to investigate sources of submicron aerosols and related atmospheric ageing processes. However, due to the inherent complexity of organic aerosol (OA) in the atmosphere, and keeping in mind current limitation in the PMF analysis, factors denomination and their scientific interpretation could be sometimes hazy or unsafe when attempting to make connections to pollution sources or atmospheric processes.

We present here a first investigation of the effectiveness of a double PMF analysis on an ACSM dataset obtained in Paris, during the 2012 late winter period. OA has been apportioned by a commonly used PMF analysis tool (Ulbrich et al., 2009). The resulted factors are then implemented in a second PMF calculation (EPA PMF v.3.0), adding inorganic ions measured by the ACSM (nitrate, sulfate, ammonium and chloride), and Black Carbon from fuel fossil and biomass burning, obtained using the Aethalometer model (Sandradewi et al., 2008). First results highlight a good agreement for some of the outputs (Biomass Burning Organic Aerosol almost 100% within the corresponding “wood burning” factor), but also evidences for a relation between Oxygenated Organic Aerosol and primary sources, and raising questions about a unique traffic origin of HOA. These results are consistent with those obtained from the characterization of two individual sources: traffic and biomass burning (via tunnel and chimney experiments), under conditions representative of the local ones.

3SA.6

Harmonization of Source Apportionment with Receptor Models in Europe. CLAUDIO A. BELIS, Philip K. Hopke, *European Commission - Joint Research Centre*

In Europe, there is a need for harmonization of the receptor model techniques aiming at: a) making the results of the different studies comparable, b) expressing the reliability of the results quantitatively, and c) establishing when a methodology is appropriate for a specific purpose.

In 2010, an initiative for the harmonization of receptor models in Europe was launched consisting in three main activities: a) accomplishing a review and meta-analysis of source apportionment studies , b) organizing European-wide intercomparsion exercises, and c) drafting a European common technical protocol.

The review, conducted on more than one hundred publications including more than 330 records, identified CMB and PMF as the most commonly used tools and reported 6 main source categories for particulate matter mass and 3 for the particulate organic carbon. The geographical and seasonal variation of these sources were mapped and discussed.

Two intercomparison exercises were carried out by comparing the source contribution estimations by 25 independent research groups from 15 countries using the same or different receptor models on the same dataset. The main outcomes of the exercises are a general agreement between the performances of the different participants and models and good expert skills in dealing with complex real-world data and synthetic data.

The third pillar of the initiative is the common technical protocol prepared by leading scientists in the field. The document, targeted mainly to practitioners but also to air quality experts and policy makers, is organized following a logical sequence of steps to be carried out in a source apportionment study, with different levels of complexity according to the reader skills. The protocol focus on the most commonly used tools, nevertheless, there is a section on advanced methods which use is likely to increase in the near future.

4AC.1

Effect of Humidity on Secondary Organic Aerosol (SOA) Formation from Biogenic Hydrocarbons and Nitrate Radicals.NGA LEE NG, Christopher Boyd, Lu Xu, Greg Huey, Xiaoxi Liu, *Georgia Institute of Technology*

The reactions of biogenic volatile organic compounds (BVOCs) with nitrate radicals (NO3) represent a direct link of anthropogenic and biogenic emissions. Half of the aerosol lifetime is in the dark where NO3 radicals and ozone can be the prevalent oxidants. Yet, compared to SOA formation from ozonolysis and photooxidation chemistry, SOA formation and evolution involving NO3 radicals have received far less study. Water is ubiquitous in the atmosphere and water vapor can affect the mechanisms, chemical composition, and physical and chemical properties of aerosols formed. This can be especially important for nighttime chemistry (where NO3 radicals can dominate) where ambient RH is high. Here we report a series of experiments to study SOA formation from the reaction of different biogenic hydrocarbons (isoprene, a-pinene, and b-caryophyllene) with NO3 radicals. Experiments are performed in the newly constructed Georgia Tech indoor chamber facility, which consists of two 8 m3 Teflon chambers suspended in a temperature controlled enclosure (4-35 oC). The experiments are performed in the dark using thermal decomposition of N2O5 as a source of NO3 radicals. Experiments are conducted under both dry and humid conditions: dry (RH< 5%), 30%, 50%, and 80% RH. Aerosol growth and composition are monitored by Scanning Mobility Particle Sizer (SMPS) and High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). The gas-phase composition and NO3 radical concentrations are monitored by a Chemical Ionization Mass Spectrometer (CIMS). The SOA yields (and parameterizations) for these experiments will be presented and the effect of water vapor on SOA formation mechanism and composition will be discussed. The presence of nitric acid under humid conditions provides an opportunity to investigate the effect of particle acidity on aerosol formation from a non-sulfur source and such results will also be presented and discussed.

4AC.2

Formation and Aging of Secondary Organic Aerosol during the β-caryophyllene Oxidation. ANTONIOS TASOGLOU, Spyros Pandis, *Carnegie Mellon University*

β-caryophyllene (C15H24) is a biogenic sesquiterpene which is emitted in the atmosphere in significant quantities and can produce secondary organic aerosol (SOA) after being oxidized. We investigate the (SOA) production during the oxidation of β-caryophyllene using the Carnegie Mellon environmental chamber. Both the initial formation of SOA and the subsequent chemical aging of the products are investigated. Three sets of experiments were conducted with three different oxidants: ozone, hydroxyl radicals, and the combination of both. The ability of β-caryophyllene to form SOA was quantified as a fractional aerosol mass yield. Seed particles were used in some experiments for determining their potential effects on the SOA yields. The potential photo-dissociation of the produced β-caryophyllene SOA was studied by exposing the formed SOA to UV-light for several hours. Oxidation of the SOA was also studied using a HR-ToF-AMS by exposing the particles to high concentrations of hydroxyl radicals. We also investigate the evaporation of β-caryophyllene SOA by heating the chamber to 40 degrees Celcius and by using a thermodenuder. The corresponding volatility distributions of the products and an effective vaporization enthalpy are estimated.

4AC.3

Characterization of Organic Aerosol from Mixed Biogenic / Anthropogenic Emissions. DHRUV MITROO, Brent Williams, Raul Martinez, Yaping Zhang, William Brune, Munkhbayar Baasandorj, Lu Hu, Dylan Millet, *Washington University in St. Louis*

Chemical reaction mechanisms have been studied in detail for single component or simple mixtures of volatile biogenic (e.g., isoprene, a-pinene) and anthropogenic (e.g., xylene) aerosol precursor gases. Recent studies to determine secondary aerosol yields from the oxidation of these volatile species under variable conditions (e.g., over a range of VOC concentrations, NOx concentrations, and RH values) have been performed in controlled laboratory settings using static smog chambers and flow-tube steady state reactors. It has been observed in the field and shown through these laboratory studies that secondary organic aerosol (SOA) yields can be increased with a mixture of biogenic and anthropogenic emissions. The details of the controlling chemical mechanisms remain highly uncertain, leaving current models unable to accurately predict aerosol concentrations in regions with mixed emission sources.

Here, we present preliminary data from controlled laboratory experiments to offer insight on active chemical pathways that may be controlling enhanced SOA formation in the atmosphere. We use a custom-built emission chamber for complex source emissions coupled with the Potential Aerosol Mass (PAM) reactor, a flow tube reactor, to mimic atmospheric oxidation, and finally, a variety of mass spectral detection techniques to determine organic gas and particle composition before and after various degrees of mimicked atmospheric aging.

4AC.4

Fluorescence, Photobleaching, and Molecular Level Analysis of Brown Carbon Aerosol. HYUN JI LEE, Paige Aiona, Sergey Nizkorodov, Alexander Laskin, Julia Laskin, *University of California, Irvine*

Brown carbon (BrC) compounds can either be directly emitted from combustion sources as primary organic aerosol (POA)(Bond et al., 2006) or be formed in the atmosphere through multi-phase reactions, such as aging of secondary organic aerosol (SOA) mediated by ammonium sulfate (AS)(Galloway et al., 2009). Chemical composition and atmospheric transformations of both primary and secondary BrC are highly uncertain. This presentation will discuss the molecular level composition, absorption spectra, fluorescence spectra, and the mechanism of photodegradation of several different types of BrC. The secondary BrC samples included products of reaction between AS and chamber-generated SOA or methylglyoxal, as well as SOA prepared by high-NOx photooxidation of aromatic compounds. The primary BrC samples included aerosol produced by wood combustion. In all cases, the evolution of the absorption and fluorescence spectra of aqueous extracts of BrC were measured during irradiation by a known flux of UV or visible light. The compositional changes between the aged and photobleached samples were characterized by liquid-chromatography coupled to a photodiode array detector and to a high-resolution electrospray ionization mass spectrometer (LC-UVVIS-ESI/HRMS). Photodegradation of BrC occurs on atmospherically relevant time scales and significantly changes its absorption properties. In contrast, the molecular level composition of BrC exhibits only subtle changes suggesting that the optical properties of BrC are controlled by minority compounds. The fluorescence of BrC is significant in some cases, and it can be potentially mistaken for bioaerosols in fluorescence-based methods. Overall, the results demonstrate a high degree of variability in optical properties and dynamic nature of atmospheric BrC.

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4AC.5

Secondary Organic Material Formation from Isoprene Photooxidation Products Induced by Particle Phase Reactions.

MIKINORI KUWATA, Yingjun Liu, Karena McKinney, Scot Martin, *Harvard University*

Particle phase reactions have been considered as one of the important mechanisms for secondary organic material (SOM) formation, especially for SOM forming from isoprene photooxidation products. However, elucidating the contributions of particle phase reactions to chemical composition and mass concentrations using traditional chamber experiment techniques has been difficult because condensational growth by saturated organic vapor also occurs. In the present study, a novel experimental setup was developed to exclusively investigate particle phase reactions.

Isoprene photooxidation products were continuously sampled from the Harvard Environmental Chamber (HEC). The concentration of isoprene in the HEC was controlled as sufficiently low to prevent particle formation in the HEC. The oxidation products were mixed with seed particles to induce SOM formation using another chemical reactor. SOM formation was monitored using both an aerosol mass spectrometer (AMS) and a scanning mobility particle sizer (SMPS), while reactive uptake of gaseous species was quantified using a proton transfer reaction mass spectrometer (PTR-MS).

Significant SOM formation was observed after mixing isoprene oxidation products with seed particles, depending on the type of seed particles. The AMS mass spectra were significantly different from those observed for previous isoprene photooxidation experiments. They were very similar to PMF factors found during atmospheric observations in tropical rain forests such as Borneo Island and the Amazon. Therefore, the present result strongly suggests the importance of particle phase reactions on SOM formation in actual atmospheric environments.

4AC.6

Quantification of Organosulfate Formation in the SOA with Preexisting Acidic Sulfate Aerosol.

JIAYING LI, Myoseon Jang,*University of Florida*

In this study, organosulfates were produced in the secondary organic aerosol (SOA) from the photooxidation of various volatile organic compounds (VOCs), such as α-pinene, toluene, and isoprene, in the presence of NOx and acidic sulfate aerosols using an outdoor Teflon film chamber. The aerosol proton concentration ([H^+], mol/L) of the SOA collected on the filter was measured using colorimetry integrated with a reflectance UV-Visible spectrometer (C-RUV). As the organosulfates form in the aerosol, the C-RUV data showed a decrease of aerosol acidity due to the consumption of preexisting acidic sulfate. The reduction of aerosol acidity measured by the C-RUV technique was used to quantify the organosulfates production in the SOA. FTIR equipped with a small flow chamber that holds an optical window for aerosols collected by impaction was used to characterize functional groups of organic compounds in the SOA. The reactivity of a certain functional group (e.g., hydroxyl, carbonyl, keto) to form organosulfates in the SOA will be investigated. Hydroxy and carbonyl groups are expected to give high organosulfates yields.

4AC.7

A Dual-Chamber Enhancement (DUCE) Method for Quantifying Secondary Organic Aerosol from Biomass Burning Emissions. DANIEL S. TKACIK, Ellis Shipley Robinson, Rawad Saleh, Adam Ahern, Albert A. Presto, Ryan Sullivan, Neil Donahue, Allen Robinson, *Carnegie Mellon University*

Biomass burning emissions are a large contributor to the global budget of gas- and particle-phase material in the atmosphere, and thus play an important role in atmospheric chemistry, human health, and climate. Current estimates on secondary organic aerosol (SOA) formation from these emissions are highly uncertain. A few biomass burning SOA studies have been conducted, but a challenge is the physiochemical makeup of these emissions is highly variable and depends on characteristics like burn and fuel conditions that are difficult to characterize. Smog chamber experiments typically consist of exposing emissions from a single biomass burn to one type of perturbation (ie: photo-oxidation), so the specific environmental conditions that promote or hinder SOA formation across all burn types are difficult to decipher.

In this study, a dual-chamber experimental setup was used to perturb biomass burning emissions using three different perturbations: high-NOx photo-oxidation, low-NOx photo-oxidation, and dark ozonolysis. During an experiment, dilute emissions from the same biomass burn were injected into two identical Teflon smog chambers. Each chamber was then subjected to a different perturbation using UV lamps (for photo-oxidation), nitrous acid (HONO, for high-NOx conditions), or ozone. Organic aerosol (OA) mass enhancements were derived for each chamber and used to calculate a dual-chamber enhancement (DUCE), a metric that describes the relative behavior of the emissions in response to different perturbations. In the high-NOx photo-oxidation vs. low-NOx photo-oxidation experiments, the high-NOx chamber showed lower OA mass enhancements in half of the experiments (n=4), regardless of fuel type, suggesting that NOx may play a role in hindering SOA formation in biomass burning emissions. In dark ozonolysis vs. low-NOx photo-oxidation experiments, the emissions subjected to dark ozonolysis showed higher OA mass enhancements in almost all experiments (n=7), suggesting that ozone may play an important role in SOA formation from biomass burning emissions.

4BA.1

Structure and Function of Airborne Bacterial Communities: From Classrooms to Mountaintops. ANN M. WOMACK, James F. Meadow, Dan Jaffe, G.Z. Brown, Brendan J. M. Bohannan, Jessica L. Green, *University of Oregon*

Our understanding of bioaerosol-associated microbial communities is expanding as variation in the structure and diversity of airborne communities among environments and over space and time is beginning to be quantified. However, there remain fundamental knowledge gaps in our understanding of the forces that shape this variation and of the ecological function of these communities. Our group uses targeted high-throughout sequencing methods to elucidate the drivers of diversity and structure in bacterial bioaerosol communities in indoor and outdoor environments. In the built environment, we have applied DNA-based molecular methods to study the relative roles of occupancy, ventilation strategy, and outdoor air communities in shaping the diversity and composition of airborne bacterial communities in a high-traffic university building. Ventilation and outdoor air communities had a significant effect on indoor airborne bacterial community composition; changes in outdoor air communities were detected inside following a time lag associated with differing ventilation strategies. However, this study and others using similar methods have a significant drawback in that DNA-based methods census the entire bacterial community, which includes dead and dormant cells. Surveying the total community without partitioning the active members complicates our ability to make inferences about the function of microbial communities particularly in systems where a large proportion of cells are expected to be dead or dormant. In order to distinguish between the dead/dormant and metabolically active portions of the community, we have developed methods to sample and study bioaerosols using RNA-based methods. We have applied these methods at a high-elevation site to characterize the diversity and composition of metabolically active bacterial communities following long distance transport. Partitioning airborne bacterial diversity into the total community versus the active community will allow us to identify important functional groups and will yield important clues about the function bacterial communities in the atmosphere.

4BA.2

Exploring Bacterial, Fungal, and Viral Diversity in Indoor and Outdoor Air. JOANNE B. EMERSON, Noah Fierer, *University of Colorado Boulder*

Although the prevalence of microorganisms in the atmosphere and their influences on atmospheric processes are beginning to be appreciated, we have a limited understanding of the diversity and abundances of bacteria, fungi, and viruses in indoor and outdoor air. Likewise, we have only just begun to understand the biotic and abiotic factors that regulate the diversity and abundances of these microbes in the atmosphere, both outdoors and within buildings. Our group uses molecular methods (targeted gene sequencing and viral metagenomics) to characterize bacterial, fungal, and viral community composition in air samples from a variety of environments. Sampling sites include the near-surface atmosphere above marine and terrestrial systems, inside and outside family residences, and above the boundary layer (accessed via a 300 m tower and through airplane sampling). We will discuss the integration of microbial DNA sequencing data and abundance estimates with measurements of environmental parameters to assess ecological influences on microbial community composition, dynamics, and biogeography in indoor and outdoor air. Results indicate seasonal patterns in both indoor and outdoor microbial community structure and abundance, along with biogeographic differences in near-surface atmospheric community composition that are driven by changes in source environments.

4BA.3

Indoor and Outdoor Size-Resolved Airborne Microorganism to Particle Number Ratios. DENINA HOSPODSKY, Naomichi Yamamoto, William Nazaroff, Jordan Peccia, *Yale University*

Accumulation of sufficient airborne material for DNA-based species enumeration and identification methods is a reoccurring challenge in field studies that use low volume aerosol samplers. A better understanding of the ratios of microbial aerosols to total aerosols would aid in decision-making on sampler type and sampling times for DNA based downstream bioaerosol analyses. Previously documented mass fractions of biological particles range from less than 1% to 80% depending on location, measured particle size, as well as height and type of measurement, and little consensus exists on the common proportions for indoor and ambient air.

We present number based bacteria to total aerosol particle and fungi to total aerosol particle ratios in indoor and outdoor air in five size bins. These ratios were calculated from optical particle counter (OPC) data and quantitative DNA-based bacteria and fungi estimates on size fractionating particle impactors from ten environments in four countries (U.S., Germany, Denmark, and China). Particle number concentrations in the size range from 0.4 to larger than 10 micrometers were quantified during occupied and vacant scenarios in school classrooms in parallel to fungal and bacterial collection and enumeration on filters of multistage impactors using quantitative PCR targeting universal fungal and bacterial genes. OPC data was converted to time averaged particle number concentrations for comparison purposes. The overall outcomes were fungal cell to particle number as well as bacterial cell to particle number ratios for each size bin.

Results indicate the low abundance of bioaerosols in size bins smaller than 2.5 micrometers and higher microorganism to aerosol particle number ratios in the indoor air of occupied buildings. Ratios increase with increasing particle size. The higher abundance of bacteria in occupied indoor air compared to outdoor air or unoccupied indoor air indicates and confirms indoor sources for bacteria.

4BA.4

Biological Components in PM2.5 in Boulder, Colorado Latino Homes.

LUPITA MONTOYA, Luis Escobedo, Ning Li, *University of Colorado Boulder*

The Environmental Protection Agency has established methods and metrics for qualifying and regulating outdoor air quality; however, indoor air quality (IAQ) has not enjoyed the same level of attention. Indoor levels of many pollutants, however, are often several times higher than those found outdoors. Indoor air pollutants can also concentrate due to poor circulation within a home. Since Americans spend most of their time indoors, understanding IAQ is important in order to protect public health because sustained exposures can result in poor respiratory and cardiovascular health.

This investigation targeted low-income Latino communities in Boulder, Colorado and focused on the indoor air quality of their homes. Participants were administered a survey, which included questions on their health conditions and indoor air pollution sources (e.g., cigarette smoke, combusted fuel used for heat and building materials). In addition, the indoor and outdoor air in each home was sampled for a period of 24 hours using Tactical Air Samplers (MiniVol, Airmetrics, Eugene OR). Air samples were collected onto two different filters (47 mm Teflon and Tissuquartz) to measure the quality of the air. The Teflon filters were analyzed gravimetrically and tested for the presence of endotoxin and proteins in the air. The Tisuquartz were analyzed for elemental and organic carbon, and other biogenic components in the samples collected. Early results indicated that indoor air contained a higher concentration of pollutants than the ambient air. Currently, the study is quantifying the indoor air pollutants and investigating the correlation between health outcomes and indoor air quality.

4BA.5

Wildfire Impact on Indicators of Primary Biological Load and Genotoxic Potential of Airborne Particulate Matter in Pristine Sub-Alpine Forests.

ALINA M. HANDOREAN, Odessa Gomez, Jane Turner, Benjamin J. Miller, Mark T. Hernandez,*University of Colorado Boulder*

Primary biopolymers can contribute to a significant fraction of airborne organic carbon (OC) pools in some atmospheric environments, yet the potential biological activity of these pools remains relatively unknown. In an effort to better characterize organic aerosols as they exist in relatively pristine settings, we monitored and compared the polysaccharides, lipids, and DNA recovered from size segregated particulate matter (PM) during several summer seasons in a sub-alpine forest belt (Colorado, USA) — including a season with a large wildfire. Particulate matter was eluted from filters which continuously collected aerosol during July and/or August of three years between 2008 and 2012. As judged by specific carbohydrate, phospholipid and gene content, airborne PM analyzed for this primary biological load was juxtaposed to relative microbial abundance, as well as the potential to induce genotoxic activity.

Carbohydrate content was measured using a colorimetric assay of monosaccharide phenol conjugates, with glucose as a standard. Phospholipid content was measured using a colorimetric assay of chloroform-methanol extracts subjected to persulfate digestion, and calibrated against a ß-glycerol phosphate standard. Genomic DNA was extracted with ammonium acetate using glycogen as a carrier, and amplified by polymerase chain reaction using universal ribosomal subunit primers for bacteria and fungi. The mass and OC fraction of these biopolymers was significant in most cases (c.a. > 10 %) and presented a conservative index of airborne vegetative detritus and microbial biomass (PMBIO), considering microorganism types. Biopolymer load was relatively consistent across seasons and sites; however, biopolymer contributions were significantly different near the fire site. As judged by SOS induction in Salmonella typhimurium cultures genetically engineered to report genotoxic activity, PM collected in the proximity of a week-long wild fire presented greater genotoxic potential than summer samples collected from nearby pristine forests.

4BA.6

Seasonal Variability in Bacterial and Fungal Diversity of the Near-Surface Atmosphere across Urban and Rural Sites.

ROBERT M. BOWERS, Nicholas Clements, Joanne B. Emerson, Christine Wiedinmyer, Michael Hannigan, Noah Fierer, *University of Hawaii*

Bacteria and fungi are present throughout Earth's lower atmosphere. These airborne microbes are highly diverse and likely originate from a mixture of source environments. Microbial cells in the atmosphere are just beginning to be recognized as an important component of total atmospheric aerosol loads. Given that some airborne microbes may act as direct human pathogens while others likely trigger seasonal allergies and asthma, a better understanding of airborne microbial ecology will help us understand their roles in human health and atmospheric dynamics. To address these knowledge gaps, we performed a comprehensive analysis of airborne microbes across time, space and aerosol size fraction. We characterized total microbial abundances (via flow cytometry) and bacterial and fungal diversity (via high-throughput sequencing) at an urban and rural site in the Colorado Front Range over a one-year time period. Samples were collected at weekly intervals across the coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) aerosol size fractions. Microbial concentrations were on average 1×10^5 cells m^{-3}, showing little variability over time, city or aerosol size fraction. However, microbial community composition was much more dynamic. Fungal 18S rRNA relative abundances peaked in late spring to early summer especially in the coarse size fraction, and bacterial diversity peaked during the late summer, suggesting that a complex set of environmental factors including changes in atmospheric dynamics and available sources influences the composition of airborne microbial communities. To expand on this, we used a bacterial source tracking approach to determine likely sources of bacteria to the atmosphere. We tracked airborne bacteria to leaves and soils throughout most of the year, however cow fecal material was also an important source of airborne bacteria in the Greeley air samples during the fall and spring months. Taken together, airborne microbes are an important yet understudied component in aerosol research that should be integrated into future surveys of the atmosphere.

4BA.7

Characterization of Atmospheric Biological Particles Collected at the Storm Peak Laboratory.

VERA SAMBUROVA, Alison Murray, Anna Gannet Hallar, Lynn Mazzoleni, Douglas Lowenthal, Barbara Zielinska, *Desert Research Institute*

Recent studies have shown that biological particles, which include bacteria, fungal spores, and plant pollen, may represent a significant portion of the organic atmospheric particulate matter. Airborne microbial cells have strong effects on human health and can cause allergic respiratory diseases such as allergenic asthma. In addition to their health effects, bacteria, fungal spores, and plant pollen can influence significantly physical and chemical properties of atmospheric organic aerosols and therefore atmospheric processes. To our knowledge, ambient airborne biological particles have received relatively little attention in atmospheric sciences. Based on our literature research, only a few studies have measured ambient airborne biological species and the results of these studies are limited and vary substantially.

Aerosol samples collected at the Storm Peak Laboratory on Mt. Werner, Steamboat, CO (3210 m AMSL) were extracted, combined into six composites and analyzed for chemical and physical properties with different analytical techniques such as ultrahigh resolution mass spectrometry (formula assignment of individual organic compounds), ion chromatography (quantitative analysis of low molecular weight organic acids), gas chromatography mass spectrometry (quantitative analysis of sugars, sugar alcohols, lignin derivatives, and organic acids), H-NMR (characterization of the main functional groups), etc. In this study, the collected samples have been characterized for biological species. The diversity and relative abundances of ambient atmospheric bioaerosols (e.g. fungal spores, plant pollen, etc.) were analyzed using electron and fluorescence microscopy. In order to identify and specify biological species, including bacteria, fungal spores, and pollen, DNA analysis based on rRNA genes sequencing technique have been used. Finally, comparison of the relative abundance of biological aerosols with individual organic species determined in the collected PM2.5 samples will be presented.

4CA.1

Single Particle Characterization Using a Soot Particle Aerosol Mass Spectrometer (SP-AMS) with a Light Scattering Module in Dowtown Toronto. ALEX K. Y. LEE, Megan D. Willis, Robert Healy, Jonathan Abbatt, *University of Toronto*

Atmospheric black carbon (BC) particles play an important role influencing air quality and radiative forcing on both regional and global scales. However, BC particles can be coated by other aerosol components during their lifetime in the atmosphere, thus introducing a significant modification to their physical and chemical properties. Better understanding of the mixing state of BC and the characteristics of its associated coatings is therefore important. In this study, we demonstrate the use of the Aerodyne soot particle aerosol mass spectrometer (SP-AMS) with a light scattering module to determine the mixing state of BC and non-refractory aerosol components (i.e. organics, ammonium, sulfate and nitrate) in downtown Toronto during September 18-22, 2012 This is the first report of single particle mass spectra of BC-containing particles measured by the SP-AMS. The individual single particle mass spectra clearly show that atmospheric BC can be coated with different types of organics (e.g., hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA)) and inorganic species (e.g., ammonium sulfate). Clustering analysis was performed to categorize a large single particle mass spectral dataset into a few clusters. The K-means algorithm extracts a cluster that is dominated by a BC fragmentation signature and separates the organic aerosol signal into three cluster types, including HOA, OOA, and cooking organic aerosol (COA). By examining the size distribution of each cluster, our results suggest that most of the BC likely coexists with the HOA component. The clustering analysis will also be compared to the results obtained from positive matrix factorization analysis of the ensemble data measured by the SP-AMS.

4CA.2

The SP-AMS Inter-Comparison Campaign. AMEWU A. MENSAH, Joel Corbin, Sanna Saarikoski, Axel Eriksson, Martin Gysel, Raphael Färber, Berko Sierau, Manuel Abegglen, Veronika Hladnik, André Welti, Ulrike Lohmann, *ETH Zurich, Institute for Atmospheric & Climate Science*

Black carbon (BC) has gained increasing attention by the society since the WHO has declared diesel soot as carcinogenic. Up to now, the quantitative measurement as well as the chemical characterization of BC is still a challenging task. Recent instrumental advances allow to evolve a better understanding of soot in general and individual features of different types specifically. Lately, the Aerodyne aerosol mass spectrometer (AMS), an instrument well established in the atmospheric research community, was extended by a 1064 nm laser to allow for the evaporation and mass spectrometric analysis of soot particles (Soot Particle (SP-)AMS).

Here, we present first results of the SP-AMS inter-comparison campaign, which took place 7. - 22.03.2013 at ETH Zurich. Main focus of the campaign was the investigation of the qualitative and quantitative sensitivity of the SP-AMS to different types of soot (Regal Black, propane flame generated CAST brown/black, Palas GFG, fullerene soot a.p., and ambient). Beside the thorough mass spectrometric investigation by three SP-AMS' from Lund University, FMI Helsinki, and ETHZ a whole range of physical parameters were analyzed. A combination of particle mass analyzers (CPMA and APM), single particle soot photometer (SP2), differential mobility analyzer (DMA) and thermodenuder was used to obtain independent measurements of total particulate and BC mass concentrations as well as the mass fraction of non-refractory coatings.

We discuss the mass calibration factor of BC in the SP-AMS, the individual mass spectrometric features of the different soot types, and new insights into the fragmentation pattern of BC. Additionally, we present direct application of our laboratory findings to ambient measurements, which were performed in a street canyon of a heavily trafficked road during that campaign.

4CA.3

Enhanced Light Absorption by Internally Mixed Atmospheric Black Carbon in Europe. SHANG LIU, Allison Aiken, Kyle Gorkowski, Manvendra Dubey, Scott Herndon, Leah Williams, Paola Massoli, Edward Fortner, Andrew Freedman, Douglas Worsnop, Nga Lee Ng, Claudia Mohr, Felipe Lopez-Hilfiker, Joel Thornton, James Allan, Christopher Cappa, *Los Alamos National Lab*

Solar absorption by black carbon (BC) particles from fossil fuel and biomass combustion could be responsible for the second largest radiative forcing after carbon dioxide. Control of the short-lived BC would slow climate warming immediately and improve air quality. BC's large radiative forcing results from model formulation that as BC ages it mixes with other species, a process that enhances its specific light absorption significantly consistent with laboratory studies. However, recent field observations show negligible absorption enhancement calling into question the large role of BC in climate forcing. To address this discrepancy, optical and chemical properties of ambient particles were measured continuously during 15 January to 15 February 2012 at Detling, UK as part of the ClearfLo (Clean Air for London) campaign. A three-laser photoacoustic spectrometer (PASS-3) was used to quantify the absorption and scattering coefficients of submicron particles. By evaporating the volatile components using a thermal denuder that operated that 250 Celsius degree, the absorption enhancement was directly measured. We find significant absorption enhancement (40%) due to the internal mixing by BC and other non-absorbing components, which is in contrast to previous measurements. In addition, the enhancement factor increases with photochemical aging and is consistent with theoretical predictions constrained by the in situ measurements. Furthermore, we find for the first time that the non-volatile, light-absorbing organic (brown) carbon (BrC) accounts for 22% of the absorption at 405 nm wavelength. The non-volatile BrC correlates with the oxygenated organic aerosol factor retrieved from the positive matrix factorization analysis, suggesting its secondary formation in the atmosphere. Our field results support parameterizations of enhanced light absorption by BC in climate models and show that diverse regimes need to be sampled to improve quantification.

4CA.4

Identify Major Oxalate Salts in PM2.5. Shiguo Jia, Liming Yang, LIYA YU, *National University of Singapore*

Oxalate salts are reported as the major component of total oxalates (oxalic acid and oxalate salts) in PM2.5, and can exhibit a concentration >10 times of oxalic acid. Nevertheless, the dominant species among the oxalate salts remain to be identified. This study develops a thermal evolution method to speciate oxalates in PM2.5 as thermal sensitive vs. thermal resistant oxalates. The method coupled with a previously established analytical method is tested with individual oxalate standard compounds, verified with standard mixture oxalate salts, and applied to PM2.5 samples collected in a warm humid tropical atmosphere.

The sampling period was accompanied with ample daily rainfall (up to 23 mm) and an averaged PM2.5 concentration of 17.1±4.8 µg/m3 (n = 8). Results show that ammonium oxalates, which are thermal sensitive, are the most dominant oxalate salt in PM2.5 with a concentration ranging from 148–255 ng/m3. This is 9–18 times of the concentration of oxalic acid, and corresponds to 84–89% of total oxalates. Non-ammonium oxalates which are thermal resistant are responsible for 3–7% of total oxalates in the collected PM2.5 samples, contributing little to the tropical urban atmosphere. The amount of ammonium associating with oxalates ranged from 30–104 ng/m3, corresponding to 3–10% of the total ammonium in PM2.5 collected from the relatively clean atmosphere. This suggests that the amount of ammonium in PM2.5 which is available to neutralize acidic components can be lower than the quantifiable amount.

4CA.5

Hourly Measurement of the Concentration and Gas-Particle Partitioning of Oxygenated Organic Tracers in Ambient Aerosol: First Results from Berkeley, CA and Rural Alabama. GABRIEL ISAACMAN, Nathan Kreisberg, Lindsay Yee, Arthur Chan, David Worton, Susanne Hering, Allen H. Goldstein, *University of California, Berkeley*

Hourly and bi-hourly time-resolved measurements of organic tracer compounds in ambient aerosols have been successfully used to elucidate sources and formation pathways of atmospheric particulate matter. Here we extend the Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SVTAG), a custom in-situ instrument that collects, desorbs, and analyzes ambient aerosol and semi-volatile compounds with hourly time resolution, to include on-line derivatization and a second, parallel collection cell that provides simultaneous collection of both particle-phase and particle-plus-gas-phase organic compounds. By introducing a silylating agent upon desorption, SVTAG can measure highly oxygenated compounds that are not easily detected using traditional gas chromatography including most previously reported oxygenated tracers for biogenic and anthropogenic secondary organic aerosol. The use of a pair of matched collection cells with parallel sampling and serial analysis provides direct gas-particle partitioning information. One cell collects total organic fraction of compounds with a volatility lower than that of approximately a C_{13} hydrocarbon, while the other cell samples through an activated carbon denuder to remove the gas-phase. Taken together these measurements provide a direct measurement of gas-particle partitioning to yield a direct check on classical absorption based partitioning theory while providing insights into important aerosol formation chemistry, such as oligomerization and salt formation. We present here the capabilities of the dual cell SVTAG with derivatization, including tests on ambient Berkeley air and the first results from the Southern Oxidant and Aerosol Study (SOAS). Correlations between oxygenated biogenic and anthropogenic tracers are explored. Tracers that have typically been available only from offline chemical analyses of filters with lower time-resolution (several hours to several days) are accessed using this instrument and presented here, including several tracers for isoprene oxidation under varying chemical regimes, i.e. 2-methyltetrols under low-NO_x conditions, and 2-methyl glyceric acid under high-NO_x conditions. The diurnal variation of tracers such as these elucidates the influence of anthropogenic emissions on biogenic aerosol formation.

4CA.6

A Sensitivity Analysis of Organic Aerosol Retrieved Volatility Distributions to Kinetic Parameters. JAMES HITE, Kate Cerully, Athanasios Nenes, *Georgia Institute of Technology*

Atmospheric secondary organic aerosol (SOA) generated through the partitioning of semi-volatile organics into the condensed phase has both epidemiological and climatic impacts through the growth of particulate matter into relevant sizes for respiratory interactions and cloud condensation nuclei activity. SOA is often described in models by treating it as a mixture of components with differing partitioning coefficients through the volatility basis set (VBS) approach rather than explicitly resolving the complex chemistry (Donahue et al., Env. Sci. Tech., 40, 2635-2643, 2006).

A method of estimating the volatility parameters of monodisperse, single-component aerosol samples through measurements made with a thermodenuder built in-house and operated as part of a volatility tandem differential mobility setup has been developed and shown to produce results comparable to those in the literature (AS&T, in review). A similar approach is employed to interpret the volatilization rates of organic aerosol mixtures of dicarboxylic acids and ammonium sulfate with a kinetic model that resolves the gas to particle partitioning of aerosol, obtaining a condensed-phase volatility distribution using the VBS approach. An iterative optimization routine is utilized to obtain the partitioning coefficients, and different approaches to the volatility distribution retrieval are considered in the analysis. These experiments serve as a test for the optimization procedure as the mixtures are of known chemical composition – a necessary validation step prior to applying this technique to actual complex SOA mixtures.

4CA.7

First Field Measurements of Volatility- and Polarity-Resolved Organic Aerosol Using the Volatility and Polarity Separator (VAPS). RAUL MARTINEZ, Brent Williams, Yaping Zhang, Nathan Kreisberg, Susanne Hering, David Worton, Allen H. Goldstein, Jose-Luis Jimenez, Thorsten Hohaus, John Jayne, Douglas Worsnop, *Washington University in St. Louis*

Discrepancies between modeled and measured atmospheric organic aerosol (OA) have shown the need for in situ instrumentation to better characterize the sources, formation mechanisms, and atmospheric evolution of ambient OA. We have developed the Volatility and Polarity Separator (VAPS) for hourly measurements of volatility- and polarity-resolved OA detected using high-resolution time-of-flight mass spectrometry (HR-ToFMS). Here, atmospheric OA is inertially impacted for a half hour, thermally desorbed into an oven for volatility separation, thermally pulsed through a short polar GC column for polarity separation, and finally detected by HR-ToFMS. This novel instrument increases the mass throughput of ambient OA in comparison to traditional GC due to shorter transfer paths and passivated coatings. Molecular separation resolution is sacrificed for this increased mass transfer, but the high-resolution mass spectral data recovers information such as elemental composition to determine aerosol oxidation state.

Here we report on laboratory testing and the first field deployment of the VAPS system. Preliminary results of volatility- and polarity-resolved OA measured from the surface site in Centreville, AL during the Southern Oxidant and Aerosol Study (SOAS) will be presented. VAPS data is explored to provide new insight into the underlying chemistry and chemical evolution of anthropogenically influenced biogenic SOA.

4CC.1

The Influence of Molecular Structure and Photochemical Aging on Organic Films Coating Microscopic Aqueous Droplets.CHRIS RUEHL, Kevin Wilson, *Lawrence Berkeley National Laboratory*

Although the surface activity of many atmospheric samples of particulate and dissolved organic matter has been well documented, the importance of surface activity in the prediction of cloud condensation nuclei (CCN) activity is still debated. We measured the CCN activity and high-RH (>99%) growth factors of both single-component organic particles and secondary organic aerosol (SOA) generated from either alpha-pinene or squalane. The partitioning of organic matter (OM) to the droplet surface is modeled in one of two ways: either as a “soluble” surfactant, in which OM exists in equilibrium between the surface and bulk phases as described by the Szyszkowski equation, or as an “insoluble” surfactant which exists almost completely in a film whose surface pressure depends on molecular area. In the latter case, droplet surface tension is insensitive to bulk concentration and therefore depends primarily on droplet surface area, while in the former case it depends on bulk surfactant concentration (i.e., droplet volume). The CCN activity of photo-oxidized squalane particles was best predicted when reduced surface tension was taken into account, equally well assuming the OM was soluble or insoluble surfactant; however, the scale bulk concentration in the Szyszkowski equation had to be reduced by several orders of magnitude to account for depletion in the bulk phase of microscopic droplets. The high-RH growth factors of individual compounds and alpha-pinene secondary organic aerosol, on the other hand, could only be modeled well as insoluble surfactants. For individual compounds, the film had properties similar to macroscopic observations of the same compounds, although no evidence for monolayer collapse was seen. For particles generated by ozonolysis of alpha-pinene, the modeled film thickness was 0.8 +/- 0.1 nm. When these particles were further photo-oxidized, modeled film thickness (i.e., surface concentration) decreased to ~0.5 nm.

4CC.2

Hygroscopic Growth of Super-micron Particles in the Coastal Marine Atmosphere. XIAOLU ZHANG, Christopher Cappa, Paola Massoli, Patricia Quinn, Timothy Bates, *University of California, Davis*

Aerosol hygroscopicity is a key factor in determining the direct aerosol radiative forcing of Earth's climate, as much of the aerosol light scattering is attributable to water uptake by aerosols at high RH. Here we investigate the hygroscopic growth of aerosols in the marine atmosphere using optical measurements made during the TexAQS-GoMACCCS in 2006. Bulk sub-saturated growth factors (GF) for both sub- and super-micron aerosols were derived from light extinction coefficients at 532 nm under dry and elevated RHs measured with a cavity ring-down aerosol extinction spectrometer. The calculated growth factors at 85% RH for sub- and super-micron aerosols were averaged at 1.58(±0.14) and 1.71(±0.18), respectively. Variability in super-micron GFs (GFsup) during the campaign appeared to be driven by changes in the chemical composition of super-micron aerosols. Sea-salt and dust are the dominant components, together accounting for 78% on average of the dry super-micron aerosol mass. GFsup was well correlated with the volume fraction of sea-salt aerosols for most of the study, with the exception of when substantial contribution from organics was observed. Two types of dust with distinct hygroscopicities were identified based on their sources and composition. The dust aerosols that originated from North Africa were somewhat hygroscopic, with an average GF of ~1.34, whereas dust from local sources was less hygroscopic, with an average GF ~1.0. A hygroscopic closure calculation based on a volume-weighted mixing rule was performed using literature documented GFs for the non-dust inorganic components and GFs for the two dust types determined in this study. Minimization of the difference between observed and predicted GFs indicated a campaign-averaged GF of 1.59 at 85% RH for the super-micron organics, suggesting super-micron organics may be largely different from sub-micron organics in terms of hygroscopicity. This study provides new insights on hygroscopicity of super-micron aerosols in the marine atmosphere.

4CC.3

Aerosol Optical Hygroscopicity Measurements during the 2010 CARES Campaign. Dean Atkinson, James Radney, JANELL LUM, Christopher Cappa, Katheryn Kolesar, Daniel Cziczo, Mikhail Pekour, Qi Zhang, Ari Setyan, Chen Song, *Portland State University*

Optical hygroscopicity (the variation in aerosol extinction or scattering with relative humidity) was measured during the 2010 Carbonaceous Aerosols and Radiative Effects Study, CARES. CARES was designed to gather information on aerosol changes during transport; specifically, urban aerosols as they were transported over rural and forested areas with extensive biogenic emissions. Changes in aerosol hygroscopicity, size and composition during atmospheric transport is a major emphasis of current experimental and modeling research. Hygroscopicity is an important property because water uptake changes particle size increasing light scattering (and perhaps absorption depending on particle morphology). This increases the particle's single-scattering albedo leading to more negative radiative forcing. Increases in hygroscopicity also may change the particle from solid to a water droplet, increasing the potential transformations to include aqueous phase reactions. The distinctly different hygroscopic behavior of salts versus organics and of supermicron (defined here as particles over 800 nm in mobility diameter Dp) and submicron (Dp < 800 nm) particles were incorporated into a model of the extinction or scattering change with relative humidity (RH). The model used measured size distributions and composition and the kappa formalism for hygroscopic growth.

An expectation was that the organic loading on particles would increase during transport. The goal of this poster is to present a model for particle extinction and scattering values for both low and high-RH aerosols that achieved optical hygroscopic closure for the CARES data. It also provides values for the hygroscopicity of the oxidized organic aerosol component characterized by the Aerosol Mass Spectrometer. Evolution in particle composition and hygroscopicity can allow better understanding of particle changes in urban to rural transport. This understanding may help in producing parameterizations of optical hygroscopicity for regional and global climate models.

4CC.4

Contribution of Biomass Burning to CCN Number and Hygroscopicity during Summertime in the Eastern Mediterranean.AIKATERINI BOUGIATIOTI, Spyros Bezantakos, Iasonas Stavroulas, George Biskos, Nikolaos Mihalopoulos, Athanasios Nenes,*Georgia Institute of Technology*

Biomass burning-influenced air masses and associated aerosol particles from wildfires on the Greek islands of Chios, Euboea and Andros, as well as at the Dalmatian Coast in Croatia and southern Bosnia-Herzegovina, were studied during late summer 2012 at the remote background site of Finokalia on Crete. The plumes traveled several hundreds kilometers, mostly during night-time, before arriving at the measurement station and physicochemical properties were studied using an Aerosol Chemical Speciation Monitor (ACSM), a 7-wavelength aethalometer and a Scanning Mobility Particle Sizer (SMPS). The origin of the air masses was confirmed by back-trajectory analysis, enhanced black carbon concentrations and m/z 60 and 73 mass fragments present in spectra derived from the ACSM. Positive Matrix Factorization (PMF) analysis of the ACSM spectra indicate a strong biomass burning influence, while most (~80%) of the organic mass consists of “aged”, oxidized organic aerosol, divided between two separate factors (semi-volatile organic aerosol, SVOA and low volatility organic aerosol, LVOA).

The CCN activity of the biomass burning-influenced aerosol was studied using a Continuous-Flow Streamwise Thermal-Gradient Cloud Condensation Nuclei Counter (CCNC), operated in Scanning-Flow CCN Analysis mode. The flow rate through the CCNC column varied in a controlled manner, while maintaining a constant streamwise temperature difference and pressure. This results in high time-resolution measurements of CCN spectra, which are critical for determining the size-resolved hygroscopicity of individual biomass burning plumes that are transported to the sampling site. The diurnal variability of the aerosol hygroscopicity parameter determined by the CCNC measurements is contrasted against subsaturated hygroscopicity measurements by a concurrent Hygroscopic Tandem DMA. The results of this study provide valuable insights into the chemical and physical aging of smoke emissions in the atmosphere.

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4CC.5

Quantifying Water Diffusion in High-viscosity Atmospheric Aerosol Proxies. HANNAH PRICE, Benjamin Murray, Johan Mattsson, Daniel O'Sullivan, Theodore Wilson, Kelly Baustian, *University of Leeds*

Some secondary organic aerosol (SOA) have been shown to be highly viscous under atmospheric conditions. These semi-solid/solid amorphous particles may equilibrate with the surrounding gas phase on very long timescales. This could have important consequences for understanding SOA growth, heterogeneous chemistry, water uptake and role as ice nuclei.

The timescales on which high-viscosity aerosol particles interact with gas species can be quantified if the diffusion coefficients of relevant gas species within aerosol particles are known. Previously, diffusion coefficients have been estimated from viscosity measurements using the Stokes-Einstein equation. However, this is not valid at high viscosity, with mobilities of different species diverging as diffusion slows. It is therefore more relevant to directly measure the diffusion coefficient.

In this work, diffusion coefficients of D_2O in highly supersaturated aqueous solutions were measured using a Raman spectrometer. Disks of atmospheric SOA surrogates, e.g. sucrose and levoglucosan, were first allowed to equilibrate in gas with controlled H_2O partial pressure. H_2O vapor was replaced with D_2O vapor of the same dewpoint and Raman spectroscopic information allowed us to fit an analytical solution of Fick’s second law to determine the diffusion coefficient. Results covering six orders of magnitude are reported, which compare well with literature data across the humidity range.

The results suggest that 150 nm semi-solid atmospheric aerosol particles equilibrate over milliseconds, whilst just below the glass transition the half lives for equilibration are on the order of seconds. Previously, a viscosity consistent with the glassy state has been assumed to indicate very long equilibration times. This work suggests this may not be the case: for the long timescales typically assumed to exist in amorphous solid aerosol, conditions must be deep into the glassy regime; simply identifying whether a particle is above or below its glass transition is insufficient if timescales are to be inferred.

4CC.6

Understanding and Constraining Global Secondary Organic Aerosol Amount and Size-Resolved Condensational Behavior.STEPHEN D'ANDREA, Silja Häkkinen, Daniel Westervelt, Chongai Kuang, Ezra Levin, Richard Leaitch, Dominick Spracklen, Ilona Riipinen, Jeffrey Pierce, *Dalhousie University*

Secondary organic aerosols (SOA) are major contributors to ultrafine particle growth to climatically relevant sizes in the continental boundary layer (BL). Many models treat SOA solely as semivolatile, which leads to condensation of SOA onto the aerosol mass distribution. However, closure studies with field measurements show that a significant fraction of SOA condenses to the aerosol surface area suggesting that the organics have very low volatilities. Additionally, many global models contain only biogenic sources of SOA (emissions generally 10-30 Tg yr^{-1}), but recent studies have shown that an additional source of SOA around 100 Tg yr^{-1} (correlated with anthropogenic CO emissions) may be required to match measurements. Recent studies on sub-20nm particle growth also show the importance of including a size-dependent growth rate parameterization (GRP) to match measurements. We explore the significance of these findings using GEOS-Chem-TOMAS global aerosol microphysics model and observations of aerosol size distributions around the globe. The change in the concentration of particles of size $D_p > 80$ nm (N80) within the BL assuming surface area condensation compared to mass distribution condensation yielded a global increase of 9% but exceeded 50% in biogenically active regions. The change in N80 within the BL with the inclusion of the additional SOA compared to the base simulation (19 Tg yr^{-1}) both using surface area condensation yielded a global increase of 30%, but exceeded 100% in regions with large CO emissions. The inclusion of two different GRP in the additional SOA case both yielded a global increase in N80 of <1%, however exceeded 5% in some cases. These model simulations were compared to measured data obtained from diverse locations around the globe and the results confirmed a decrease in the model-measurement bias when surface-area condensation and the extra SOA were used.

4CC.7

Sub-grid Aging: When is the Internal Mixture Assumption Good Enough? LAURA FIERCE, Nicole Riemer, Tami Bond, *University of Illinois at Urbana-Champaign*

The characteristics of emitted particles change by condensation of secondary aerosol and coagulation with other particles, processes known collectively as aging. In many cases, aerosol properties evolve rapidly near the emission source, at spatial scales much smaller than global model boxes. This is largely due to conditions near emission being very different compared to the average over a global grid cell. Therefore, sub-grid processes must be included in global simulations to adequately represent the evolution of particle characteristics.

In this work, we introduce an aging routine that accounts for sub-grid aerosol dynamics in emission inventories, based on results from the particle-resolved model PartMC-MOSAIC. To obtain this aging routine, we simulated the evolution of black carbon emissions in a set of nearly 300 plume scenarios and identified the environmental parameters that most influence aging rates. Condensational aging depends on the flux and hygroscopicity of secondary aerosol, and coagulation aging depends on the number concentration and size-distribution of pre-existing particles. These parameters are used as inputs to the aging routine, along with the size distribution and composition of fresh aerosol emissions. The aging routine returns the size distribution and composition of modified emissions, accounting for sub-grid changes in particle hygroscopic properties by condensation and loss in particle number by coagulation.

4CH.1

Behavior of Fibrous Filter Media Loaded with Agglomerate Particles. QISHENG OU, David Y. H. Pui, Da-Ren Chen,*Washington University in St. Louis*

Filtration is considered as the most economical control technique to effectively remove airborne particles. Many studies have been performed and published to investigate the filtration behavior of filter media under the particle loading. Most of these studies assume that particles under investigation are spherical in shape. In real world, agglomerate particles are often encountered, especially for those generated from combustion sources. It is believed that the particle morphology is one of the factors that may influence the behavior of particle filtration. Fundamental investigation on the filtration of agglomerate particles is however limited in the literature.

The behavior of fibrous filter media loaded with agglomerate particles, especially in the depth and transition phases, was investigated in this study. Based on the existed model proposed by Thomas and his co-workers for spherical particle loading, a revised model was proposed to estimate the filter loading behavior for agglomerate particles, providing the better prediction in penetration evolution in the loading process. By introducing the equivalent interception length of agglomerate particles into the proposed model, the depth and transition loading behavior of filters for agglomerate particles can be better predicted. The newly proposed model was further verified by the loading experiments on three fiberglass filter media. Testing agglomerate particles with the fractal dimension of ~1.8 and ~1.0 were produced by a diffusion burner via the use of different precursors. The time evolution of both pressure drop and particle penetration efficiency was measured during the loading process. Reasonably good agreement was found between the model calculation and the experimental data. The detail of this work will be presented in this talk.

4CH.2

Collection Performance of Nanofiber Filters. YOSHIO OTANI, Hiroaki Matsuhashi, Yoshikazu Mizutori, Takafumi Seto,*Kanazawa University*

Nanofiber filters are of great interest for application to air cleaning because they are believed to have a high collection efficiency and a low pressure drop. In the present work, the pressure drop and collection efficiency of nanofiber filters were predicted based on the conventional filtration theory and the determination of pressure drop and collection efficiency were performed. Furthermore we also measured the pressure drop and collection efficiency of microfiber filters at reduced pressures. As a result, we found that the collection efficiency of 20-nm particles becomes higher because of an increase in interceptional effect due to slip flow. For nanofiber filters, we were not able to show the effect of slip flow because of the filter inhomogeneity and extremely high collection efficiency.

4CH.3

Numerical Modeling of the Influence of Nanofibers Covering the Fibrous Filter Surface on the Filtration Cake Removal Efficiency. JAKUB GAC, Leon Gradoń, *Warsaw University of Technology*

The filtration of aerosols using the fibrous filters is very important process from the point of view of the environmental and health protection problems. One of the main features of the filters behavior for aerosol particles removal is its lifetime. This time is limited by the filtration cake formation on the surface of the filter, what results with the filter blocking. For this reason the efficient methods of removal of the cake is extensively investigated in both experimental and theoretical works.

In our present work we use the discrete element method for the numerical modeling of the filtration cake formation and its removal from the fibrous filter. We consider the case where the microfibrous structure of the filter is covered with the monolayer of nanofibers. Two techniques of filtration cake removal are applied: the shaking of a filter and the cleaning gas flow in the direction tangent to the filter surface. For both of these methods we compute the efficiency of cake removal at the absence as well as at the presence of nanofiber layers. We observe that at the presence of nanofibers the filtration cake is less adhesive and thus the efficiency of its removal (with both of two removal techniques considered) is higher than at the absence of nanofiber layer. We also investigate the influence of nanofibers diameter and the mean distances between nanofibers on the efficiency of cake removal, what allows us to design the optimal nanofiber cover of the filter.

4CH.4

Determination of the Single Fiber Collection Efficiency for Fibrous Filters through Mean First Passage Time Analysis.BENJAMIN HUNT, Thaseem Thajudeen, Christopher Hogan Jr., *University of Minnesota*

We propose and present a new method of determining the single fiber efficiency for the fibrous filtration of arbitrarily-shaped particles. Specifically, this method utilizes mean first passage time calculations for determination of the collision rate between nanoparticles and a filter fiber, and through these calculations a relation between the collision rate and single fiber efficiency is derived. In addition to demonstrating this new method of single fiber efficiency calculation, there are a number of advantages to this approach and new insights into filtration that can be found. First, single fiber collection efficiency calculations require integration of the efficiencies for individual streamlines. Collision rate calculations, on the contrary, can be performed in the absence of flow and in the zero-flow continuum limit have a known solution. By comparison to this solution, it becomes apparent that many single fiber collection efficiency equations do not have the correct scaling with the Peclet number, Pe, as Pe approaches zero. Second, with the use of dimensionless calculations, the dimensionless collision rate/efficiency can be determined as functions of dimensionless numbers that also describe the equations of motion for the particles. This enables determination via regression of a single function describing the rate/efficiency accounting for the effects of diffusion, interception, and filter solidity together, mitigating the need to assume additivity or to incorporate interaction terms. Finally, we show that with a properly defined length scale for nonspherical entities, the resulting collision rate and single fiber collection efficiency equations can be extended to particles of arbitrary shape, including fibers and agglomerates.

4CH.5

On the Electrical Properties of Carbon Sorbents and Their Impact on Electro-Hydrodynamic Phenomena within Utility ESPs: Numerical Simulation and Field Data. HEREK CLACK, *University of Michigan*

Powdered activated carbon (PAC) injection upstream of an electrostatic precipitator (ESP) has emerged as a leading technology capable of reaching the 90% target for reducing mercury emissions mandated in 2012 by the U.S. EPA’s Mercury and Air Toxics Standard. However, in previous studies we have measured and reconfirmed that the electrical resistivity of PAC falls well below the accepted range for optimal ESP removal efficiency, and the addition of PAC to fly ash significantly lowers the bulk electrical resistivity of the mixture. Further, our previous analyses estimated that the lower removal efficiency for PAC could increase particulate carbon emissions from ESPs by more than 100%. The present study offers fundamental details of the internal gas-particle dynamics of ESPs that govern particle collection, mercury adsorption, and undesirable particulate carbon emissions associated with PAC injection. Using a multi-physics computational software suite to solve the coupled set of fluid dynamic and charged particle transport equations that govern the electro-hydrodynamic (EHD) fluid-particle phenomena within ESPs, the computed solutions provide insight into how these EHD-driven phenomena vary as a result of the addition of PAC to the suspended fly ash and the resulting change in electrical properties of the bulk particulate matter. Performance trends that are extracted from these computed solutions are compared against particulate samples collected from the hoppers of a full-scale utility ESP during PAC injection that have been analyzed for both their mercury and carbon content. The comparison provides a full-scale validation of a computational model of combined fly ash and PAC EHD and adsorptive behavior within ESPs, contributing to improved ESP performance in the simultaneous control of both mercury and PM.

4CH.6

Performance of Electrostatic Battery for Emissions Control (ESBEC) when Challenged with Diesel Emissions. TAEWON HAN, Huajun Zhen, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

We recently developed a novel diesel emissions control device, Electrostatic Screen Battery for Emissions Control (ESBEC), where exhaust particles are removed using an electrostatic mechanism. Unlike traditional diesel particulate filters (DPFs), this device features high particle collection efficiency without contributing to exhaust backpressure and there is no need for thermal regeneration of collected particles. As part of the continuing development of this technology, the 3rd generation ESBEC was fabricated using 3D printing, where a cylinder-shaped housing integrates a charger and collector. A carbon fiber brush is positioned perpendicular to the direction of the air flow and ions are produced once high voltage is applied between the brush and a grounded screen. The collector of 1.5 inches in diameter consists of two half-cylinders holding several sets of screens. One screen of each set is supplied with high voltage opposite to the sign of the charger and the other is grounded, producing an electrostatic field across the screens.

This optimized and improved version showed high collection efficiency of ~87% for 0.2 micro-meter fluorescent polystyrene latex particles when 10kV were applied to the charger and 12kV to the collector. As a next step in the development of this diesel control device, ESBEC was built with seven sets of screens and challenged with diesel exhaust of concentrations varying from 5 to 120 mg/m^3 and flow rates of ~103 L/min. ESBEC removed about 82 - 94% of diesel exhaust particle mass entering the battery. During 6 hours of continuous operation, the collection efficiency of ESBEC did not decrease and its pressure drop increased only minimally. Particle deposition across the screen was also relatively uniform. In the next tests, ESBEC will be scaled-up to 6 inches in diameter and its performance compared with a conventional DPF during long term operation.

4CH.7

Electrostatic Lunar Dust Collection. NIMA AFSHAR-MOHAJER, Chang-Yu Wu, Nicoleta Sorloacia-Hickman, *University of Florida*

Levitation and consecutive deposition of the naturally charged particles on the lunar surface were troublesome in previous NASA exploration. Protecting sensitive surfaces from dust deposition in the limiting condition of the lunar atmosphere is imperative for future space exploration. Earlier theoretical and numerical models demonstrated that an electrostatic lunar dust collector (ELDC) is a highly efficient way of particle collection in the vacuum.

In this study, the collection efficiency of an ELDC is investigated experimentally. The experiments were conducted inside a sealed cylindrical chamber connected to the rotary vane vacuum pump (10^-6 torr). A dual-purpose particle charger/dropper was designed and installed on the chamber wall to tribocharge a certain amount of previously sieved 20-µm-sized lunar dust simulants, JSC-1A and Chenobi. The particle charger was remotely controlled by an electric circuit to stop rotating and to start dropping the simulants. The adequate times for saturatedly charging the samples were determined before the ELDC-involved experiments. Connected to a KEITHLEY 6514 electrometer working in nC charge range, a Faraday cup was placed in the bottom of the chamber, and the ELDC stood on top of the Faraday cup. The difference between terrestrial and lunar gravitational acceleration was taken into account by modifying the ELDC dimensions and distances. Each experiment was performed with the ELDC turned off or on. The ELDC collection efficiency was defined based on the difference between the measured total charges of the delivered particles inside the Faraday cup for each paired condition over the total charge in the absence of the ELDC. The obtained results and findings will be presented in the conference.

Keywords: Lunar dust, Particle collection, Electrostatic field

4HA.1

Relationship between the Redox Cycling Activity and Chemical Properties of Oxidized Soot Particles. MARIA ANTIÑOLO, Megan D. Willis, Shouming Zhou, Jonathan Abbatt, *University of Toronto*

The formation of carbon containing particles in combustion processes has been widely studied, and it is believed that such soot particles have toxic health effects. However, the reactivity of these particles with different tropospheric oxidants remains unclear, including how these aging processes can drive health effects. Oxidative stress is one of the major mechanisms thought to induce the toxicological effects of the particulate matter (PM). In these redox-cycling reactions, a catalyst such as quinones or transition metals is reduced whereas reducing agents within the cell are consumed. The catalyst is then reoxidized by reducing oxygen to Reactive Oxygen Species (ROS), allowing the cycle to repeat. To assess the capability of a species to be a catalyst in this cycle, the dithiothreitol (DTT) assay has been widely used.

In this work, soot was obtained from a propane-air diffusion flame. Different measurements were performed on untreated soot and soot exposed to ozone. In particular, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used to observe changes in chemical composition of the surface of soot collected on a filter. Other experiments were done in an atmospheric simulation chamber, where a Scanning Mobility Particle Sizer (SMPS) allowed monitoring the physical properties of the soot, and the chemical properties of the particles were observed with a Soot Particle Aerosol Mass Spectrometer (SP AMS). The DTT assay was performed with oxidized and non-oxidized soot collected from the DRIFTS cell and from the chamber to evaluate the effect of ozone oxidation on the redox cycling activity of the carbonaceous particles.

4HA.2

Chemical Characterization and Toxicological Properties of PM2.5 Emissions from Commercial Cooking. POORNIMA DIXIT, Nicholas Gysel, David R. Cocker III, Georgios Karavalakis, Arthur K. Cho, Debra A. Schmitz, *University of California, Riverside*

Restaurants, kitchens, grills and other sources of cooking, charbroiling, and high temperature frying are sources of fine and ultrafine particles, organic aerosols, volatile organic compounds that make significant contributions to urban air pollution (Schauer et al., 1999; Kabir and Kim, 2011). It is a well-established fact that exposure to particulate matter (PM) with aerodynamic diameter of less than 2.5 micrometer has been associated with increases in pulmonary/cardiovascular morbidity and mortality. In addition, PM emissions from cooking are expected to surpass heavy-duty trucks and off-road vehicles in the South Coast Basin by 2014. Therefore, it is important to understand the chemical and toxicological characteristics of emissions from commercial cooking.

Cooking emissions have relatively high rates of organic mass which include several PAHs (polycyclic aromatic hydrocarbons), nitro-PAHs, organic acids, and quinones. The PAHs and nitro-PAHs are known for their mutagenic and carcinogenic effects, while the quinones are highly reactive derivatives of PAHs that are capable of catalyzing redox cycling reactions and forming covalent bonds with tissue nucleophiles. These organic compounds were collected using 47 mm Teflon filters, during real-time meat cooking using standard cooking methods, and subsequently characterized using a GC-MS. The toxicological properties, which include the chemical reactivity of these organic species, were determined using the DTT (dithiothreitol) and GAPDH (glyceraldehyde-3-phospahet dehydrogenase) assays. The results from these assays provide a direct link to the adverse health effects associated with emissions from cooking operations and ultimately urban air pollution. The chemical composition of cooking originated particles, and their redox and electrophilic properties will be discussed.

4HA.3

Use of a Comprehensive Suite for the Toxicological Analysis of Airborne Particulate Matter. JANE TURNER, Kevin McCabe, Alina M. Handorean, Mark T. Hernandez, *University of Colorado at Boulder*

Epidemiological studies have provided compelling statistical evidence for associations between airborne particulate matter (PM) exposure and negative health effects. Additionally, numerous toxicological studies have demonstrated that beyond certain thresholds, airborne PM has the potential to introduce DNA damage, cytotoxicity and oxidative stress. Recent toxicological research on PM focuses on singular biomarkers, generalizing cellular damage pathways to solitary mechanisms. There is a need for the development of broader screening approaches which are capable of quickly and comprehensively describing the conglomerate of biological activity that PM may carry. In response to this paucity, a suite of toxicological assays, which utilizes flow cytometry for quantification, has been adapted to assess the major toxicological modes associated with airborne PM. The assay panel employs human cell lines (lung epithelial and phagocytic monocytes) and addresses the following classes of fundamental cellular responses previously linked with PM exposure: necrotic and apoptotic cytotoxicity, genotoxicity and oxidative stress. These assays are relatively rapid, and can indicate the potential of individual toxicity mechanisms, as well as provide for the analysis of combined biological effects. In order to demonstrate the capabilities of this suite, human cell lines were challenged with well-characterized diesel exhaust particles (DEP). Preliminary results demonstrate DEP induced cyto- and genotoxicity via induction of necrosis, apoptosis and interruption of cell cycling when thresholds were exceeded. This platform can now be utilized to elucidate mechanisms driving synergistic effects between DEP and model bioaerosols.

4HA.4

Contrasting Profiles of the Oxidative Properties of Ambient Aerosols Collected from Urban and Rural Environments in Atlanta. VISHAL VERMA, Ting Fang, Rodney Weber, *Georgia Institute of Technology*

In recent years, numerous studies have been conducted to trace the oxidative properties of ambient particulate matter (PM) from their specific components. Many of these studies were focused in typical urban environments where the atmospheric PM is heavily dominated by primary vehicular emissions and their secondary reaction products. The chemical properties of ambient particles can dramatically vary depending upon their sources and meteorology in a particular environment such as rural and near-road site. The variations in the chemical composition of ambient aerosols lead to their dissimilar oxidative properties and the subsequent health effects.
As part of our SCAPE center (Southeastern Center for Air Pollution & Epidemiology), we aim to measure the oxidative potential of ambient aerosols in different environmental settings ranging from urban background to rural environment. Here we present the contrast in the oxidative potential of ambient particles collected from two characteristically different sites in Atlanta – Jefferson street which is characterized as an urban background site, and Yorkville which represents a typical rural environment. Ambient fine particles (Dp< 2.5 micro-meter) were collected at both sites on the quartz filters (23 hours integrated samples, N = 32 for each site) using a high-volume sampler (Thermo Anderson) in summer (June-July) 2012, and the particles were extracted in deionized water. Oxidative potential of the extracted water-soluble particles was measured by the dithiothreitol (DTT) assay. To better understand the sources of PM oxidative potential, hydrophobic compounds from the PM extracts were removed using a C-18 column and the remaining hydrophilic fraction was also analyzed for DTT assay. Preliminary results show that there is significant variability both at the spatial and temporal scales in the oxidative potential of ambient particles. The DTT activity was unsymmetrically partitioned in the hydrophobic and hydrophilic components for different samples; however, the average contribution of hydrophobic compounds was significantly higher in Yorkville (56±17 %) compared to Jefferson street (44±21 %). Chemical analyses of these samples are underway but these findings indicate that PM components governing the aerosol oxidative potential at two sites have different chemical signatures, some of which could potentially be revealed by their sequential extraction in a series of non-polar solvents such as hexane, dichloromethane, and methanol. The sources of these differential profiles of oxidative potential in relation to their specific driving components would be further explored by extending this comparison to different seasons and sites in Atlanta.

4HA.5

A Comprehensive Study on the Composition and the Biological/Health Effects of Combustion-Derived Aerosols: First Results of the Virtual Helmholtz Institute HICE on Ship Diesel Aerosols. RALF ZIMMERMANN, Gunnar Dittmar, Jeroen Buters, Hanns Paur, Carsten Weiss, Horst Harnsdorf, Jorms Jokiniemi, Thorsten Streibel, Olli Sippula, Karsten Hiller, et al., *Helmholtz Zentrum München and Rostock University*

The Virtual Helmholtz Institute-HICE address-es health effects of anthropogenic combustion emissions. This is performed by comprehensive chemical/physical characterization of combustion aerosols and studying of biological effects on human lung cell-cultures. A new ALI air-liquid-interface (ALI) exposition system and a mobile S2-biological laboratory were developed for the HICE-measurements. Human alveolar basal epithelial cells (A549 etc.) are ALI-exposed to fresh, diluted (1:10-1:100) combustion aerosols and subsequently were toxicologically and molecular-biologically characterized (transcriptomics, proteomics and metabolomics). By using stable isotope label-ling technologies (13C-Glucose/metabolomics; 2H-Lysine/SILAC-proteomics), high sensitivity and accuracy for detection of molecular-biological effects is achievable even at sub-toxic effect dose levels. Aerosols from wood combustion and ship diesel engine (heavy/light fuel oil) have been already investigated. The effect of wood combustion and ship diesel PM e.g. on the protein expression of ALI-exposed A549 cells was compared. Filtered aerosol is used as gas-reference for the isotope labelling based method (SILAC). Therefore the effects of wood combustion- and shipping diesel-PM can be directly compared. Ship diesel aerosol causes a broader distribution in the observed fold changes (log2), i.e. more proteins are significantly up- or down-regulated in case of shipping diesel PM-exposure. This corresponds to a stronger biological reaction if compared to wood combustion-PM exposure. The chemical analysis results on wood combustion- and ship diesel-PM depict more polycyclic aromatic hy-drocarbons (PAH)/oxidized-PAH but less of some transition metals (V,Fe) in the wood combustion case. Interestingly, alkylated PAH are more abundant in shipping PM, suggesting that PAH/Oxy-PAH may be less relevant for observed acute-toxic effects. The influence of transition metals and alkylated PAH needs to be further investigated. The differential biolog-ical effects of LFO- and HFO-ship emissions were investigated as well, resulting in HFO-PM showing considerably higher toxic- and biological-effects. Further results will be dis-cussed in the contribution. This work/HICE (www.hice-vi.eu) is supported by the Helmholtz Association (HGF).

4HA.6

Non-Symmetrical pMDI Aerosol Deposition on a Spacer.

ELIZABETH SPRIGGE, Sandra Fiset, Edgar Matida, *Carleton University*

Spacer devices are used alongside pressurized metered dose inhalers (pMDIs) to assist in the delivery of beta-2 agonist medication to the lungs. A number of volumes are available, all of which are proven to increase the efficacy of the pMDI, as well as reducing the amount of medication deposited in the oropharyngeal and oropharynx regions. It has been found that medication is lost in the spacer device itself.

In this study, a large volume (750 ml) spacer device has been tested to determine the areas at which the most deposition of medication (Salbutamol) occurs. By considering the spacer in four quarters, UV spectrophotometry has been used to calculate the concentration (and hence amount) of deposition in each area as well as the amount of medication released to the patient and that which is lost in the actuator. Inhalation for five different flow rates (7.5, 15, 30, 45, and 60 L/min) was simulated using a vacuum pump.

Simulations have been performed with ANSYS CFX to further study the deposition occurring within the spacer. Using unsteady Reynolds averaged Navier-Stokes (URANS) equations; flow through a simplified model of the spacer has been recreated to further study effects of deposition.

Results reinforce previous literature suggesting that the spray angle of the actuator is downwards, as a greater amount of deposition occurs on the lower half of the spacer, and also suggest that the amount of medication that will reach the patient increases with increasing inspiratory flow rate. Both experimental and numerical results indicate that inertial impaction, rather than turbulence, will affect the deposition within the spacer.

4HA.7

Deposition of Carbon Nanotubes in the Human Respiratory Tract.

WEI-CHUNG SU, Yung-Sung Cheng, *Lovelace Respiratory Research Institute*

Carbon nanotubes (CNTs) have been used in a variety of commercial applications because of their unique physical properties. CNT materials might become airborne in the workplace or laboratory during the manufacturing and handing processes. Animal studies have shown that inhalation of the CNT aerosols may lead to adverse pulmonary effects. Therefore, from the viewpoint of occupational health, it is important to obtain associated deposition data of CNT in the human respiratory tract in order to well assess the risk of exposure to CNT aerosols in related workplaces. To achieve this goal, a series of CNTs lung deposition experiments were conducted in our lab using a realistic human respiratory tract replica with various CNT aerosols. The CNT materials employed in the study were Staked-cup CNT, Single-walled CNT, and Multi-walled CNT. These CNT materials were aerosolized either by a nebulizer-based wet method or by a vortex mixer-based dry method. The deposition experiments were conducted by delivering DMA classified CNT aerosols (dB = 50, 100, and 200 nm) into the human airway replica, and then use a SMPS to indirectly measure the deposition of the CNT aerosols in the airway replica. The deposition results acquired showed that very few CNT aerosols were found deposited in the airway replica. The fractional deposition as well as the deposition efficiency in each airway section is generally below 5%. This result implies that most of the inhaled CNTs will transit down to the lower lung airways, which might induce adverse health effects in the deep lung.

5AC.1

Alkane SOA Formation: Effect of Alkane Structure, NOx Conditions, Relative Humidity and Acidity. KATHERINE SCHILLING, Matthew Coggon, Jill Craven, Christine Loza, Tran Nguyen, Rebecca Schwantes, Lindsay Yee, Xuan Zhang, John Seinfeld,*California Institute of Technology*

Alkane SOA was generated in the Caltech Environmental Chamber from the photooxidation of structural isomers of dodecane to investigate the effects of structure, NOx conditions, relative humidity, and aerosol acidity on the formation of oligomeric species in the aerosol phase. Oligomer formation through acid-catalyzed condensation reactions has been predicted to be a significant contributor to SOA growth and mass in alkane photooxidation. n-Dodecane, 2-methylundecane, cyclododecane, hexylcyclohexane were subjected to photooxidation under moderate and high NOx conditions to probe the effect of structure and NOx on the gas-phase chemical mechanism and the chemical composition of the resultant SOA. To investigate the role of water on particle-phase chemistry, relative humidities (~5% and ~65% RH) were chosen to create seed particle surfaces mostly devoid of water and with multilayer coverage of water, respectively. Acidity was modified by varying seed particle composition; sodium chloride, ammonium sulfate, and ammonium sulfate with sulfuric acid were each used. The gas-phase precursors to oligomeric species in the aerosol were monitored by on-line chemical ionization mass spectrometry. SOA growth and chemical composition was monitored on-line by a time-of-flight aerosol mass spectrometer (Aerodyne, Inc.). Off-line analysis of alkane SOA collected by filters was done by solvent extraction and gas chromatography/mass spectrometry, and by direct analysis in real time (DART) – mass spectrometry. Together, these methods of analysis show the evolution of each parent compound’s resultant SOA population, and provide chemical insight into the products that partition into the particle phase and the oligomers that form in the aerosol phase.

5AC.2

Effect of Ozonolysis Chemistry on SOA Formation from Alkane Photooxidation. XUAN ZHANG, Katherine Schilling, Matthew Coggon, Rebecca Schwantes, Richard Flagan, John Seinfeld, *California Institute of Technology*

Long-chain alkanes, which are categorized as intermediate volatile organic compounds (IVOCs), are important source of secondary organic aerosol (SOA). The mechanism for the gas-phase OH-initiated oxidation of long-chain alkanes has been well documented. Particle-phase chemistry, however, has received less attention. Previous studies found that 1,4-hydroxycarbonyl, generated from the isomerization of alkoxy radicals, could undergo heterogeneous cyclization to form substituted dihydrofuran. Due to the presence of C=C bonds, substituted dihydrofuran is predicted to be highly reactive with OH and even more so with O3 and NO3. This work focuses on studying how substituted dihydrofuran formation and its subsequent reaction with ozone affects our current understanding of SOA formation from the photooxidation of long-chain alkanes. Experiments were carried out in the Caltech Environmental Chamber using n-dodecane as a target to investigate the difference in chemical composition of aerosols generated from “OH-oxidation dominating” vs. “ozonolysis dominating” environments. A detailed model incorporating the specific gas-phase photochemical mechanism, together with the heterogeneous formation of substituted dihydrofuran and its subsequent oxidation, was developed to evaluate the importance of this reaction channel and its impact on the SOA yield and oxidation state. We conclude that the ozonolysis of substituted dihydrofuran opens a reaction pathway that is not usually accessible to alkanes, expands the product distributions from alkane photochemistry, and possibly contributes significantly on the alkane SOA formation in the urban atmosphere.

5AC.3

Insights into SOA Formation Chemistry from the Isolation of Individual Reactive Pathways. ANTHONY CARRASQUILLO, Kelsey Boulanger, James Hunter, Sean Kessler, Kelly Daumit, Jesse Kroll, *MIT*

Our understanding of the chemistry of secondary organic aerosol (SOA) formation from precursor organic species is hindered by the complexities arising from multiple reaction pathways and generations of oxidation. Here, we constrain radical oxidation chemistry to a single reaction pathway by forming SOA from the direct photolytic generation of alkoxy radicals from alkyl nitrite (RONO) species. Direct photolysis of RONO species yields one specific alkoxy radical, which greatly simplifies the subsequent chemistry by allowing for individual reaction steps and pathways to be examined. Laboratory chamber experiments under added NO conditions (to ensure RO2 + NO chemistry dominates) were conducted with a series of C10 RONO species to investigate how the structure of the parent alkoxy radical species influences the formation of SOA. We examined the role of radical substitution (primary, secondary, and tertiary), radical position along the carbon backbone, and the structure of the carbon skeleton (linear, branched, and cyclic) on SOA formation. SOA yields and the distribution of major products from each precursor species as well as bulk aerosol properties (O/C, H/C, and N/C) were determined using an Aerodyne Aerosol Mass Spectrometer and compared to analogous alkane oxidation experiments. The evolution of individual product species provides new insight into SOA formation from alkanes, and highlights the importance of molecular structure in SOA formation chemistry.

5AC.4

Secondary Organic Aerosol Formation from Aromatic Compounds: Describe SOA Yield Using [OH]/[HO2] Ratio. Ping Tang, Shunsuke Nakao, Chia-Li Chen, DAVID R. COCKER III, *University of California, Riverside*

Formation of secondary Organic Aerosol (SOA) from benzene, toluene, ethylbenzene, xylene isomers, ethyltoluene isomers, thrimethylbenzene isomers, propylbenzene, isopropylbenzene, tetramethylbenzene, pentamethylbenzene and hexamethylbenzene was investigated in a series of over 150 smog chamber experiments. Previous studies show that aerosol yields from the photooxidation of aromatic hydrocarbons are highly sensitive to NO_x level (Song et al., 2005; Ng et al., 2007b, Wyche et al., 2009). In this study, experiments were performed in dry air under no-NO_x and low-NO_x conditions. NO_x levels control the partitioning of HOx between OH and HO_2 and are integrally linked to the production of ozone in the unpolluted atmosphere (Monks, 2005). For this work, experimental observations were modeled using the gas-phase kinetic model SAPRC 2011. The OH to HO_2 ratio ($[OH]/[HO_2]$) obtained is used to describe aerosol formation of different aromatic compounds. It is observed that more aerosol is formed at lower $[OH]/[HO_2]$ ratios under both low-NO_x and no-NO_x conditions. Mz43 ($C_2H_3O^+$)/mz44 (CO_2^+) ratio determined by ToF-HR-AMS were observed to decrease with increasing $[OH]/[HO_2]$ ratio. Additionally, aromatic compounds with more carbon number tended to have higher $[OH]/[HO_2]$ ratios correlating with their lower SOA yields.

5AC.5

Secondary Organic Aerosol Formation from Naphthalene and Methylnaphthalene Photooxidation. CHIA-LI CHEN, Mary Kacarab, Ping Tang, David R. Cocker III, *University of California, Riverside*

Polycyclic aromatic hydrocarbons (PAHs) play a significant role in semivolatile gas-phase emissions from anthropogenic sources, which include incomplete combustion emissions, wood-burning, and may be a major “missing” source of SOA. Secondary organic aerosols can be formed from oxidation of PAHs and their contributions to ambient fine particulate matter are not well understood. Large uncertainties in PAH derived SOA, fine particle aging properties, SOA formation mechanisms and their gas-particle transformation reaction pathway in the atmosphere promote further investigation. The characteristics of SOA formation from oxidation of PAHs such as naphthalene and methylnaphthalene under the absence and presence of NOx conditions were conducted in the UCR CE-CERT chamber. SOA composition characteristics were identified by the HR-ToF-AMS, particle size distributions, particle density, SOA yield and particle volatility were obtained. SOA formations from naphthalene and methylnaphthalene photoxidation were found to favor higher SOA yields under H2O2 conditions more so than high NOx and low NOx conditions. The characteristic indicator of m/z 44 (CO2+) dominated the total organic aerosol formation and f44 and O/C ratio increased during the course of experiment from naphthalene and methylnaphthalene photooxidation. In addition, the VRF (Volume Remaining Fraction) increased from 20% to 88% which indicates that low volatility aerosols aged with reaction time. This research will provide a foundation for the prediction of SOA formation from PAH precursors.

5AC.6

Secondary Aerosol Production from Modern Diesel and Gasoline Light Duty Vehicles. Stephen Platt, Imad El Haddad, Simone Pieber, Alessandro Zardini, Ricardo Suarez-Bertoa, Jay Slowik, Ru-Jin Huang, Stig Hellebust, Brice Temime-Roussel, Nicolas Marchand, Luka Drinovec, Grisa Mocnik, Covadonga Astorga, Urs Baltensperger, ANDRE PRÉVÔT, *Paul Scherrer Institute*

On road vehicles are a significant source of particulate matter (PM), particularly in urban areas where population densities therefore and health impacts are higher. Under ambient conditions, most vehicular PM is likely secondary, produced via atmospheric reactions of volatile organic compounds (VOCs) from the exhaust. How this secondary PM production varies by vehicle type (e.g. diesel or gasoline, vehicle legislative standards etc) must be understood to improve atmospheric model predictions, inform policymakers and the general public, and ultimately reduce the health impacts of internal combustion vehicles.

Unfortunately very little information on the secondary aerosol production potential (SAPP) of vehicle exhaust is available. Meanwhile, recent ambient measurements combined with fuel consumption data (Bahreini et al., 2012) and estimations using raw fuels (Gentner et al., 2012), gave conflicting results as to whether diesel or gasoline vehicle emissions have a higher SAPP. Furthermore, the effect of low temperature ambient conditions (already known to increase primary PM and VOC emissions), or ambient relative humidity on vehicular SAPP is poorly constrained.

We report results from novel smog chamber experiments characterizing primary and secondary exhaust emissions from diesel and gasoline passenger cars (Euro 5) during the New European Driving Cycle. Primary emissions were diluted to atmospherically-relevant concentrations and injected into the chamber. Formation and aging of secondary products was initiated by OH photochemistry. Experiments were performed at 263K and 288K and at 40% and >90% relative humidity (RH).

VOC emission was generally lower for diesel vehicles, resulting in lower SAPP. Cold ambient conditions increased VOC emission and SAPP significantly for the gasoline vehicles studied but not for diesel vehicles. Increasing RH was also observed to increase SAPP.

5AC.7

Secondary Organic Aerosol Formation from Photo-oxidation of Evaporated Fuel: Experimental Results and Implications for Aerosol Formation from Combustion Emissions. SHANTANU JATHAR, Marissa Miracolo, Daniel S. Tkacik, Neil Donahue, Peter Adams, Allen Robinson, *UC Davis*

We conducted photo-oxidation experiments on evaporated fuels to investigate the role of fuel composition on secondary organic aerosol (SOA) formation from evaporated fuel and determine its implications on the atmospheric formation and composition of SOA from combustion emissions. We used a smog chamber to perform hydroxyl radical-initiated, high NOx experiments at typical atmospheric organic aerosol concentrations on gasoline, three types of jet fuel and six different diesel fuels. For a unit mass of fuel reacted, evaporated diesel formed the most SOA followed by Jet Propellent-8, Fischer-Tropsch (natural gas), gasoline and Fischer-Tropsch (coal). Qualitatively, these trends are consistent with the differences in fuel volatility and molecular structure. Aerosol mass spectrometer data indicate that the SOA is moderately oxygenated (O:C~0.2-0.4), which is similar to the semi-volatile oxygenated organic aerosol (SV-OOA) factor derived from ambient data. The estimated SOA mass yields for the evaporated jet and diesel fuel (SOA/Fuel reacted) are within a factor of two of SOA mass yields of dilute emissions from combustion sources operated on those fuels. This suggests that fuels are able to explain the variability in SOA formation observed with combustion emissions. However, for gasoline vehicle emissions, the vehicle emissions certification standard appears to play an important role in SOA formation potential, suggesting that other variables in a combustion system also influence SOA formation.

5AC.8

Comparison of Gasoline and Diesel Vehicles - Emission Factors of Volatile Organic Compounds from EURO5 Diesel and Gasoline Vehicles and Their Potential Integrated Influence on Air Quality. STIG HELLEBUST, Brice Temime-Roussel, Amelie Bertrand, Stephen Platt, Imad El Haddad, Simone Pieber, Alessandro Zardini, Ricardo Suarez-Bertoa, Jay Slowik, Ru-Jin Huang, Covadonga Astorga, Andre Prévôt, Nicolas Marchand, *Aix Marseille Université, Laboratoire Chimie Environnement*

Volatile Organic Compounds, VOCs, including nonmethane hydrocarbons (NMHCs) and oxygenated VOCs, are emitted from a wide range of sources, such as solvents, industrial combustion, petroleum vapour and biogenic sources. Vehicle exhaust is recognised as a significant source of VOCs in urban areas, and therefore is under strict regulatory control.

Furthermore, VOC emissions can impact on other air quality parameters, such as particulate matter (PM), because chemical reactions of VOCs in the atmosphere can produce PM in the form of secondary organic aerosol (SOA) through gas-to-particle formation processes.

We present VOC emission factors from modern gasoline and diesel vehicles compliant with the latest European emission standard (Euro 5). The vehicles were tested during the New European Driving Cycle, at 295K and 263K at a purpose built vehicle emissions test laboratory (VELA) of the European Commission Joint Research Centre (JRC) in Ispra, Italy. Subsequent chemical processing of the VOC emissions was studied in a smog chamber at the two different temperatures and at 40% and 90% relative humidity.

The experiments have shown that primary VOC emissions from the gasoline cars tested were typically higher in aromatic compounds, while primary VOC emissions from the diesel vehicles contained higher levels of oxidised hydrocarbons.

We compare different fuels and vehicle technologies in terms of primary VOC emission, and investigate how differences in VOC composition of modern gasoline and diesel vehicles influence atmospheric processing, including SOA formation. We also discuss the total integrated effects of VOC emissions from modern vehicle technologies on local air quality.

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The test facility experiments were provided by the European Commission.

5CA.1

Comparing Ambient Organic Aerosol Volatility at an Urban and a Remote Site in Europe. ANDREA PACIGA, Lea Hildebrandt Ruiz, Gabriella Engelhart, Evangelia Kostenidou, Monica Crippa, Andre Prévôt, Urs Baltensperger, Spyros Pandis, *Carnegie Mellon University*

The composition and volatility of ambient organic aerosol were measured in a major urban (Paris, France) and a remote area (Finokalia, Greece) during five month-long campaigns. The measurements were performed combining CMU’s variable residence-time thermodenuder, the Aerodyne Aerosol Mass Spectrometer (AMS) and a Scanning Mobility Mass Spectrometer (SMPS).

The OA measurements in Paris were part of the MEGAPOLI campaigns and were collected in the summer of 2009 and winter of 2010, providing contrasting meteorological conditions. During the summer the OA concentrations were relatively low, with mostly aged OA that was transported to the site from other areas. Half of the OA evaporated at 90 degrees Celsius and 90 percent at 190 Celsius at a centerline residence time of 25 seconds. During the winter the OA levels were higher with local sources becoming more important. The OA volatility was higher than in the summer with half of the OA evaporating at 80 degrees Celsius.

The most recent FAME campaign took place in October 2011 in a remote site on the island of Crete, Greece. This dataset is added to the collection of studies at Finokalia performed during the summer of 2008 and winter of 2009. This particular site is far from local emission sources, allowing the aerosol to reach a highly aged, oxygenated state. During periods with intense sunlight the aged OA has quite low volatility (requiring a temperature of 120 degrees Celsius to evaporate half of its mass at a centerline residence time of 15 seconds). During periods with lower photochemical activity the OA volatility increased with half the OA evaporating at 100 degrees Celsius.

A dynamic mass transfer model is used to estimate the OA volatility distribution for the different areas and seasons, evaluating changes in O:C of the OA, photochemical conditions, and OA sources (using positive matrix factorization).

5CA.2

An Improved Volatility Basis Set for Modeling Organic Aerosol in both CAMx and CMAQ. BONYOUNG KOO, Greg Yarwood, Eladio Knipping, *ENVIRON International Corporation*

Due to the complex nature of atmospheric organic aerosol (OA), it is impractical to explicitly simulate evolution of thousands of atmospheric organic compounds in photochemical grid models (PGMs). Therefore, PGMs adopt some kind of simplified representation where organic compounds with similar properties and/or origin are lumped together. The first generation volatility basis set (VBS) approach grouped OA compounds by volatility and provided a unified framework for gas-aerosol partitioning of both primary and secondary OA and their chemical aging. However, a VBS approach with one dimension of variation (volatility) is unable to describe observed variations in OA oxidation state (i.e., O:C ratio) at a fixed volatility level. A two-dimensional VBS approach was recently introduced where degree of oxidation is also tracked in addition to volatility but further study is needed to fully parameterize the 2-D VBS model.

In this study, a new OA module based on the VBS approach is implemented in two widely-used PGMs. Our scheme uses four basis sets to model ambient OA with different oxidation state: two sets for oxygenated OA (anthropogenic and biogenic) and two for freshly emitted OA (from anthropogenic sources and biomass burning). Each basis set has five volatility bins including a zero-volatility bin for essentially non-volatile compounds. The scheme adjusts both carbon number and oxidation state in response to chemical aging by simplifying the 2-D VBS scheme. The new organic PM module is implemented in both the CAMx and CMAQ PGMs and evaluated with a modeling database that simulates a 2005 summer episode over the entire continental US.

5CA.3

Average Chemical Properties and Potential Formation Pathways of Highly Oxidized Organic Aerosol. KELLY DAUMIT, Sean Kessler, Jesse Kroll, *MIT*

Measurements of ambient organic aerosol indicate that a substantial fraction is highly oxidized and low in volatility, but this fraction is generally not reproduced well in either laboratory studies or models. From field measurements, we know that low-volatility oxidized organic aerosol (LV-OOA) is highly oxidized (with an average carbon oxidation state of approximately 0-1), exceedingly low in volatility (c* ~0.1 to $<10^{-7}$ ug m^{-3}), and generated relatively quickly (over time scales of ~1-3 days). Thus the atmospheric formation of LV-OOA must involve reactions that rapidly increase the oxidation state of organic carbon (i.e., increasing O:C and decreasing H:C) while also rapidly decreasing the vapor pressure of the organics. In this work, we describe a new approach for constraining the viable precursors and formation pathways of LV-OOA, by starting with the oxidized product and considering the possible reverse reactions, using a simple set of chemical rules. The elemental composition and volatility of the aerosol enables the determination of its position in three-dimensional chemical space (defined by H:C, O:C, and carbon number) and its average chemical formula. Consideration of possible back-reactions then defines the movement taken through this chemical space, constraining potential reaction pathways and precursors. Results suggest that potential LV-OOA formation pathways include functionalization reactions that add multiple functional groups per oxidation step, oligomerization of highly oxidized precursors, and, in some cases, fragmentation reactions that involve the loss of small, reduced fragments.

5CA.4

The Influence of Aerosol Water in the Organic Phase on the Mass, Properties and Source Apportionment of Organic Aerosol in a Source-oriented Model. SHANTANU JATHAR, Abdullah Mahmud, James F. Pankow, Michael Kleeman, *UC Davis*

Ambient organic aerosol (OA) is hygroscopic meaning that water partitions into the organic phase to a degree determined by the organic chemical composition and the ambient relative humidity. In addition to contributing to the OA mass, the absorbed water also alters the mean molecular weight of OA and the activity coefficients of OA’s constituent compounds, which in turn influences OA’s gas-particle partitioning. Classical OA treatment in aerosol transport models does not account for water uptake and its subsequent impacts.

In this work, we use the UCD/CIT source-oriented air quality model to simulate water uptake by OA on different internal mixtures or source-oriented particle types and assess its influence on the mass, properties and source-apportionment of OA. The model is run for a summer (July 2002) and winter (January 2003) month over two distinct regions in California: the South Coast Air Basin (dominated by motor vehicle emissions) and the San Joaquin Valley (dominated by agricultural and wood burning emissions). The internally mixed OA calculations predict very little water in the organic phase ($<$ 0.3 µg m^{-3}) in the summer but modest amounts of water in the organic phase during the winter ($>$ 1 µg m^{-3}). The water in the organic phase is sufficient to substantially change the mean molecular weight of the OA-water mixture, which ends up increasing the partitioning coefficient of the organic constituents or pushes gas-particle equilibrium towards the particle phase. Hence, in winter, the absorbed water contributes significantly to OA enhancement which improves model performance. Tests of water uptake into the organic phase on source-oriented aerosols are ongoing. We anticipate that the source-oriented calculations will reveal that particles with a more hygroscopic OA (emitted from wood smoke or biomass burning) absorb more water in their organic phase than particles with less hygroscopic OA (emitted from gasoline or diesel combustion). This would have a strong influence not only on the water mass absorbed by OA but also on the properties and source apportionment of OA.

5CA.5

Wintertime Organic Aerosols in Fresno, California: Characteristics, Sources and Aqueous-phase Processing. XINLEI GE, Ari Setyan, Yele Sun, Qi Zhang, *Univeristy of California, Davis*

California's San Joaquin Valley (SJV) suffers from severe aerosol pollution problem, especially during wintertime. Here, we present results on characterization of the organic aerosols (OA) in Fresno, one of the most populated city in this region, during January 2010 using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). OA dominated the submicron aerosol (PM1) mass, with major contributions from three primary sources – traffic, food cooking, and residential wood combustion. Specifically, traffic-related hydrocarbon-like OA (HOA; O/C=0.09), cooking OA (COA; O/C=0.11), and biomass burning OA (BBOA; O/C=0.33) on average accounted for 22%, 19%, 16% of the OA mass during this study. Primary OA (POA) were particularly prominent during nighttime, contributing up to 80% of the OA mass between 6-9 PM, owing to elevated emissions from evening traffic, dinner cooking and residential heating exacerbated by lower mixed layer height. BBOA correlated best with the polycyclic aromatic hydrocarbons (PAHs) indicating that residential wood burning is a significant source of PAHs. Secondary oxygenated OA aerosol (OOA; O/C=0.42) correlated strongly with both nitrate and sulfate (R>0.84) and accounted for an average 43% of the OA mass. The mass-based size distributions of different OA factors were estimated using a multilinear regression algorithm. Both HOA and BBOA peaked at ~140 nm in vacuum aerodynamic diameter, OOA peaked at ~460 nm, while COA exhibited a unique behavior with two size modes centering at ~200 nm and ~450 nm respectively. Three dense fog events and a persistent rainy period were encountered during this study, allowing us to investigate the effects of aqueous-phase processing on the aerosol chemistry and size distributions. Our results indicate that fog processing enhanced the formation of SOA and other secondary species like sulfate and nitrate. It also shifted the size distributions of secondary species to a larger mode size and enhanced the O/C of SOA.

5CA.6

Black Carbon Containing Particles at a Rural Site Southeast of London, UK during ClearfLo (Winter 2012). LEAH WILLIAMS, Scott Herndon, John Jayne, Andrew Freedman, William Brooks, Jonathan Franklin, Paola Massoli, Edward Fortner, Puneet Chhabra, Mark Zahniser, Timothy Onasch, Manjula Canagaratna, Douglas Worsnop, Felipe Lopez-Hilfiker, Claudia Mohr, Joel Thornton, Nga Lee Ng, Lu Xu, Berk Knighton, Manvendra Dubey, Allison Aiken, Kyle Gorkowski, Shang Liu, Andre Prévôt, et al., *Aerodyne Research, Inc.*

Clean Air for London (ClearfLo) is a large, multidisciplinary study of the London urban atmosphere aimed at understanding the relationships between surface meteorology, gas-phase composition and particulate matter at city sites and at rural locations that sample the inflow to or outflow from the London urban area. We deployed a suite of instruments at a rural site approximately 50 km southeast of London in Detling, UK during January-February, 2012. Measurements included aerosol chemistry and microphysics, gas-phase tracers, secondary organic aerosol (SOA) precursors, and radiative and meteorological conditions. This talk will focus on black carbon containing particles measured at Detling. The soot particle aerosol mass spectrometer (SP-AMS) instrument made in situ measurements of the chemical composition and size distributions of black carbon containing particles, including both the black carbon component and any coatings. The mass spectra were analysed with positive matrix factorization (PMF) yielding three factors. The first factor has dominant peaks at m/z 60 and 72, indicative of solid fuel burning. The second factor has a mass spectrum suggesting hydrocarbons associated with fresh vehicle emissions, while the third factor has a mass spectrum associated with oxygenated organics and more aged aerosol particles. The PMF factors are linked to air mass sources using dispersion model back trajectories and local wind measurements. Connections between the chemical, microphysical, and optical properties of the black carbon containing particles in the different air masses will be presented.

5CA.7

A Study of Secondary Organic Aerosol Formation Influenced by Mixed Anthropogenic and Biogenic Emissions in Atlanta Area by High Resolution Mass Spectrometer. LU XU, Hongyu Guo, Laura King, Vishal Verma, Rodney Weber, Nga Lee Ng,*Georgia Institute of Technology*

Secondary organic aerosol (SOA) accounts for a major fraction of particulate mass and significantly affects the Earth's climate and human health. However, SOA formation is controlled by complex processes which are not well understood. Specifically, to which extent human activities affect SOA formation and evolution is highly uncertain. The Atlanta area is an ideal location to investigate the effect of SOA production in mixed anthropogenic and biogenic emissions since this area is characterized by high emissions of both anthropogenic and biogenic sources. In this study, the formation of SOA is investigated by a comparison among Jefferson Street Site (Atlanta urban area), Yorkville Site (rural, 55km NW of Atlanta), and a roadside site (next to Interstate 75/85). Real-time particle instruments included an Aerodyne High-Resolution Time-of-Flight Mass Spectrometer (HR-ToF-AMS), a Multi-angle Absorption Photometer (MAAP), a Particle Into Liquid Sampler (PILS), and a Total Organic Carbon Analyzer (TOC). The HR-ToF-AMS was deployed to measure the size-revolved chemical composition of non-refractory submicron aerosol. Total mass concentrations of five major aerosol compositions, organics, nitrate, sulfate, ammonium, and chloride, at each sampling site are reported. In addition, elemental analyses are carried out to determine the oxygen/ carbon (O/C) and hydrogen/carbon (H/C) ratios of the bulk OA, which are indications of aerosol aging. Positive Matrix Factorization (PMF) is conducted on high mass-resolution (HR) organic aerosol (OA) spectra to deconvolve OA into different components. Hydrocarbon-like organic aerosol (HOA) and oxygenated organic aerosol (OOA), which are surrogates of primary and secondary OA respectively, are found at all sites. Besides, isoprene-derived SOA is only detected in Yorkville during summer. The effect of anthropogenic emissions on SOA formation would be discussed based on the measurement results obtained at the three different sampling sites at different times.

5CA.8

Spatially and Seasonally Resolved Estimate of the Global Organic Matter to Organic Carbon Ratio Inferred from Aerosol Mass Spectrometer Measurements and Satellite-Derived Ground-Level Nitrogen Dioxide Concentrations. SAJEEV PHILIP, Randall Martin, Jeffrey Pierce, Caroline Nowlan, Dominick Spracklen, Jose-Luis Jimenez, Qi Zhang, Lok Lamsal, Nickolay Krotkov,*Dalhousie University, Canada*

Particulate organic matter (OM) is of intense interest for air quality and climate research, but the relationship between OM and organic carbon (OC) remains poorly constrained. We present a novel method to estimate the spatially and seasonally resolved global OM/OC ratio. First, we develop a parameterization for the OM/OC ratio using the hydrocarbon-like organic aerosol (HOA) fraction of total OM measured globally with the Aerosol Mass Spectrometer (AMS). Second, we use ground-level NO_2 concentrations derived from the Ozone Monitoring Instrument (OMI) satellite sensor to serve as a proxy for fresh emissions that have a high HOA fraction. The combination of these two methods yields predictions of OM/OC from NO_2 measurements. We use two-thirds of a database of AMS field measurements (47 observations) to formulate a prediction model of the OM/OC ratio; evaluation of the full NO_2 --> OM/OC relationship with the remaining data yields significant agreement (r = 0.76, slope = 0.96, n = 21). The global OM/OC ratio ranges from 1.3 to 1.9 (micro-gram/micro-gram Carbon), with distinct spatial variation that clearly reflects the difference between urban and rural regions. The seasonal OM/OC ratio has a summer maximum and a winter minimum over regions dominated by high combustion emissions. This parameterization could be included into models for estimating the OM/OC ratio using the simulated NO_x or NO_2 concentrations.

5CC.1

Aircraft Measurements of Aerosol and CCN activation Properties during TCAP. FAN MEI, Jason Tomlinson, John Shilling, Jennifer Comstock, John Hubbe, Larry Berg, Beat Schmid, *Pacific Northwest National Laboratory*

Currently, the indirect effects of atmospheric aerosols remain the most uncertain components in forcing of climate change over the industrial period (IPCC, 2007). This large uncertainty is partially due to our incomplete understanding of the ability of particles to form cloud droplets under atmospherically relevant supersaturation. In addition, there is a large uncertainty in the aerosol optical depth (AOD) simulated by climate models near the North American coast and a wide variety in the types of clouds are observed over this region. The goal of the US Department of Energy Two Column Aerosol Project (TCAP) is to understand the processes responsible for producing and maintaining aerosol distributions and associated radiative and cloud forcing off the coast of North America.

During the TCAP study, aerosol total number concentration, cloud condensation nuclei (CCN) spectra and aerosol chemical composition were in-situ measured from the DOE Gulfstream 1 (G-1) research aircraft during two Intensive Operations Periods (IOPs), one conducted in July 2012 and the other in February 2013. An overall aerosol size distribution was achieved by merging the observations from several instruments, including Ultra High Sensitivity Aerosol Spectrometer – Airborne (UHSAS-A, DMT), Passive Cavity Aerosol Spectrometer Probe (PCASP-200, DMT), and Cloud Aerosol Spectrometer (CAS, DMT)(Tomlinson, et al., 2013). Aerosol chemical composition was characterized using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Inc.). Based on the aerosol size distribution, CCN number concentration (characterized by a DMT dual column CCN counter with a range from 0.1% to 0.4%), and chemical composition, a CCN closure was obtained. The differences in aerosol/CCN properties between two columns, and between two phases, were investigated. The overall aerosol hygroscopicity, estimated from the relationship between the aerosol oxidation level and organic aerosol hygroscopicity (Mei et al., 2013), will be discussed.

5CC.2

The Limitations of Electrical Mobility Diameter for Biomass Burning CCN Activation. MICHAEL GIORDANO, Carlos Espinoza, Akua Asa-Awuku, *University of California, Riverside*

Biomass burning is a large contributor of aerosols to the atmosphere. Aerosols can impact the earth’s radiative balance through their ability to activate into cloud condensation nuclei (CCN). Electrical mobility is often used to size-select aerosols to determine their critical activation diameter. The electrical mobility diameter is subsequently used to estimate the volume and moles of solute dissolved in the activated droplet. This approach assumes that a particle is spherical and that the electrical mobility diameter is equivalent to the volume equivalent diameter. In this study we explore the fractal nature of biomass burning aerosol and its influence on CCN activity. Controlled burns were conducted at UC-Riverside’s College of Engineering-Center for Environmental Research and Technology facility to determine the sphericity of the aerosol. Two common southwestern brush species, manzanita and chamise, were burned in a wood stove. The emissions were diluted and injected into a 12 m^3 Teflon environmental chamber. Emissions were aged with ultraviolet light over 6-8 hours. A Kanomax Aerosol Particle Mass (APM) analyzer in conjunction with a scanning mobility particle sizer (SMPS) determined the effective particle density and fractal dimension of the aerosol. A continuous flow streamwise thermal gradient CCN Counter determined the CCN activation diameters at supersaturations of .2-1%. Results show that biomass burning aerosol can be non-spherical, the degree of which can change with aging (effective densities from .6 to .8 g cm^{-3} over the experiment). The sensitivity of single parameter estimates of CCN activation, assuming a spherical aerosol, is compared to measurements. Accounting for the sphericity of biomass burning aerosol can be important in predicting CCN activation.

5CC.3

A New Experimental Approach toward Determining Cloud Nucleating Activities of Haze Particles. SHUNSUKE NAKAO, Sonia Kreidenweis, *Colorado State University*

The atmospheric aqueous phase plays an important role in the interactions between atmospheric particles, cloud droplets, and gas-phase compounds. The presence of an aqueous phase may enhance secondary organic aerosol (SOA) formation from water-soluble organic compounds that are too volatile to partition to an organic phase solely based on volatility. Water may affect formation of oligomers, acting as a plasticizer that reduces organic aerosol viscosity. The hygroscopicity of an aerosol can be determined by measuring its activity in serving as a cloud condensation nucleus. A common experimental approach to evaluation of cloud-nucleating activity is to remove the aqueous phase before measurement, due to the technical need to know the amount of (dry) solute in the aerosol for correlation with the measured critical supersaturation. However, the drying step may lead to uncertainties such as changes in aerosol phase/shape, loss of semi-volatile compounds, and incomplete drying. This study eliminated the drying step, utilizing an additional chemical measurement to account for the presence of the aqueous phase. A humidity-controlled differential mobility analyzer was used to produce mono-disperse, equilibrated wet aerosol, and subsequently cloud nucleating activities and chemical compositions of wet particles were measured. The evaluation of this experimental approach using inorganic salts and low-volatile/semi-volatile organic compounds will be presented.

5CC.4

Weak Global Sensitivity of Cloud Condensation Nuclei and the Aerosol Indirect Effect to Criegee+SO2 Chemistry. JEFFREY PIERCE, Mat Evans, Catherine Scott, Stephen D'Andrea, Delphine Farmer, Erik Swietlicki, Dominick Spracklen, *Colorado State University*

H2SO4 vapor is important for the nucleation of atmospheric aerosols and the growth of ultrafine particles to cloud condensation nuclei (CCN) sizes with important roles in the global aerosol budget and hence planetary radiative forcing. Recent studies have found that reactions of stabilized Criegee intermediates (CIs, formed from the ozonolysis of alkenes) with SO2 may be an important source of H2SO4 that has been missing from atmospheric aerosol models. We investigate the impact of this new source of H2SO4 in the atmosphere. We use the chemical transport model, GEOS-Chem, with the online aerosol microphysics module, TOMAS, to estimate the possible impact of CIs on present-day H2SO4, CCN, and the cloud-albedo aerosol indirect effect (AIE). We extend the standard GEOS-Chem chemistry with CI-forming reactions from the Master Chemical Mechanism. H2SO4 concentrations increase by over 100% in forested tropical boundary layers and by over 10-25% in forested NH boundary layers (up to 100% in July) due to CI+SO2 chemistry, but the change is generally negligible elsewhere. The predicted changed in CCN were strongly dampened to the CI+SO2 changes in H2SO4 in these regions: less than 15% in tropical forests and less than 2% in most mid-latitude locations. The global-mean CCN change was less than 1% both in the boundary layer and the free troposphere. The associated cloud-albedo AIE change was less than 0.03 W/m^2. The model global sensitivity of CCN and the AIE to CI+SO2 chemistry is significantly (approximately one order-of-magnitude) smaller than the sensitivity of CCN and AIE to other uncertain model inputs, such as nucleation mechanisms, primary emissions, SOA and deposition. We conclude that improvement in the modeled CI+SO2 chemistry would not likely to lead to significant improvements in present-day CCN and AIE predictions.

5CC.5

The Contribution of Sub-Grid, Plume-Scale Nucleation to Global and Regional Aerosol and CCN Concentrations. ROBIN STEVENS, Jeffrey Pierce, *Dalhousie University*

New-particle formation in the plumes of coal-fired power plants and other anthropogenic sulphur sources may be an important source of particles in the atmosphere. It has been unclear, however, how best to reproduce this formation in global and regional aerosol models with grid-box lengths that are 10s of kilometres and larger. The predictive power of these models is thus limited by the resultant uncertainties in aerosol size distributions.

Based on the results of the System for Atmospheric Modelling (SAM), a Large-Eddy Simulation/Cloud-Resolving Model (LES/CRM) with online TwO Moment Aerosol Sectional (TOMAS) microphysics, we develop the Predicting Particles Produced in Power-Plant Plumes (P6) parameterization: a computationally-efficient, but physically-based, parameterization that predicts the characteristics of aerosol formed within sulphur-rich plumes based on parameters commonly available in global- and regional-scale models. Given large-scale mean meteorological parameters, emissions from the source, the desired distance from the source, and the mean background SO_2, NO_x, and condensation sink, the parameterization will predict the fraction of the emitted SO_2 that is oxidized to H_2SO_4, the fraction of that H_2SO_4 that forms new particles instead of condensing onto preexisting particles, the median diameter of the newly-formed particles, and the number of newly-formed particles per kilogram SO_2 emitted.

We implement the P6 parameterization in the GEOS-Chem global chemical-transport model in order to evaluate the contributions of coal-fired power plants globally to particle number and CCN concentrations.

5CC.6

Investigating Sensitivities of Ice Crystal Concentration: The Evaluation of the Adjoint of a Physically-Based Cirrus Activation Parameterization. BENJAMIN SHEYKO, Shannon Capps, Donifan Barahona, Athanasios Nenes, *Georgia Institute of Technology*

Ice clouds have the potential to significantly influence climate through their impact on Earth's radiative balance, stratospheric circulation, and liquid and ice water paths. Even with their climatic importance, the aerosol-cloud-climate connection is still poorly understood due to many complexities including cirrus activation. Historically efforts to understand this connection have been made through comprehensive sensitivity studies which involve making small perturbations in global climate model (GCM) inputs and observing the results of the perturbation. While being conceptually straightforward, this finite difference approximation of sensitivities is time consuming and forces the state of the system to be altered when the evaluations are made as well as lacks the ability to simultaneously evaluate output sensitivity to multiple inputs parameters. Investigating sensitivities using an adjoint has the potential to alleviate these problems.

Here we develop and evaluate the adjoint of the Barahona and Nenes (2009) cirrus activation parametrization. This physically-based activation scheme considers competition between homogeneous and heterogeneous freezing and is unique in the sense that it is able to use any ice nuclei (IN) spectrum (provides the number of crystals that freeze heterogeneously). The adjoint was validated against finite difference sensitivities and then applied globally to study the relative importance of input parameters to cirrus ice crystal number concentration for several IN spectra. Lastly sensitivities were used to determine to what extent input parameters contribute to crystal number variability, elucidating their importance spatially. The adjoint model was driven using daily averaged fields including: aerosol size distribution, ice nuclei characteristics, and meteorology from version 5.0 of the Community Atmosphere Model (CAM5).

5CC.7

The Composition of Droplet-Forming Aerosol as a Function of Supersaturation. BETH FRIEDMAN, Eleanor Browne, Karin Ardon-Dryer, Anthony Carrasquillo, Kelly Daumit, Kelsey Boulanger, Jesse Kroll, Joel A. Thornton, Daniel Cziczo, *University of Washington*

Aerosol-cloud interactions represent a significant uncertainty with respect to radiative forcing and climate with both particle composition and size playing key, yet poorly understood, roles in determining the cloud nucleating capabilities of aerosols. Cloud condensation nuclei (CCN) and aerosol composition measurements were conducted during February 2013 as part of the Department of Energy Two Column Aerosol Project (TCAP). Located in North Truro, MA, the site provides access to a variety of air mass sources, including marine, continental, and urban.

A CCN closure study was conducted with measurements from a commercial Cloud Condensation Nuclei Counter (CCNC, Droplet Measurement Technologies) at a range of supersaturations, as well as an Aerosol Mass Spectrometer (AMS, Aerodyne). Further measurements were conducted utilizing a Pumped Counterflow Virtual Impactor (PCVI) in order to separate the activated droplets, as a function of supersaturation, from un-activated aerosol at the output of the CCNC. Subsequent composition analysis of the residual droplet aerosol was conducted with the AMS. High-resolution residual aerosol composition will be presented as a function of instrument supersaturation and air mass, and will be compared to the total ambient aerosol composition. Preliminary results suggest an enhancement of nitrate in the activated fraction, as well as compositional differences in organics between the unactivated aerosol and the droplet residuals. The advantages and disadvantages of a combination of a CCN / PCVI / AMS will be discussed with a focus on how this new technique can improve our understanding of warm cloud formation.

5CC.8

Effect of Rain on Evolution of Aerosol Concentration Distribution in Air Pollution Plumes. BORIS KRASOVITOV, Tov Elperin, Andrew Fominykh, *Ben-Gurion University of the Negev*

Although it is commonly accepted that air pollution is dominated by local emissions many studies report that plumes of harmful pollutants can waft across oceans and continents and warn about the growing danger of long-distance smog. Scavenging of aerosols by rain contributes to the evolution of concentration distribution of aerosols and reduces concentration of aerosols in pollutants emissions. In the present study we suggest a model of scavenging of aerosol particles by rain in Gaussian air pollution plume. Analytical approach was developed using a Gaussian plume dispersion model and taking into account raindrops size distribution by using the Monte Carlo simulation. In simulations we used the log-normal size distribution of raindrops with Feingold and Levin parameterization based on the long-time measurements of rain drops size spectra in Israel. The developed model allows analyzing spatial and temporal evolution of aerosol concentration in the gaseous phase as well as in the raindrops. In the calculations we use as input parameters for a Gaussian plume dispersion model meteorological data such as wind speed, wind direction and atmospheric stability class. It is shown that the dynamics of below-cloud scavenging of aerosols is described by an explicit analytical expression. Aerosol concentration distributions are calculated for different values of rain intensity and different sizes of aerosol particles in the plume. The obtained results can be useful in the analysis of different meteorology-chemistry models including scavenging of aerosols in air pollution plumes by rain and, in particular, in various parameterizations of global air pollution scavenging by precipitation.

5EN.1

Origin, Cure and Control of Nanosilver Toxicity. Georgios Sotiriou, Kakeru Fujiwara, SOTIRIS E. PRATSINIS, *ETH Zurich*

Nanosilver is considered the most commonly used engineered nanomaterial, for example, in antibacterial textiles, polymer films for food packaging, paints and pigments, filters for water or air treatment to name a few applications (1). Concerns however about released Ag^+ ions during dispersion of nanosilver in liquids have limited its broad use. Here nanosilver supported on nanostructured silica is made with closely controlled Ag size both by dry (flame aerosol) and wet chemistry (impregnation) processes without, however, any surface functionalization that could interfere with its ion release (2). The dispersion method of nanosilver in solutions affects its dissolution rate but not the final Ag^+ ion concentration. By systematically comparing nanosilver size distributions to their equilibrium Ag^+ ion concentrations, it is revealed, that the latter correspond precisely to dissolution of one to two surface silver oxide monolayers, depending on particle diameter. When, however, nanosilver is selectively conditioned by either washing or H_2 reduction, the oxide layers are removed, drastically minimizing Ag^+ ion leaching and its antibacterial activity against E. coli. That way the bactericidal activity of nanosilver is confined to contact with its surface rather than to rampant ions. This leads to silver nanoparticles with antibacterial properties that are essential for medical tools and hospital applications. Complete cure of nano-Ag toxicity is achieved by its hermetic coating by nanothin inert silica films.

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2. G.A. Sotiriou, A. Meyer, J.T.N. Knijnenburg S. Panke, S.E. Pratsinis, “Quantifying the origin of nanosilver ions and their antibacterial activity”, Langmuir, 28, 15929–15936 (2012).

5EN.2

Single Particle Characterization of Nanoparticle Metal-Oxides by ICP-MS. BRIAN MAJESTIC, Manuel Montano, James Ranville, *University of Denver*

Metal oxide nanoparticles (NP) (e.g. Fe_2O_3, Al_2O_3, SiO_2) are used in a variety of products ranging from groundwater remediation, photoactive cosmetics and polishing slurries in microchip fabrication, but can also be effective vectors for contaminant transport in the environment and may be responsible for inhalation health effects. Single-particle (sp) inductively coupled plasma mass spectrometry (ICP-MS) is a powerful tool capable of detecting, counting and sizing nanoparticles in complex matrices. Individual nanoparticles in their pure elemental state (e.g., Ag and Au) have been successfully sized by ICPMS at sizes down to ~ 20 nm. Metal oxides are more difficult to detect using ICPMS because 1) they often suffer from significant molecular interferences, as is the case for ^{56}Fe ($^{40}Ar^{16}O$) and ^{28}Si ($^{14}N_2$) and 2) there is less analyte mass per particle due to the presence of oxygen. In these cases, a collision cell pressurized with helium gas can be used to reduce/remove the interferences allowing for sizing of the analyte. In the current study, collision cell sp-ICP-MS has been used to study silica (SiO_2) nanoparticles and alpha-hematite (Fe_2O_3) colloids to develop a method for detecting these particles in environmental samples. alpha-Hematite particles as small as 60 nm and silica particles as small as 200 nm have been detected by sp-ICP-MS. However, the sizing of the particles has proven to be troublesome and requires further method development. Research is ongoing to not only characterize these particles, but to also study adsorbed contaminants onto nanoparticles (e.g., copper adsorbed onto hematite or metals adsorbed onto black carbon). When paired with a water-trap type of sampler, such as a particle-into-liquid sampler (PILS), this technique has the capability to potentially size and detect, in semi-real time, individual airborne nanoparticles.

5EN.3

Performance of a Personal Thermal Precipitator to Assess Nanoparticle Exposures. David Leith, John Volckens, DAN MILLER-LIONBERG, Traci Lersch, Gary Casuccio, *Colorado State University*

A thermal precipitatation sampler (TPS) has been developed and evaluated to assess personal exposure to engineered nanoparticles. The TPS is about the size and weight of a smart phone and collects particles on a standard TEM grid. It contains a sampling head, pump, mass-flow controller, and batteries that allow sampling for up to sixteen hours. Sampling parameters can be set or adjusted using surface-mounted buttons and a digital display. After sampling and removal of the TEM grid, a high resolution electron microscope is used to analyze the nanoparticles collected on the grid. This presentation describes the development and use of a “transfer function” that relates the number and sizes of the nanoparticles collected on the TEM grid to the concentration and size distribution of the nanoparticle aerosol sampled. The validity of this transfer function is evaluated through experiments for particles between 20 and 600 nm in diameter. Further analysis of the collected nanoparticles using energy dispersive spectroscopy allows discriminating engineered nanoparticles that may be of particular concern, from nanoparticles of natural or incidental sources. We have demonstrated TPS performance for sampling and discriminating engineered and non-engineered nanoparticles in the laboratory and in the field. Thus, the TPS allows evaluation of the potential health risk due to exposure to specific, engineered nanoparticles independently of the potential risk posed by exposure to other aerosol particles that may be present at the same time.

5EN.4

Carbon Nanotube Penetration through Different Respirator and Nuclepore Filters: Models and Experiments. SHENG-CHIEH CHEN, Jing Wang, Yeon Kyoung Bahk, Heinz Fissan, David Y. H. Pui, *University of Minnesota*

Animal studies have shown asbestos-type pathology associated with exposure to longer and straighter CNTs. Respirators are usually used as the final personal protective equipments to mitigate the exposure of workers who are manufacturing and handling CNTs. However, the performances of respirators were usually obtained by challenging spherical particles; therefore the penetration curves may not be accurate and suitable for CNTs. It has been found that CNTs had a much lower penetration through screen filters at 5 cm/s face velocity than the same mobility diameter spherical particles due to a much longer interception length of CNTs. This result indicates the performance data are applicable for the CNTs. However, the penetration of open Ag agglomerates, which have a similar high length-to-diameter ratio, was found to be close to spherical particles in Nuclepore filter at face velocities higher than 10 cm/s (close to the face velocity for N-95 certification) due to the effect of alignment. This finding attracts our attentions to study whether the penetration could be higher for CNTs than the same mobility diameter spherical particles at face velocity around 10 cm/s and higher velocities. In this study, three different respirator filters (two electrets and one glassfiber) were challenged with different mobility diameter, 30-500 nm, monodisperse CNTs at 5.3 and 10.6 cm/s face velocities. The CNTs were functionalized by the nitric acid refluxing method. The penetration data were compared with that of NaCl particles obtained earlier by us. Results showed that the penetrations of CNTs were mostly lower than NaCl at the same mobility diameter at both face velocities for all three filters. However, it was found the CNTs had higher penetrations than NaCl for sizes larger than 300 nm at 10.6 cm/s face velocity. Finally, the collection mechanisms of CNTs were studied experimentally and theoretically by using Nuclepore filters and capillary tube models, which is a potential method to assess the CNT exposure of workers.

5EN.5

Characterisation of Emitted Particles during Maintenance of Common Nano Particle Generator. Patrik Nilsson, Linus Ludvigsson, Jenny Rissler, Maria E Messing, Christina Isaxon, Axel C. Eriksson, Maria Hedmer, Håkan Tinnerberg, Knut Deppert, ANDERS GUDMUNDSSON, Joakim Pagels, *Lund University*

The production of engineered nanoparticles is rapidly growing and measurement and characterization of the particle exposure of the whole manufacturing processes is important to obtain reliable risk assessments. In this work we characterized particle emissions during maintenance of common particle generators: a Spark Discharge Generator and a High Temperature furnace. Both generators were operated upstream a sintering furnace.

Online characterization of as-produced particles was carried out with a Scanning Mobility Particle Sizer and filter sampling for analysis with transmission electron microscopy. During the maintenance sampling was carried out within the expected emission zone using an Aerodynamic Particle Sizer and a Condensation Particle Counter. Filters for scanning electron microscopy analysis were collected. Time-resolved chemical identification was obtained using a Laser Vaporization Aerosol Mass Spectrometer (LV-AMS, Aerodyne Inc.) of both the as-produced and emitted particles.

During maintenance the emissions in terms of particle mass and surface area were dominated by particles larger than1µm. SEM analysis revealed that the particles were highly agglomerated and consisted of both the originally as-produced aggregates and the sintered particles. The chemical identification using LV-AMS of the emitted particles showed that they were dominated by the metal elements used during the particle synthesis sessions prior to the maintenance.

The geometric mean diameter of the as-produced and the emitted particles were ~0.03 µm and ~1.8 µm, respectively, which coincides with the lower and the upper maxima of the pulmonary deposition curve.
This work shows the importance of including measurements of particles larger than1µm in assessments of emissions and exposure to manufactured engineered nanoparticles.

This work was supported by the Consortium for Aerosol Science and Technology, the Nanometer Structure Consortium at Lund University (nmC@LU), the Swedish research council FAS and the FAS-centre METALUND.

5EN.6

Assessing the Environmental Impact of Cerium Additives for Diesel Fuel Vehicles. SHAMIA HOQUE, Kathleen Fahey, Havala Pye, Garnet Erdakos, Prakash Bhave, K. Max Zhang, *Environmental Protection Agency*

Nanoparticle fuel-borne catalysts (FBCs) can be used to modify the emissions of particulate matter from diesel vehicles. Laboratory studies examining the effect of cerium FBCs indicate a potential increase in ultrafine particles and decrease in particle mass. In this investigation a representative set of aerosol emissions from a diesel vehicle is tracked from near – road to ambient urban conditions by applying a multi-component aerosol dynamics model. A series of simulations were conducted to determine the effect of the cerium additive and wind speed on the particle size distribution.

The simulations show that application of the cerium additive results in an increased number of nanoparticles (<50 nm) compared to undoped fuel. Particle number decreases as a function of distance from the roadway due to coagulation, deposition, and dilution. However, use of cerium results in a higher number (95% versus 99% reduction) of nanoparticles at 300m from the road. The additive has a mixed effect on number concentration for diameters of 50 nm – 100 nm and reduces the number of particles > 100 nm. Cerium particle number is reduced by ~80% at a distance of 300 m from the road reaching mass concentrations of 0.02 micrograms per cubic meter and ~1% of the cerium agglomerated with soot. 30 to 40% reduction of low- , semi-, and non- volatile organic emissions occur in the presence of the additive at 300m. A wind speed reduction from 1 m/s to 0.5 m/s, decreases dispersion resulting in higher number and mass concentrations at a given distance. Conversely, doubling the wind speed results in lower concentrations.

This study shows how vehicular emissions running on cerium-doped diesel fuel may influence the particle size/composition distribution and cerium concentrations in the near-road environment. Understanding these changes is crucial to assessing the potential impacts of the cerium fuel additive on human health and the environment.

5EN.7

Oxidation of Aerosolized C60 by Ozone. Andrea Tiwari, LINSEY MARR, *Virginia Tech*

Manufactured carbonaceous nanoparticles, such as C_{60} fullerenes, will enter the atmosphere during production, use, and disposal. There, they will be subject to chemical and physical transformations that could modify their properties and ultimately their fate, transport, and toxicity within the environment. The objective of this research is to determine the products and possible environmental impacts of the reaction of C_{60} aerosols with atmospherically relevant concentrations of O_3. C_{60} was aerosolized into a 6 m^3 Teflon chamber through dispersion of the powdered nanomaterial, producing a size distribution that peaked around 100 nm. The aerosols were then exposed to O_3 concentrations of 45-120 ppb at relative humidities of ~15% and ~65%. Following exposure to ozone, aerosols were collected onto filters, copper tape, and copper grids for chemical and physical analysis by high performance liquid chromatography (HPLC), x-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). Results indicated that the reaction proceeded within minutes and appeared to be complete in less than 1 h. Reaction products included $C_{60}O$, $C_{60}O_2$, and $C_{60}O_3$. Continued O_3 uptake and the appearance of a brownish, toluene-insoluble residue suggested the formation of a C_{60} polymer on the aerosol surface. The presence of water vapor enhanced ozone loss, oxygen uptake, the oxygen content of the aerosol surface, and the initial rate of formation for oxide reaction products. Results of assays for reactive oxygen species and mutagenicity indicated that exposure to ozone may affect the toxicity of C_{60} aerosols. At atmospherically relevant O_3 levels, C_{60} may be rapidly oxidized, and this process may affect its fate, transport, and toxicity in the environment.

5EN.8

Physicochemical and Toxicological Characterizations of Laser Printer Emissions. SANDRA PIRELA, Georgios Pyrgiotakis, Bingtao Zhao, Philip Demokritou, *Harvard University*

There is evidence associating the use of laser printers and emission of PM, ozone and VOCs. Recently, there have been concerns associated with the incorporation of engineered nanomaterials into toner formulations to improve quality but the implications on exposures are unknown. In this study, a realistic exposure system was developed to generate exposure atmospheres associated with commonly used laser printers. The printers were placed in a controlled environmental chamber and their emissions monitored during a continuous print job lasting 60 minutes. Real time instrumentation was used to measure emitted particle number concentration, size distribution, mass concentration, ozone, carbon dioxide, carbon monoxide levels, relative humidity and temperature. The effect of various operational parameters, such as warm-up period, drum temperature and page coverage, on the emission profile was investigated. The printers were then ranked based on their emission profiles and the 3 highest emitters underwent further physico-chemical and morphological analysis. Emitted PM was sampled and size-fractionated using the Harvard Compact Cascade Impactor. Morphological examination of the laser printer emissions and toner powder was performed using TEM. Surface chemistry was assessed using EDS. Furthermore, the collected PM was then extracted from the impaction substrates and stabilized in deionized water, followed by characterization for hydrodynamic diameter and zeta potential via DLS. Chemical evaluation included SF-ICP-MS, GC/MS, and organic and elemental carbon analysis. An in vitro toxicological evaluation was done to investigate the biological response of various cell lines to the collected PM. Results show peak emissions to be model-dependent and varied between 3,000 to 1,200,000 particles/cm^3 with modal diameters ranging from 49 to 208 nm. Preliminary toxicological data showed that laser printer emissions may induce biological responses, such as increased pro-inflammatory cytokines and decreased cell viability. These results suggest that printer-emitted particles may be deleterious to lungs of those exposed to them.

5HA.1

Association of Respiratory and Circulatory Hospitalizations with $PM_{2.5}$ Elemental Carbon (EC), Organic Carbon (OC), and Gaseous Co-Pollutants in Pittsburgh, Pennsylvania, during 2001-2002. RICHARD BILONICK, Daniel Connell, Evelyn Talbott, Judith Rager, *University of Pittsburgh*

Time series structural equation models (SEMs) were fitted separately to daily respiratory and circulatory hospitalization counts from Allegheny County, Pennsylvania, from August 2001 to August 2002. Models included two independent daily measurements of fine particulate EC and OC (made using a $PM_{2.5}$ speciation sampler and a collocated semi-continuous carbon analyzer), as well as daily measurements of gaseous co-pollutant concentrations (SO_2, NO, NO_2, CO, and O_3) and mean daily temperature. All air quality measurements were made at a monitoring site located in Schenley Park in the City of Pittsburgh. Respiratory and circulatory hospitalization counts were adjusted for day-of-week effects and holidays. A calibration model encompassing the four carbon measurements was included in each SEM. Ordinarily, calibration with only two methods is not possible without making strong assumptions that cannot be verified. However, given the strong correlation between EC and OC, the use of two correlated congeneric measurement error models (two correlated latent factors - one for EC and one for OC, each with two indicators) allowed estimation of separate scale bias and method imprecision (random error) components for EC and OC. Results indicated that EC and OC had similar and statistically significant scale biases between the two measurement methods, but with substantially different intercepts. Hospitalizations were allowed to depend on latent EC and OC (0-4 day lags), gaseous co-pollutants (0-1 day lags), and temperature (both directly and indirectly through the dependency of latent EC and OC on temperature). In addition, hospitalizations, EC, OC, gaseous co-pollutants, and temperature were each allowed to depend on its previous day's value. In every case, autocorrelation with previous day's values was statistically significant as were temperature dependencies. Preliminary results indicated a differential effect between EC and OC on hospitalizations, although not statistically significant. Among air pollutants, only NO_2 had a statistically significant association with respiratory hospitalization.

5HA.2

Linking Different Exposure Patterns to Internal Lung Dose for Heterogeneous Ambient Aerosols. CHONG KIM, Jung-il Choi,*USEPA*

Particulate matter (PM) in the ambient air is a complex mixture of particles with different sizes and chemical compositions. Because potential health effects are different for different size particles, specific dose of each size and their combination under realistic exposure conditions would be of interest in health risk assessment. In the present study we investigated deposition characteristics of typical bi-modal distribution aerosols under three different inhalation conditions: resting, mild exercise and moderate exercise. Oro-nasal breathing was used for exercise. The bimodal aerosols are composed of two uni-modal distributions having the mass median diameter of 0.3 um and 5 um with GSD of 1.8 and 2.0, respectively. Mass ratios (MR) between the two distributions were varied to simulate various types of aerosols. Total and compartmental lung deposition (TB and AL) were obtained for three size fractions, Ultrafine (PM0.1), Fine (PM0.1-2.5) and Coarse (PM2.5-10), by dynamic transport mathematical model. Results show that for mass deposition, both F and C deposit together in TB and AL with their absolute doses being approximately following MR. During exercise, deposition increases particularly in TB but shows a slight decrease in AL for C while Fine decreases in both TB and AL. UF’s contribution was minimal. For surface area, F and UF deposit at a ratio of 8:2 in both TB and AL. C can contribute substantially only in TB during exercise at MR< 0.5. For number deposition, both UF and F deposit together in both TB and AL at a ratio of approximately 6:4 regardless of exposure conditions. Absolue doses were higher at rest vs. exercise. Contribution of C was negligible. In conclusion, for typical bimodal aerosols UF, F and C deposit together at the same site with varying proportions. Their interactions may be a factor for altering heath risk outcome for multipollutant mixtures.

5HA.3

Effects of Traffic-related Air Pollution on School Children's Pulmonary Function. AFRIM TABAKU, Dile Gjonaj, Mehedi Ndreu, Besnik Serjanaj, *Aldent University*

Introduction: Several studies have indicated that exposure to traffic related air pollutants, proximity of schools and homes to roadsides and motorways, as well as exposure to high rates of road traffic and in particular to truck traffic, increases the risk of respiratory symptoms, and have been associated with decrease of school children pulmonary function. The airborne dust plays a major part in the overall atmospheric pollution and the motor vehicle emissions constitute the most significant source of ultrafine particles in an urban environment.

Material and methods: A cross sectional survey was carried out in 2012 on 114 children living in urban area and in 45 children of suburban area of Shkodra City, measuring pulmonary function and the levels of air pollution of particulate matter, sulfur dioxide, nitrogen oxides, and ozone. The purpose of this survey was to put into evidence differences in pulmonary function of children living and attending schools in urban area, with those of suburban area.

We have used a questionnaire to collect data on sex, current respiratory symptoms, allergy diagnosed by the physician, parent education, smoking habit of parents, presence of animals, synthetic carpets and moulds in their houses. The selection of schools, and children was done by randomized method.

Results: Data obtained by this survey, have shown significant differences between two groups of children, regarding pulmonary function FVC (P=0.0003), FEV1 (P=0.0004), and PEF (P<0.0001). OR of symptoms were for cough 1.92 (CI 1.13–3.56) and phlegm 1.08 (CI 0.95–2.10).

The concentration of PM10 oscillated 10.24-97.00 mcg/m3 and of PM2.5 2.82-71.94 mcg/m3, whereas the levels of other measured pollutants have resulted within recommended levels.

Conclusions: The results of this survey have shown significant differences in values of pulmonary function of the two groups of children. The average concentration of PM10 and PM2.5 in air exceeded recommended TLVs.

5HA.4

Assessment of Gaseous and Particulate Air Pollutants at ATTO and Manaus: The Implication to the Health of Manaus Population. RICARDO H. M. GODOI, Cybelli G. G. Barbosa, Sarah L. Paralovo, Ana Flavia L. Godoi, Rodrigo A. F. Souza, Claudomiro M. Silva, Antonio O. Manzi, Yara S. Tadano, *Federal University of Parana - Curitiba, PR, Brazil*

Amazon region is one of the most significant natural ecosystems on the planet. A major study area involves the interface forest-city, especially by adverse impacts on the human population and vegetation. Therefore, the chosen sampling sites are Manaus city and ATTO, located in Amazon rainforest.

Daily sampling of 2.5 micrometers particulate matter are carried out in both sites. Gravimetric and reflectance data clearly differentiate the dry and rainy seasons, with average of 180 micrograms and 70 micrograms respectively for the urban area, representing a decrease of 0.23 percent in life expectancy for the local population, but considering just the dry season it increases to 1.5 percent, with a daily level peak around 38 percent. XRF indicates presence of significant levels of sodium, aluminum, sulfur, iron, magnesium and calcium, that when combined, may enhance the risk of respiratory diseases. The forest area shows average mass about 50 micrograms, where primarily biogenic elements plus aluminum and silicon are observed.

Size segregated aerosol samples are collected at ATTO for analyses of bulk and single particle elemental and molecular compositions, analyzed by micro Raman spectrometry and electron probe micro-analysis, utilizing facilities for low-Z element determination and XRF.

Considering the harmful effects of gaseous pollutants and the possible influence of BTEX in the formation of secondary organic aerosols, monthly sampling of BTEX, NO_2, SO_2, O_3 and acetic and formic acids from both sites are also studied. Partial results present high concentration of formic acid in the forest area.

Results are interpreted separately and as a whole with the specific aim of identifying compounds that could affect the population's health in Manaus and/or could act as CCN. Chemical analysis supports the elucidation of the possible origins, transport mechanisms, health and main effects of the assessed pollutants in those environments.

5HA.5

A Computationally Efficient Model for Estimating the Social Costs of Air Pollutant Emissions.

JINHYOK HEO, Peter Adams, *Carnegie Mellon University*

The social cost of emitting an air pollutant is defined as the monetized value of the various societal damages caused by that pollutant, including morbidity and mortality, visibility degradation, crop damage, etc. Estimates of the air pollutant social costs are used in a variety of policy analyses such as U.S. EPA's Regulatory Impact Analyses. It involves the quantification of the changes in air quality, the estimation of social impacts from the changes, and the economic valuation of the impacts. Typically, premature mortality due to exposure to PM2.5 is the major contributor to social costs. Existing social cost estimates rely on a reduced-form air quality model, which often does not reflect major achievements made in air quality science in the past decades, resulting in unsatisfactory estimations. That is because even though such achievements are implemented in state-of-science 3-D chemical transport models (CTMs) they have often been too computationally expensive for social costs analysis. Based on the latest version of a 3-D CTM, the Particulate Matter Comprehensive Air Quality Model with extensions (PMCAMx), we developed a computationally efficient model for estimating the social costs of marginal emissions that embraces recent major achievements in air quality science.

5HA.6

Modeling Secondary Particulate Matter Concentrations and Sources for Health Effects Research in California.

JIANLIN HU, Hongliang Zhang, Michael Kleeman, *UC Davis*

Particulate matter (PM) mass is associated with adverse health effects but routine PM measurement data does not provide the exposure information needed to test the detailed relationships between health effects and PM trace chemical components, size fractions smaller than 2.5 µm, or sources other than the top six contributors to PM mass. In previous work we have developed a chemical transport model (UCD_Primary model) to predict exposure fields for ~20 primary PM trace components from ~900 sources in multiple size fractions (including $PM_{0.1}$) over a 7-year period (2000-2006). This study has provided useful information for epidemiological studies to examine the associations between primary PM and health effects. In the present study, we develop and apply the UCD/CIT air quality model to predict the secondary PM concentrations and sources in the same time period to improve our understanding of the relationships between health and secondary PM.

The UCD/CIT model is applied to estimate hourly population weighted concentrations of primary and secondary PM. Source apportionment calculations are included for secondary organic aerosol from 9 sources: onroad gasoline, offroad gasoline, onroad diesel, offroad diesel, wood smoke, food cooking, high sulfur-content fuel, biogenic, and other sources. Gas-phase reactions are simulated using the SAPRC11 chemical mechanism.

The model predictions for gaseous and secondary PM composition are compared to ambient measurements. The current results demonstrate that O_3, NO_2, $PM_{2.5}$, EC agree well with measurements, with monthly mean fractional bias within ±0.2. NO_3^-, NH_4^+ and OC are currently under-predicted in all months. The underlying causes for this discrepancy will be discussed. The model results are used to estimate regional concentration fields and population-weighted exposure for gaseous pollutants and size/chemistry/source resolved secondary PM broken down by source types. Relationships between health effects and secondary PM are explored using the same epidemiological framework employed previously for primary PM health effects.

5HA.7

Deposition of Aerosolized Perfluorocarbon (PFC) in the Lungs of Sprague Dawley Rats. Bahman Asgharian, OWEN PRICE, Jeff Schroeter, Gene McClellan, Jason Rodriguez, Tim Bentley, *Applied Research Associates, Inc.*

The family of perfluorocarbon (PFC) compounds exhibits a strong intra-molecule bonding and high capacity for dissolving a variety of medium and high vapor pressure chemicals. Hence, PFCs have been proposed as a vehicle for pharmaceutical drug delivery. Feasibility testing of this pharmaceutical use is ongoing in different laboratories with large and small animals, such as Sprague Dawley rats. A mathematical model of aerosolized PFC transport and deposition in the lungs of Sprague Dawley rats was developed to determine the amount of the drug deposited in the pulmonary region and, thus, availability for systemic transport to other tissues and organs. A symmetric, typical-path model of the lung geometry for Sprague Dawley rats was developed based on digitized images of the lower respiratory tract. The geometry was used in a multiple-path particle dosimetry model (MPPD, ARA, Raleigh NC) to predict site-specific deposition of PFC particles for different breathing rates, lung volumes, and initial droplet sizes. The model accounted for particle size change by hygroscopic growth and evaporation due to phase change. Deposition in the pulmonary region was highly dependent on the initial size of the particles and PFC physico-chemical properties; thereby allowing the selection of a PFC candidate which demonstrates the greatest deep-lung deposition and delivery to other tissues. By simulating different exposure and inhalation scenarios, the mathematical model of PFC deposition may be used as a fast and inexpensive means to conduct a feasibility study and identify an ideal PFC candidate based on its ability to deliver drugs to target sites. This study was funded by the Office of Naval Research, contract number N00014-12-C-0624.

5HA.8

Probabilistic Modeling and Bayesian Updating of Concentrations of Carbon Monoxide and Fine Particulate Black Carbon in Fort Collins, Colorado for Exposure Estimation. DANIEL MENDOZA, Amy L. Stuart, Getachew Dagne, *University of South Florida*

Estimates of commuter exposure to air pollution are necessary to inform urban design and public health policy. The lack of highly resolved spatial and temporal exposure estimation methods along with incomplete uncertainty estimates have been major hindrances toward obtaining representative exposure information.

We present the development and first stage of application of a modeling system that will ultimately estimate urban commuter exposures at high resolution with specific representation of uncertainty. We first generated emissions of select traffic-related pollutants at a high spatiotemporal resolution for the study area of Fort Collins, Colorado. Uncertainty and variability in dispersion model input data, including emissions, were also identified and tabulated. This information was used to define probabilistic distributions of inputs. A stochastic code was applied to sample the input distributions and perform ensemble dispersion simulations. The sampling strategy was designed to produce probabilistic estimates of spatial fields of concentration for a sample defined by hour of the day, day type, and season. Fields were produced at 500m x 500m spatial resolution for the 10 km x 10 km study region. Concentration results were compared to monitoring data for evaluation of the concentration estimates. A Bayesian updating procedure was subsequently developed to assimilate monitoring data into posterior estimate of concentrations. The next step of modeling system development will use the posterior concentrations to estimate route- and mode-specific exposures.

Prior estimates of spatial fields of ensemble mean concentration for two pollutants (carbon monoxide and fine particulate black carbon) are presented and discussed. Fields representing cumulative distribution statistics for these estimates highlight spatial locations and hours of high variability/uncertainty. Results of the graphical and statistical comparison of prior model estimates with data from stationary and personal monitoring provide evaluation information. Preliminary results of posterior concentration distributions produced by the Bayesian updating procedure are also provided.

5ST.3

A Novel Method for Reliable Long-term Assessment of Exposure to Traffic-related Air Pollution Mixtures. NATALIA MYKHAYLOVA, Kelly Sabaliauskas, Jon M Wang, Ezzat Jaroudi, Cheol-Heon Jeong, Jeff Brook, Greg J. Evans, *SOCAAR, University of Toronto*

Exposure to air pollutant mixtures at high temporal and spatial resolution is an important predictor for many respiratory and cardiovascular conditions and its accurate assessment remains the holy grail of air quality monitoring. However, attaining high temporal resolution data of multiple pollutants, while maintaining low cost and reliable long-term performance, remains a challenge.

To address this issue, we conducted a thorough investigation of 30 different low-cost commercial gas and particulate matter sensors from 5 manufacturers. The types compared included n-type MOS, p-type MOS, optical, and electrochemical sensors. We identified the best-performing sensors through controlled lab calibrations and long-term ambient inter-comparisons between sensors and standard real-time measuring techniques. Best-performing sensors for detection of nitrogen dioxide, carbon monoxide, ozone, volatile organic compounds, fine particulate matter and coarse particulate matter, were selected, further optimized and integrated into a portable sensor array system. Temperature and humidity sensors were included for data normalization. We evaluated the performance of sensors in field during two 2-week deployments in winter and summer, using a network of high time-resolution sensor array devices deployed at 5 different locations within a 30km radius of downtown Toronto. These deployments allowed long-term sensor performance to be evaluated under different meteorological conditions as well as different ranges of pollutant concentrations.

The portable sensor array system was shown to be sensitive enough to measure ambient levels of pollutants even in Toronto's relatively clean air. Specifically the system could detect concentrations as low as 5ppm level for total volatile organic compounds, 20 micrograms per meter cubed for fine particulate matter, 5ppb for ozone, 15ppb for nitrogen dioxide and 400ppb for carbon monoxide. The pollutant levels showed large variation both temporally and spatially, indicating the importance of high resolution monitoring. Methods for evaluating measurement accuracy and precision as well as reducing measurement biases will be discussed.

5ST.4

Personal Exposure Results for the M-Pod, a Portable Low-Cost Air Quality Monitor. MICHAEL HANNIGAN, Ricardo Piedrahita, Nicholas Masson, John Ortega, Yifei Jiang, Xiang Yun, Kun Li, Qin Lv, Robert Dick, Li Shang, *University of Colorado at Boulder*

Portable low-cost air quality monitors (M-Pods) were deployed in a two-week user study in Boulder and Denver, Colorado. Personal exposure assessment and instrument validation results are presented. M-Pods use metal oxide semiconductor sensors for measurement of NO2, CO, O3, and total VOCs, while CO2 is measured using an NDIR sensor. 10 M-Pods were carried by 6 users, with 4 users carrying 2 M-Pods each. Pre and post calibrations were performed by co-locating the instruments with reference monitors operated by the Colorado Department of Health and Environment (CDPHE). Inter-M-Pod variability was assessed, and data quality was checked by placing reference monitors for O3, CO2, and CO, in a location that was frequented by the users. The check-ins with reference instruments were used to analyze sensor drift and inter-M-Pod agreement over time. The M-Pod sensors exhibited low inter-sensor variability and little drift over the study period in most cases. Personal exposure data is presented for CO2, NO2, CO, O3, and total VOCs. Concentrations were generally quite low, but exhibited significant spatial variability. User experiences are recounted, and thoughts on sensor quantification and feasibility of wide adoption are shared.

5ST.5

Laboratory and Field Evaluation of the UCB-PaCO (Particle and Carbon Monoxide) System: A Portable, Robust, and Low-cost Platform for Monitoring Combustion-related Household Air Pollution. AJAY PILLARISETTI, David Holstius, Michael Johnson, Tracy Allen, Dana Charron, David Pennise, Edmund Seto, Kirk Smith, *University of California, Berkeley*

The UCB-PaCO (Particle and Carbon Monoxide) is a modular, low-cost, robust, portable data-logging sensor platform for assessing concentrations of combustion byproducts related to household energy use in the developing world. PaCO monitors combine an off the shelf light-scattering chamber with commercially available CO sensors. Each monitor can log continuous 1-minute data for over three weeks on three AAA batteries. The Platform for Integrated Cookstove Assessments (PICA) ingests data from both UCB-PaCO sensors. Additional datastreams from commercial pollution monitors and from simple data-logging thermometers used as stove use monitors can also be processed in PICA.

Multiple UCB-PaCOs were tested in the laboratory against other commercially available CO and PM instruments and against the previous generation UCB-PATS (Particle And Temperature Sensor). Simultaneous gravimetric sampling was also conducted, allowing for calibration of light-scattering devices. Two CO sensors were evaluated and were calibrated against span gas before and after laboratory testing. Inter- and intra-device comparisons are presented.

Laboratory testing showed high correlation between the particle responses of UCB-PaCO and commercial devices (r = .87). The CO sensors evaluated differ in sensitivity and design. Newly available electrochemical CO sensors were found to have fast response and good precision, low sensor-to-sensor variability in baseline and sensitivity parameters, minimal power requirements, and linear responses even at low (0.10–10 ppm CO) concentrations.

UCB-PaCOs were deployed for 48 hour periods each during household air pollution assessments in Kaski District, Nepal, where they were collocated with the UCB-PATS and other commercially available PM and CO sensors and gravimetric samplers. Factors affecting performance and usability were assessed, including battery life, simplicity of operation, and overall utility of PICA in the field. Kitchen and ambient concentration data are presented for CO and PM. Inter- and intra-device comparisons are highlighted.

5ST.6

Air Quality Networks using Amperometric Gas Sensors and Providing the Required Temporal and Spatial Spaces. JOHN SAFFELL, Roderic Jones, Mohammed Mead, Ronan Baron, Dean Kavanaugh, Wah On Ho, *Professor, Atmospheric Chem Group, Univeristy of Cambridge*

Wireless air quality networks are being deployed throughout North America and Europe. Deployment of both mobile and fixed site networks in Cambridge, Valencia etc. as well as Heathrow airport have taught us the value of fine temporal and spatial resolution, required by the urban fluid dynamics modellers.

Additionally, mobile mapping with GPS has shown the importance of mapping in real time whilst also referencing to AQMs for data that is accurate and on time. Trials with these low cost networks located adjacent to AQMs shows that these networks are not only trending networks but also reliable absolute measurements.

We will demostrate the combined capabilities of:

1 ppb capable amperometric gas sensors
2 low noise potentiostatic circuitry
3 Geotech capability to broadcast measurements with required time resolution
3 Cambridge University data analysis which ensures reliable sensor data transfer into useful citizen data.

5ST.7

Validating the Performance of the RTI MicroPEM to Support Indoor Air Pollution Exposure Health Studies. Charles Rodes, Ryan Chartier, J. Randall Newsome, James Carlson, JONATHAN THORNBURG, *RTI International*

The RTI MicroPEM Personal Exposure Monitor was recently developed to measure sized particulate matter (PM) for both personal and indoor exposures, including strong source indoor air pollution (IAP) settings such as cookstove environments. Performance validation data have yet to be summarized to gauge level of readiness and improvement in uncertainty over prior art technologies.

Currently, MicroPEM performance is being validated via a combination of domestic and in-country IAP settings. Performance parameters investigated include precision, accuracy, representativeness, data capture rates, and ease of deployment. We used data from a 50 residence Sri Lanka cookstove study to determine consistency with these findings.

Integrated and real-time MicroPEM data were collected during laboratory, domestic and in-country deployment settings. Available performance data were compiled, including in-country usability and deployability information, to characterize MicroPEM performance as related to performance goals, as well as to compare to alternative filter and real-time sampling techniques.

The accuracy of the MicroPEM against a pseudo-referee sampler (MSP PEM) during simulated solid fuel cookstove IAP showed a positive bias of 3.8 percent for PM2.5. Collocated MicroPEMs deployed in Sri Lankan homes yielded a relative standard deviation (RSD) of 11.6% for PM2.5. A smaller RSD value of 2.4% was obtained during a domestic (US) exposure study. Ease of deployability led to a valid data capture rate in Sri Lanka that exceeded 97.5%.

To date, the v3.2 MicroPEM has met all performance goals. Factors such as accuracy, precision, and representativeness are excellent, even when operating in strong source IAP settings. Deployability is simple resulting in valid data capture rates exceeding 97%. In-country testing in Sri Lanka demonstrated the viability for local deployments by modestly trained non-technical field staff. Although a quantitative comparison to a true referee exposure metric is needed, the performance of the MicroPEM in IAP settings was excellent.

5ST.8

BEACON: A High Density Urban Network for Observing Air Quality and Greenhouse Gases. RONALD COHEN, Virginia Teige, Katja Weichsel, David Holstius, Andrew Hooker, Holly Maness, *UC Berkeley*

BEACON (www.beacon.berkeley.edu) is a new instrument designed to map urban concentrations of greenhouse gases a (CO2) nd criteria pollutants (CO, NO2, O3) with high spatial resolution (2km) and time resolution of minutes. The initial pilot consists of separate nodes functioning as a single instrument and spanning Oakland, CA and the surrounding cities to the north and south and extending across the Bay to San Francisco. Performance of the instrument and initial results will be described.

6AC.1

OH-initiated Heterogeneous Oxidation of Cholestane: A Model System for Understanding the Aging of Cyclic Alkane Aerosols. HAOFEI ZHANG, Chris Ruehl, Arthur Chan, Theodora Nah, David Worton, Gabriel Isaacman, Allen H. Goldstein, Kevin Wilson, *Lawrence Berkeley National Laboratory*

Aliphatic hydrocarbon aerosols play a substantial role in the urban atmosphere, in which cyclic alkanes make up a large fraction in certain types of particulate matter, such as diesel particles and motor oil particles. In the present study, cholestane ($C_{27}H_{48}$) was selected as a model compound for cyclic alkanes and OH-initiated heterogeneous oxidation experiments were conducted in a flow tube reactor. OH exposure was varied in the experiments, corresponding to a chemical lifetime in the atmosphere of up to one week. Oxidation products were collected on filters and analyzed using the soft ionization gas chromatography technique. By using this technique, most of the functional isomers can be separated and quantified. The analysis suggests that the first-generation functionalization products (cholestane ketones and alcohols) are the dominant reaction products that account for up to 80% of total speciated compounds. In contrast, fragmentation products and higher-generation functionalization products are much less abundant (less than 5%). Of the fragmentation products, $C_{21}H_{34}O$, is formed in the largest abundance, suggesting the potential importance of cleaving bonds with tertiary carbon atoms during oxidation. In addition, the concentration ratios of first generation ketones to alcohols were close to one at every oxidation level. The alcohol group was found to be more abundant on the ring (~20%) of cholestane, in contrast to the ketone groups, which form preferentially on the aliphatic side chain (~50%). These results provide new insight into the heterogeneous oxidation mechanism of cyclic alkanes.

6AC.2

O_3-initiated Heterogeneous Oxidation of Fatty Acids. Chunbo Leng, Guang Zeng, Hai Pham, Yunhong Zhang, YONG LIU,*University of Colorado Denver*

Despite recent extensive studies towards heterogeneous oxidation of unsaturated organics initiated by ozone, our current knowledge about effects of ambient temperature, physical state, relative humidity, ozone concentration, particle size, and structural isomerism on chemical transformation of organic aerosols, in particular reaction kinetics is still scarce. In this work, we used ATR-IR flow reactor and a variety of unsaturated fatty acids including oleic acid, linoleic acid, linolenic acid and erucic acid as proxies for atmospheric unsaturated organics to investigate their heterogeneous oxidation by ozone, aiming at better understanding the effects of ambient temperature, physical state, relative humidity, ozone concentration, particle size, and structural isomerism on the heterogeneous reaction and overall reactive uptake. In the work, pseudo-first order rate constants and overall reactive uptake coefficients were acquired from absorbance changes in peak located near 1710 cm-1 which can be assigned to C=O in carboxylic acid. Experimental results showed that heterogeneous loss of ozone onto fatty acids could have very strong temperature dependence, depending on species and their physical states. Particle size and ozone concentration appeared to play important roles in reaction kinetics; in contrast, the effects of relative humidity and structural isomerism were seemingly less significant. Results also showed that heterogeneous reactions proceeded via Langmuir-Hinshelwood mechanism.

6AC.3

Hydroxyl Radical Mediated Aging of Oxidized Dodecanoic Acid Particles. JOSEPH KLEMS, W. Sean McGivern, *National Institute of Standards and Technology*

The hydroxyl (OH) radical initiated oxidation of organic species in the atmosphere represents a major source of secondary organic aerosol (SOA) and plays an important role in aerosol aging. In this work, the evolution of SOA generated from the oxidation of dodecanoic acid (DDA) was investigated as a function of OH radical exposure. In these experiments, OH radicals were generated in a quartz flow tube outfitted with 254 nm ultraviolet lamps and an adjustable shade via the photolysis of ozone in the presence of water. The OH radical exposure was varied by changing the length of the shade, and the resulting particles were collected on a filter and subjected to offline LC/MSn and GC/MS analyses. The use of a carboxylic acid precursor greatly facilitated the identification of a number of products, as they produced an abundance of ions in the negative mode mass spectrum. The major products were then quantified using chemical derivatization coupled to LC/MS2 experiments. At short OH exposures, structural isomers of oxo-DDA and hydroxy-DDA comprised the bulk of the particle mass, with some of the later undergoing cyclization to form alkyl-substituted lactones. Other SOA products detected included trace levels of DDA diketones, hydroxyketones and C6 - C10 oxo-acids, with each product demonstrating a variety of isomeric forms. Increasing the OH radical exposure decreased the relative concentration of the long chain products and substantially increased the concentration of the shorter chain products. This observation indicates that as the particles age, chain degradation becomes an increasingly important process, even for long chain organic molecules in a NOx free environment. The ability to track the aging of particle-phase products on the molecular level provides insights into the chemical processes that contribute to their formation not possible with other popular techniques.

6AC.4

Constraining the Contribution of Organic Acids to Organic Aerosol Using MOVI-HRToF-CIMS and AMS data.LAXMINARASIMHA YATAVELLI, Harald Stark, Douglas Day, Samantha Thompson, Brett Palm, Pedro Campuzano-Jost, Joel Kimmel, Manjula Canagaratna, Michael Cubison, Joel Thornton, John Jayne, Douglas Worsnop, Jose-Luis Jimenez, *University of Colorado, Boulder*

Using data collected during the Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H2O, Organics & Nitrogen - Rocky Mountain Biogenic Aerosol Study (BEACHON-RoMBAS; http://tinyurl.com/BEACHON-RoMBAS, July-August 2011) we estimate organic acid contribution (f_{acid}) to organic aerosol (OA) in a ponderosa pine forest. Organic acids were measured using a micro-orifice volatilization impactor high-resolution time-of-flight chemical ionization mass spectrometer (MOVI-HRToF-CIMS; Yatavelli et al., AS&T, 2012) with acetate as the reagent ion. Organic aerosol mass concentration was measured using an Aerodyne aerosol mass spectrometer (AMS). During the BEACHON-RoMBAS, we observed strong correlations between MOVI-HRToF-CIMS measured organic acids and OA. Molecules containing one or more organic acid functional group contributed approximately 45% of the OA mass. Organic acid functional groups are also observed to correlate strongly with the AMS mass fragment (m/z 44, CO_2^+ ion) generally used as a marker for highly oxidized aerosol. We observe, on a molar basis, 2 acid molecules per CO_2^+ ion. We develop an empirical relationship between the f_{acid} and f_{44} (ratio of m/z 44 ion to total OA). Finally, using this new f_{acid} - f_{44} relationship and f_{44} data from AMS measurements at various sites worldwide (Ng et al., ACP, 2010, and other studies), we estimate that molecules containing carboxyl group constitute 30-80% of OA.

6AC.5

Synchrotron Studies of the Heterogeneous Oxidation of Organic Aerosols. MICHAEL WARD, Kevin Wilson, *Lawrence Berkeley National Laboratory*

Understanding the relative importance of individual mechanistic pathways involved in the heterogeneous oxidation of organic aerosols offers the potential to tune such reactions toward favored outcomes. An important tool in attempting to disentangle the contribution of individual mechanistic pathways to the overall oxidation process is to study the kinetic evolution of aerosol oxidation products. While mass spectrometric techniques are typically used to study the kinetics of such heterogeneous oxidation reactions, the complex fragmentation patterns of large organic molecules can make it difficult to distinguish between positional isomers of the oxidation products. On the other hand, the exact identities of the oxidation products are typically determined using chromatographic techniques which do not readily lend themselves to kinetic studies.

Using the VUV light available at the Chemical Dynamics beamline of the Advanced Light Source synchrotron to ionize the oxidation products of model organic aerosols with minimal fragmentation, we are able to distinguish between different positional isomers of these oxidation products in real time using aerosol mass spectrometry. Consequently we have been able to determine the kinetic evolution of the separate positional isomers of oxidized aerosol species for the first time. These aerosol oxidation reactions are initiated by OH radicals and studied in a continuous flow stirred tank reactor (CFSTR) at atmospheric pressure. The experimental data indicate that, at low OH exposures, the OH radicals predominantly abstract hydrogen atoms from tertiary carbons, whilst the yields of positional isomers corresponding to attack at secondary carbons are seen to reach a maximum at higher OH exposures.

6AC.6

Size Distribution Dynamics Reveal the Importance of Particle-Phase Chemistry in Organic Aerosol Formation. Manabu Shiraiwa, LINDSAY YEE, Katherine Schilling, Christine Loza, Jill Craven, Andreas Zuend, Paul Ziemann, John Seinfeld, *California Institue of Technology*

Organic aerosols are ubiquitous in the atmosphere and play a central role in climate, air quality and public health. Particle size distribution is a key in determining their optical properties and cloud condensation nuclei activity. The dominant portion of organic aerosols is formed through gas-phase oxidation of volatile organic compounds, so-called secondary organic aerosol (SOA). Combining chamber experiments and kinetic flux modeling, here we show that particle-phase chemistry needs to be considered for accurate prediction of size distribution as well as mass concentration and carbon oxidation state of SOA. The particle-phase reaction mainly proceeds at the surface and its reaction products contribute to SOA mass substantially. Chamber experiments with aldehyde injection strongly confirm that the particle-phase reactions with organic hydroperoxides forming peroxyhemiacetals can lead to large increase in SOA mass. The results highlight the need for consideration of particle-phase chemistry and size distribution dynamics in atmospheric aerosol models.

6AP.1

Calculations and Measurements of the Collision Cross Sections of Sub-2.0 nm Metal Iodide Clusters in Air. HUI OUYANG, Carlos Larriba-Andaluz, Derek Oberreit, Christopher Hogan Jr., *University of Minnesota*

In the free molecular regime, electrical mobility can be related to the collision cross section (CCS) of charged particles and ions. To distinguish possible particle candidate structures from one another, calculations of CCS with proper gas molecule scattering model are required for comparison with measurements. The elastic hard sphere scattering (EHSS) model is widely used in CCSs calculations for comparison to CCS measurements made in Helium background gas, while the gas molecule scattering law in polyatomic gas background remains under controversy. In this work, a diffusive hard sphere scattering (DHSS) model is proposed for CCS measurements in polyatomic gas, which, when applied to a spherical particles, leads to results in excellent agreement with the free molecular limit of the semi-empirical Stokes-Millikan equation. To examine this scattering law, the electrical mobility in air of singly and doubly charged Sodium, Potassium, Rubidium, and Cesium Iodide cluster ions (positively charged) are measured via a high resolution parallel-plate differential mobility analyzer coupled to a time of flight mass spectrometer (DMA-MS). Candidate structures corresponding to the measured ions are generated through density functional theory (DFT) calculations. CCSs calculations for these candidate structures are performed with both EHSS and DHSS models accounting for the influence of gas molecule polarization, and compared to the measured CCSs. In general, DHSS predictions are found in better agreement with measurements than are EHSS predictions, though the measurement agreement with DHSS predictions and disagreement with EHSS predictions both decrease with increasing cation mass in cluster ions, which suggests neither EHSS and DHSS can fully describe the scattering rule for all four salt ion clusters. Further, the influence of polarization in air is found to have a non-negligible effect on CCSs of the examined cluster ions.

6AP.2

Aggregation and Growth Kinetics in the Transition Regime. THASEEM THAJUDEEN, Hui Ouyang, Ranganathan Gopalakrishnan, Christopher Hogan Jr., *University of Minnesota*

Aerosol particle growth is driven by particle-particle collisions (coagulation/aggregation) in many instances, most notably high temperature combustion and synthesis systems. Described in this presentation, through dimensionless analysis of the collision process and Langevin based mean first passage time calculations, we have derived a universal collision rate coefficient/kernel (expressed in dimensionless form H) valid for aerosol particles of arbitrary shape across the entire diffusive Knudsen number (Kn_D: the ratio of the mean persistence path of the colliding entities to an appropriate collision length scale) range for particle-particle collisions, and further extended this collision kernel to account for the influence of van der Waals potentials. Using this collision kernel for spheres, we have used constant number Monte Carlo simulations to examine particle growth via collisions in the transition regime, in which both the average diffusive Knudsen number and momentum transfer Knudsen number (gas molecule mean free path/particle length scale) evolve over time, decreasing monotonically. A universal curve for spherical particles is found, describing the rate of change in diffusive Knudsen number relative to the change in Knudsen number, and this curve is further found valid when van der Waals potentials are considered.

After examining spherical particle growth, we have used Brownian dynamics calculations to examine the evolution in average diffusive Knudsen number and Knudsen number of aggregating particles, i.e. particles which do not coalesce upon collision and therefore do not remain spherical. Through these simulations a distinctly different evolution through the transition regime is found; this indicates that the degree of sphericity of particles undergoing isothermal collisional growth can be determined simply through monitoring the average Knudsen numbers.

6AP.3

Mesoscale Simulations of Nanoparticle Growth by Coagulation and Sintering in the Free Molecular Regime.

MAX L. EGGERSDORFER, Sotiris E. Pratsinis, *ETH Zurich*

Aerosol technology is used routinely in large scale production of commodities like pigmentary titania, carbon black and fumed silica and recently also for sophisticated materials from catalysts to devices and even biomaterials and nutritional products (Strobel and Pratsinis, 2007). The dynamics of aerosol reactors and product nanoparticle characteristics span 10-15 orders of magnitude in length and time scale and require interconnected models for systematic design that can be distinguished into continuum, mesoscale, molecular dynamics and quantum mechanics (Buesser and Pratsinis, 2012). One important, if not the most important, design criterion is the high temperature particle residence time. It determines the nanoparticle growth by gas and surface reaction, coagulation and sintering. Typically the chemistry is so rapid that coagulation and sintering control particle growth.

Here, the formation of nanoparticles by coagulation and sintering is simulated in the free molecular regime by a discrete element method (DEM, mesoscale) at volume fraction, phi=10^{-7}, following the trajectories of up to 16×10^6 particles. The formation of agglomerates is traced in time to extract the detailed collision frequency. Aggregate sintering is modeled by a multiparticle viscous flow sintering mechanism intrinsically accounting for the primary particle polydispersity and aggregate structure (Eggersdorfer et al., 2011). So the relation between structure, coagulation and sintering rate is fully resolved. It is found that the ratio of characteristic sintering, tau_s, to collision time, tau_c, solely defines the aggregate structure independent of process conditions. Modified collision kernels are proposed and applied with continuum models (monodisperse and sectional). Furthermore, detailed aggregate size distributions are studied quantitatively to determine the fractions of spherical particles, aggregates and agglomerates.

Buesser, B. and Pratsinis, S.E. (2012) Annu. Rev. Chem. Biomol. Eng. 3, 103-127.
Eggersdorfer, M.L., Kadau, D., Herrmann, H.J. and Pratsinis, S.E. (2011) Langmuir 27, 6358-6367.
Strobel, R. and Pratsinis, S.E. (2007) J. Mater. Chem. 17, 4743-4756.

6AP.4

A Collision-Based Model for the Kinetics of Bacteriochlorophyll c Self-Assembly in Methanol-Water Solution.

GERARD LAKIN, Vivek Shah, Gregory Orf, Robert Blankenship, Pratim Biswas, *Washington University in St. Louis*

Dye-sensitized solar cells (DSSCs) have received a great amount of attention in recent years as a potential low-cost alternative to single crystal silicon solar cells. To improve the efficiency of DSSCs it is necessary to develop dyes that are capable of absorbing a wide spectrum of incident wavelengths with a large extinction coefficient while maintaining effective charge transfer to the oxide substrate. Naturally occurring photosynthetic light-harvesting complexes (LHCs) have generated interest as models for highly efficient light absorption and transfer. The chlorosome LHC is capable of photosynthesis at low and diffuse illumination levels due to the high order of the bacteriochlorophyll (BChl) c pigment structures, which are assembled with almost negligible influence from proteins. It is possible to self-assemble light-harvesting antennae from BChl c for use in a DSSC. We propose to utilize electrospray to simultaneously self-assemble and deposit pigment antennae, making use of the monodispersity of electrospray droplets to control the size of deposited structures. In order to fully make use of electrospray deposition technique we must understand the kinetics of self-assembly.

In this study we have performed kinetic self-assembly experiments for BChl c in bulk methanol-water solutions and developed a collision-based empirical model that successfully describes the rate of monomer integration into self-assembled aggregates. Various methods were tested: modification of the Brownian collision rate by various interaction forces, the modification of the rate for slower growth, and others will be described in the presentation. We have performed experiments showing the time dependence of the full UV-visible absorbance spectra as well as the time dependence of the peaks at 670 nm and 740 nm which represent the monomer and self-assembled aggregate concentrations, respectively. The model fits our data to determine the time-dependent collision frequency, fraction of collisions that result in assembly, and the equilibrium monomer concentration.

6AP.5

Modeling of Nanoparticles Synthesis in Inverted Flames. IGOR NOVOSSELOV, Christopher Stipe, Rajan K. Chakrabarty, Hans Moosmuller, *Enertechnix Inc*

Combustion synthesis has proven to be a cost effective method for producing a diverse array of nanomaterials. Fundamental knowledge, gained through scientific studies of flame chemistry and aerosol kinetics, makes it possible to engineer nanoparticles with novel physical, thermal, electrical, and biological properties. Modeling of the combustion process can be used to gain insight into the fluid dynamics and flame structure, which are essential to understanding both combustion and aerosol gel formation processes.

We have investigated a recently reported phenomenon of formation of carbon superaggregates (SAs) from a reversed gravity (i.e., downward) diffusion flame. In order to investigate the process of aerosol gel synthesis, 2D transient CFD simulations were performed for acetylene and methane flames. Acetylene combustion was modeled using three-step acetylene oxidation chemistry. Reduced methane-air oxidation chemistry was used for methane combustion system. The species, flow and energy equations were coupled to the soot formation/oxidation chemistry and discrete ordinates (DO) radiation model. The simulation showed good qualitative and quantitative agreement with the experimental data for flame length, measured surface temperatures and soot production location.

6AP.6

Evaluating the Mobility of Nanorods in Electric Fields. MINGDONG LI, Rian You, George Mulholland, Michael Zachariah,*University of Maryland*

The mobility of a nonspherical particle is a function of both particle shape and orientation. In turn the higher magnitude of electric field causes nonspherical particles to align more along the field direction, increasing their mobility or decreasing their mobility diameter. In our previous works, we developed a general theory for the orientation-averaged mobility and the dynamic shape factor applicable to any axially symmetric particles in an electric field, and applied it to the specific cases of nanowires and doublets of spheres. The experimental results of doublets of NIST traceable size standard PSL particles with primary spheres larger than 127nm were shown to be in excellent agreement with the expected values based on our theory. In this work, the theory for a nanowire is compared with experimental results of gold nanorods with known shape determined by TEM images. We compare the experimental measured mobility sizes with the theoretical predicted mobility in the continuum, free molecular, and the transition regime. The mobility size shift trends in the electric fields based on our model, expressed both in the free molecular regime and in the transition regime, show in good agreement with the experimental results. For rods of dimension: width dr=17 nm and length Lr=270 nm, where one length scale is smaller than the mean free path and one larger, the results clearly shows that the mobility of an object is most controlled by the smallest dimension. In this case the free molecule transport properties best represented our nanorod. The net charge effect on the particle alignment was also evaluated and indicated for a conducting particle, that while the electrophoretic velocity is net charge dependent, the actual orientation of the particle is not.

6CA.1

Chemical and Optical Properties of Biomass Burning Aerosol. ROYA BAHREINI, Joshua P. Schwarz, Anne Perring, Daniel Lack, Justin Langridge, Francesco Canonaco, Andre Prévôt, John Holloway, Carsten Warneke, Jessica Gilman, Brian Lerner, Joost de Gouw, Ann Middlebrook, *University of California, Riverside*

Biomass burning (BB) is a large source of organic and inorganic species in both the gaseous and condensed phase. Toxicity of some of the BB components is an air quality concern in areas downwind of the fires. In addition, emissions of primary or secondary light absorbing species (black carbon (BC) or brown carbon (BrC)) may have regional and global climate impacts. Here we present results from fresh (Schultz Fire, AZ and 4-Mile Fire, CO) vs. long-range transported (ARCPAC field study) biomass burning emissions, sampled by an aerosol mass spectrometer (C-ToF-AMS) and a single particle soot photometer (SP2) for aerosol chemical characterization and by a cavity ring-down spectrometer (CRDS), a photoacoustic spectrometer (PAS), and/or a particle soot absorption photometer (PSAP) for aerosol optical characterization. Auxiliary gas phase measurements are also available for overall characterization of the air masses. We perform factor analysis on the organic aerosol (OA) mass spectra to determine the contribution of biomass-burning organic aerosol (BBOA) in the different fires and examine relations between BBOA and other tracers in the OA spectra with the optical measurements. Our analysis of the fresh BB emissions in the 4-Mile Fire indicates that there is a linear relationship between the mass absorption efficiency (MAE) of OA at 404 nm and the ratio of levoglucosan-related fragment (m/z 60) to oxidized OA fragment in the AMS (m/z 44) [Lack et al., ACP, 2013], indicating contribution of BB-related compounds in the condensed phase to BrC. Results from the factor analysis and optical measurements indicate that MAE of OA approached 1.6 m2/g in the most intense BB plumes, i.e., periods when BBOA mass fraction was ~1. We will expand our analysis of the 4-Mile Fire and extend it to the other datasets indicated above in order to link BB aerosol chemistry with climate impacts of BrC in biomass burning.

6CA.2

Secondary Organic Aerosol Formation from Gasoline and Diesel Vehicle Emissions Using a New Flow Reactor. JAY SLOWIK, Ru-Jin Huang, Stephen Platt, Simone Pieber, Imad El Haddad, Alessandro Zardini, Ricardo Suarez-Bertoa, Stig Hellebust, Brice Temime-Roussel, Nicolas Marchand, Urs Baltensperger, Covadonga Astorga, Andre Prévôt, *Paul Scherrer Institute*

Vehicle emissions significantly impact air quality, especially in urban areas with high traffic flow. Many previous studies have investigated direct emissions of vehicle trace gases and particulate matter (PM), although recent studies indicate that the secondary organic aerosol (SOA) formation dominates the total vehicle PM burden. Nevertheless, relevant studies of SOA formation from vehicle emissions remain very scarce. Flow reactor systems provide a highly oxidizing environment that simulates atmospheric oxidation processes occurring on the order of one to several days using a reaction time of only a few minutes. This provides time-resolved measurements of the secondary aerosol production potential that is particularly useful for assessing vehicle emissions as a function of engine load.

Here we present initial measurements of SOA formation potential from modern (Euro 5) gasoline and diesel cars using a new flow reactor system conducted at the vehicle test facilities at the European Commission Joint Research Centre (Ispra, Italy). Vehicle exhaust emissions from a New European Driving Cycle were sampled either i) directly into the flow tube from a constant volume sampler (CVS) or ii) first into a smog chamber and then through the flow reactor. Within the reactor, emissions are exposed to OH radicals generated from either ozone or HONO-based sources. The reactor output is sampled by a movable sampling probe, enabling OH concentration and reaction time to be varied independently while maintaining the same OH exposure (OH exposure = concentration x time). Particle and gas-phase composition were quantified using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and a time-of-flight proton transfer reaction mass spectrometer (PTRTOF-MS), respectively. The amount and composition of SOA was observed to depend on both vehicle type and driving cycle phase.

6CA.3

New Particle Formation Increases CCN Yield in Veldt Fire Plumes in Southern Africa. VILLE VAKKARI, Johan Paul Beukes, Petri Tiitta, Andrew D. Venter, Kerneels Jaars, Miroslav Josipovic, Pieter G. van Zyl, Veli-Matti Kerminen, Markku Kulmala, Lauri Laakso, *University of Helsinki, Helsinki, Finland*

Biomass burning is one of the largest sources of carbonaceous aerosol particles and several trace gases in the atmosphere. In southern Africa, barring the industrial hub around Johannesburg, wild fires and prescribed burning are the most important source of aerosol particles during the dry season, from June to September. In this study, combining remote sensing fire observations to ground-based long-time measurements of aerosol particle and trace gas properties at the Welgegund measurement station (www.welgegund.org), we have been able to follow the time evolution of veldt fire plumes up to several hours in the atmosphere in both day and night time conditions.

From May 20th 2010 to April 15th 2012 altogether 61 veldt fire plumes were observed at Welgegund. Approximately 50% of the time the plumes were transported in fully dark and 20% of the time in daylight conditions. The evolution of the aerosol size distribution was rapid for five hours after the emission: during this period the growth rate of the fire aerosol count mean diameter (size range 12 to 840 nm) was 24 nm h^{-1} in daytime plumes and 8 nm h^{-1} in nighttime plumes. The online chemical composition measurements show a factor of 2.5 higher organic aerosol emission ratio in daytime plumes compared to nighttime plumes.

New particle formation in daytime plumes was found to increase the number of particles larger than 100 nm (N100) so that after three hours the N100 emission ratio was two to three times as high as the initial emission, indicating that in daylight conditions most CCN-sized particles in a veldt fire plume originate in nucleation within the plume. In the nighttime plumes no new particle formation was observed, but during the first two hours the N100 emission ratio did increase, although substantially less than in the daytime plumes.

6CA.4

Sources and Light Absorption Properties of Water-Soluble Organic Carbon in Beijing. ZHENYU DU, Kebin He, Fengkui Duan, Yuan Cheng, Jiumeng Liu, Rodney Weber, *Tsinghua University*

We investigated the sources and light absorption properties of PM2.5 water-soluble components in Beijing via samples collected from October 2011 to November 2012. Light absorption of PM2.5 water-soluble components at 365 nm (Abs365), used as a proxy for water-soluble brown carbon, correlated well with water-soluble organic carbon (WSOC) (monthly r2 always higher than 0.84), which suggested similar sources for WSOC and water-soluble brown carbon, though concentrations varied a lot among seasons. In winter, levoglucosan correlated well with both WSOC and Abs365, suggesting biomass burning was the main source for both WSOC and water-soluble brown carbon. In summer, the absorption of low biomass burning-impacted samples exhibited low correlation with levoglucosan and element carbon, indicating that sources related to secondary organic aerosols might be important. The mass absorption coefficients (MAE) of WSOC exhibited distinct seasonal variation with mean values of 1.27 m2/g in winter and 0.57m2/g in summer, which were approximately 2-3 times of the values in southeastern US. This difference might be caused by larger contribution of biomass burning or more anthropogenic-emitted precursors. PMF analyses attribute 39% and 51% of WSOC, and 54% and 20% of Abs365 to biomass burning and sources related to secondary organic aerosol formation, respectively. In addition, a factor with high percentage of EC contribute about 20% to Abs365, indicating the existence of primary sources other than biomass burning for brown carbon. We also analyzed some near-source samples to further investigate sources of water-soluble brown carbon, and the results were in-line with our PMF findings. Our results demonstrated the abundance of WSOC and water-soluble brown carbon in China, which may greatly influence climate and atmospheric photochemical processes.

6CA.5

Biomass Burning Contribution to Beijing Aerosol. YUAN CHENG, Kebin He, Fengkui Duan, Guenter Engling, Rodney Weber,*Tsinghua University*

Biomass burning, the largest global source of elemental carbon (EC) and primary organic carbon (OC), is strongly associated with many subjects of great scientific concern such as secondary organic aerosol and brown carbon. The characteristics of biomass burning aerosol were investigated based on both ambient samples collected in Beijing and sources emission samples derived from stove combustion. The high levoglucosan concentrations and the low winter to summer ratios of levoglucosan indicated significant impact of biomass burning activities throughout the year in Beijing. Comparison of levoglucosan and water soluble potassium (K+) levels suggested that it was acceptable to use K+ as a biomass burning tracer during summer in Beijing, while the contribution of fireworks to K+ could be significant during winter (e.g., the Spring Festival period). Moreover, the levoglucosan to K+ ratio was found to be lower during the typical summer period (averaging 0.21) compared with the typical winter period (averaging 0.51). On the other hand, levoglucosan correlated strongly with mannosan throughout the winter and the levoglucosan to mannosan ratio averaged 9.49, whereas levoglucosan and mannosan exhibited relatively weak correlation during the typical summer period and the levoglucosan to mannosan ratio averaged 12.65. Results from PMF modeling showed that about 50% of the OC and EC in Beijing were associated with biomass burning processes. In addition, a new source-identification method was developed based on the comparison of the levoglucosan to K+ ratio and the levoglucosan to mannosan ratio among different types of biomass. Using this method, the major source of biomass burning aerosol in Beijing was suggested to be the combustion of crop residuals, while the contribution from softwood burning was also non-negligible, especially in winter.

6CA.6

Atmospheric Soot Superaggregates: Implications for Health and Radiative Forcing. NICHOLAS D BERES, Li Liu, Michael I Mishchenko, Rajan K. Chakrabarty, *Desert Research Institute*

The conventional view holds that fractal dimension (D_f) 1.8-2.5, mobility diameter (D_f) ≤ 1 microns, and aerodynamic diameter (D_a) ≤ 300 nanometers are the end-point physical characteristics of soot aggregates emitted from combustion sources. Recent observations of soot emissions from heavily sooting (10–100 parts per million) anthropogenic fires, such as open-air agricultural residue burning and oil pool fires, contradict this view. Last year, findings from three recent independent investigations showed soot superaggregates (SAs) – aggregates of soot aggregates having $D_f \approx 2.6$, $D_m \geq 3$ microns, and $D_a \leq 300$ nm being emitted in quantities greater than 70% in number and mass from large-scale, open-burning emissions. Average D_m and specific surface areas of these soot SAs are ten and three times greater, respectively, than those of conventional soot particles. These unusually large D_m values render these aerosols undetectable using conventional mobility sizing instruments (such as the SMPS). Alternatively, the aerodynamic diameters – used for estimating the probability of deposition within lungs – of these aerosols are similar to those of diesel soot. These observations suggest that soot SAs could be a large component of open burning emissions with the potential to have deleterious effects on human health and the environment, and previously unaccounted-for impacts on climate forcing. In this talk, we will present our findings on the microphysical properties of soot SAs, and discuss their potential impacts on climate and human health.

6HA.1

Infectivity and Survivability of Airborne Viruses Generated from Human Saliva, Artificial Saliva, and Cell Culture Media.

ZHILI ZUO, Thomas Kuehn, Aschalew Bekele, Harsha Verma, Sagar Goyal, Peter Raynor, David Y. H. Pui, *University of Minnesota*

Virus aerosols are raising more and more public concerns due to their potential involvement in disease transmission. To better understand the airborne transmission of viral diseases, many laboratory studies have been performed to study airborne viruses, which are often generated from virus suspensions using nebulizers. However, laboratory studies are sometimes criticized for generating virus aerosols from artificial nebulizer suspensions (e.g. cell culture media), which 1) does not mimic the natural release of virus from human saliva or respiratory mucus and 2) may alter the properties of airborne viruses. Therefore, it is unclear if results obtained using artificial nebulizer suspensions could represent the behavior of airborne viruses in real world situations.

The objectives of this laboratory study were to determine how human saliva affects the infectivity and survivability of airborne viruses and to compare the use of human saliva with artificial saliva and cell culture media. MS2 bacteriophage stock was diluted in the appropriate nebulizer suspension, aerosolized, size-selected (100-450 nm) using a differential mobility analyzer, and collected onto gelatin filters. Uranine dye was also nebulized with the virus, serving as a particle tracer. The resulting particle size distribution was determined using a scanning mobility particle sizer. The collected samples were analyzed by infectivity assays, quantitative PCR, and spectrofluorometry.

Compared with cell culture media, human saliva caused more inactivation of airborne MS2 bacteriophage. However, the level of inactivation was independent of particle size (200-450 nm). These preliminary results suggest that caution needs to be taken when extrapolating laboratory results to real life situations. Tests using artificial saliva and animal viruses are currently underway and results will help better understand disease transmission via virus aerosols.

6HA.2

Comparison of the Particle Size Distributions of Narghile-Waterpipe and Cigarette Mainstream Tobacco Smoke.

EZZAT JAROUDI, Alan Shihadeh, *SOCAAR, University of Toronto*

Recent studies prompted by the global upsurge in waterpipe tobacco smoking have shown that WP smoke contains alarming quantities of carcinogenic and toxic compounds. These findings suggest that WP smoke poses potential health hazards, and contradict the widespread belief that WP smoke is a low-risk activity.

Lung dosimetry models can be helpful in assessing the potential for significant uptake of these toxicants, but there is little reliable data available on the particle size distribution of mainstream WP smoke. Because of the differing combustion process, residence time, and transport mechanisms, WP particle size distribution likely varies from that of cigarettes. The aim of the current study is to measure the particle size distribution of WP and compare it to that of a common cigarette brand.

Smoke was generated using a smoking machine. Mainstream smoke particle size distributions were obtained using a TSI 3090 Engine Exhasut Particle sizer (EEPS) in series with a TSI 3302A Aerosol Diluter set at 1:250 dilution ratio. While the WP smoke was directly sampled into the EEPS, cigarette smoke was transported into the instrument via a sliding sampler diluter to accommodate the lower puff flow rate that characterizes cigarette smoking.

While the average number concentrations for cigarette smoke were higher, the total number of particles and smoke volume inhaled per session were considerably higher for WP. The average diameter for WP smoke was found to be slightly higher (155nm versus 123nm). With similar particle sizes, WP smoke and cigarette smoke are likely to be delivered to the lungs with equal efficiency estimated at 20% by the ICRP model. These findings indicate that a significant fraction of particle-phase WP smoke toxicants can be delivered to the lung.

6HA.3

Mass-mobility Measurements of Cigarette Smoke Using a CPMA-DMS System. TYLER JOHNSON, Ross Cabot, Conor Treacy, Caner Yurteri, Colin Dickens, John McAughey, Jonathan Symonds, Jason S. Olfert, *University of Alberta*

Tobacco smoke is a dynamic mixture of vapor and particulate matter. The volatile nature of this aerosol causes its properties to change over time, making particle characterization difficult. A Centrifugal Particle Mass Analyzer (CPMA) and Differential Mobility Spectrometer (DMS) were used to measure the real-time mass-mobility of cigarette smoke particles. These characteristics are important for modelling lung deposition or smoke particle aerodynamic behavior.

Smoke was produced using a Puff Inhale Exhale (PIE) simulator, which mimics the transient process of a human puffing then inhaling a cigarette. On puffing (35mL puff of 2s duration), the smoke was charged using a radioactive neutralizer, classified by mass-to-charge ratio by a CPMA, and the classified aerosol mobility size distribution measured by a DMS. Since the CPMA classifies particles by mass-to-charge ratio and multiple-charged particles were present, the measured mobility size distribution had to be corrected for this effect. This correction, outlined by Johnson et al. (2012), removed the contribution of multiple-charged particles from the measured DMS ring currents and re-inverted the data.

The effective density was determined to be constant in the 200 to 400 nm mobility diameter range with an average of 1044 kg/m^3. Lipowicz (1988) also determined the effective density to be constant in the 1.1 to 1.5 micrometer mobility diameter range with an average of 1100 kg/m^3 using aged smoke in a Millikan cell. The variation in effective density of smoke particles between different puffs, cigarettes and smoking parameters was also investigated.

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6HA.4

Comparison of Culturability and Membrane Integrity Loss of Escherichia Coli during Aerosolization by Four Aerosol Generators. HUAJUN ZHEN, Taewon Han, Donna Fennell, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Bioaerosol research often requires stable and reliable aerosol generators that could produce high particle concentrations. However, there is still a lack of information about the effect of aerosolization on the physiological status of microorganisms. Here we tested the performance of several liquid bioaerosol generators including a Collison nebulizer, a Liquid-Sparging Aerosolizer (LSA), a C-flow nebulizer and a newly designed Single-Pass Aerosolizer (SPA), which is a single-pass pneumatic nebulizer. We investigated each generator’s ability to preserve the culturability of aerosolized bacteria and to retain the structural integrity of cell membrane at different aerosolization pressures.

The bacteria aerosolized by the four generators were collected using a BioSampler. The amount of cell membrane damage was determined as the Cell Membrane Damage Index, which was expressed as the ratio of cell-released 16S rRNA gene copies in sample liquid versus the entire amount of 16S rRNA gene copies in a bioaerosol sample. The Damage Indices for E. coli aerosolized with the Collison and C-flow nebulizers at 40 psi were significantly higher than the corresponding Indices at nebulization pressures of 5 and 15 psi. However the increased aerosolization pressure for LSA and SPA did not have a substantial impact on cell membrane damage. Increased culturability loss was observed for bacteria aerosolized by Collison Nebulizer and SPA with the increased aerosolization pressure, while no significant change in culturability was found for the other two generators with increased aerosolization pressure. At a constant aerosol concentration of 100 bacteria/cm3, the SPA showed the highest bacterial culturability among the tested generators. Only the Collison nebulizer and SPA achieved aerosol concentrations of 1000 bacteria/cm3, and the SPA outperformed the Collison nebulizer with respect to cell membrane damage. Our results demonstrate that the SPA could be used to produce high bioaerosol concentrations with a relatively low amount of damage to bacterial cells.

6HA.5

Effect of Aerosolization, Air Sampling and Relative Humidity on Influenza Virus. Nathalie Turgeon, Mélissa Marcoux-Voiselle, Marie-Josée Toulouse, Caroline Duchaine, MARTYNE AUDET, *Université Laval, Canada*

Several viruses can be transmitted by the airborne route. However, few is known about their aerosolization, propagation, and survival in aerosol state. Moreover, information about sampling effect on viruses is limited. The aim of this study was 1) to evaluate the effect of aerosolization and relative humidity in airborne state as well as 2) effects of air sampling on Influenza virus integrity.

We utilized a live attenuated Influenza vaccine as viral strain. We spiked 2 liquid cyclone air samplers (SKC Biosampler and Coriolis µ) and let them run with clean HEPA filtered air in order to assess damages caused to the viruses into the air samplers. Our results demonstrated that 5% of influenza virus remains infectious into the Coriolis µ after 10 min air sampling at 300 L/min and 2.5% in the Biosmpler after 20 min air sampling. Moreover, 4% of the virus remains infectious after nebulisation with the Collison 6-jet into a 50L rotating chamber and sampling using the Biosampler. The effect of relative humidity on airborne Influenza viruses was also evaluated. Influenza viruses were arosolized into a 50L rotating environmental chamber under 20% and 80% RH. Aerosols were kept in suspension for 0h, 6h and 14h at 18°C. At 20% RH, Influenza viruses infectivity decreased of 90% in the first 6 hours and remains stable between 6h and 14h. The infectivity loss was higher under 80% RH. Indeed, Influenza viruses lose 99.6% infectivity within the first 6 hours exposure compare to the aerosols at time 0h.

Based on these results, nebulisation with the Collison 6-jet does not seem to affect the infectivity of Influenza viruses. However, air sampling causes substantial infectivity loss. Once airborne, Influenza viruses can remain infectious even after 14h. We also demonstrated that airborne Influenza viruses remain more infectious at 20% RH when compared to 80% RH.

6HA.6

Preferential Aerosolisation of Respiratory Pathogens. PHILLIPA PERROTT, Nathalie Turgeon, Marc Veillette, Caroline Duchaine, *Université Laval, Canada*

Bioaerosols have a significant impact on health, as they are a major mode of transmission of infectious respiratory diseases such as influenza. Additionally, bioaerosols exacerbate respiratory inflammatory diseases such as chronic pulmonary obstructive disease (COPD) and hypersensitivity pneumonitis (HP). In spite of this, the factors that influence the creation and transport of bioaerosols in both environmental and human-engineered settings are not well understood. Some organisms may be more readily aerosolised than others, known as preferential aerosolisation. This was first demonstrated for nontuberculous mycobacteria (NTM) in an article published in 1983 by Parker et al. More recently, ‘selective’ aerosolisation was observed by Moletta et al, where the biodiversity of bioaerosols and their liquid sources was compared. The authors found that there were higher proportions of some organisms in the bioaerosols than in the liquid source. However, further research into this phenomenon has not been undertaken. Importantly, the dynamics between bacteria during aerosolisation processes must be better understood.

We hypothesised that organisms ‘compete’ during aerosolisation processes, and that as a result, some organisms are preferentially aerosolised. A small aerosol chamber was designed for the study of the aerosolisation of several microorganisms simultaneously. Mycobacterium avium, Pseudomonas aeruginosa and Staphylococcus aureus were aerosolised both simultaneously and separately. A bubbling nebuliser was used to produce bioaerosols, to mimic natural aerosol production and an SKC biosampler was used to collect air samples from the chamber. The nebulising liquid and the air samples were analysed by culture, qPCR, and fluorescence microscopy. We found that P.aeruginosa was more easily aerosolised by bubbling when a mixed suspension was nebulised. We also found that when M.avium was aerosolised with S.aureus and P.aeruginosa, it significantly diminished the aerosolisation of P.aeruginosa, but not of S.aureus. We conclude that the presence of M.avium prevents other bacteria from being efficiently aerosolised.

6ST.1

Evaluation of Low-Cost PM Sensors, Intended for Use in a Dense Monitoring Grid. David M. Broday, Barak Fishbain, YAEL ETZION, Ilan Levy, *Technion - Israel Institute of Tehcnology*

Particulate matter (PM) was found to be associated with adverse health effects in humans, such as respiratory and cardiovascular diseases. This is particularly true in urban areas where there are multiple sources for air pollution. Measurements of particulate matter levels in urban areas are based on data collected at monitoring sites with dedicated and accurate instrumentation that is too expensive to deploy in high density. As a result, urban areas are typically monitored only at few locations. Yet the complexity of the emissions sources results in large uncertainties in the fine scale variance of particles at different size distributions, and particularly in near-road levels.

A complementary approach to the standard air quality monitoring networks is the use of low-cost sensors that are less accurate but can be deployed in large numbers over relatively small areas. Several such sensors are available in the market today. Here we present results of an evaluation of two such devices against a hi-end instrument.

Measurements were applied simultaneously by two Sharp's dust sensors onboard ambient monitoring systems (AirBase 's CanarIT 1.0), two standalone Air Quality Monitors of Dylos (DC1700), and two aerosol spectrometers (DMT's PCASP-X2 and GRIMM 1.103) . The evaluation included 1) inter-unit consistency, and 2) agreement with the particle counts by an aerosol spectrometer. The experiment was conducted under full ambient conditions, namely, no filters were used to remove coarse particles. The Sharp dust sensors are measuring all particles in ambient air. The Dylos DC1700 measures particle counts at two size fractions: particles greater than 0.5 micron and greater than 2.5 microns, while the aerosol spectrometer measured particle-size resolved concentrations in the 0.12-10 micrometer range.

Preliminary results show a very good agreement between the two Dylos DC1700 units and also a good agreement between the counts of Dylos units and the integrated counts of DMT in the 0.5-2.5 µm size range. The Sharp sensors in comparison were found less responsive to changes in ambient concentrations.

6ST.2

Strategies for Reducing the Size and Power of Partical Exposure Monitors. JOHN MUTH, Sushmit Mallik, *North Carolina State University*

There is increasing interest in the deployment of small, lightweight particle exposure monitors that can be worn, or carried in close proximity to a person to obtain a measure the concentration and type of particles they may be inhaling from the environment. Ideally a particle monitor, should be wearable for several days without replacing batteries, and should not interfere with the person’s routine behaviors. It is also important to obtain a measure of the persons ventilation rate. The goal of this presentation is to examine strategies on how the power budget, size and weight of particles monitors can be reduced. The designs of some compact light scattering nephelometers and dust sensors will be compared. A novel particle sensor using fiber optic components will be discussed.

6ST.3

PRECISE: Personal Real-time Exposure Using Cell-phone Integrated Portable SamplErs. NARESH KUMAR, Ian Longley, Sung Kim, *University of Miami*

It is known that gene-environment interactions determine the final phenotype of different diseases. In personalized medicine, we have made great strides in characterizing the genotype of individuals, but we lack the ability to characterize and quantify personal environmental exposure. Recent revolution in smartphone and optical technologies offer unprecedented opportunity to develop inexpensive portable samplers. PRECISE is an example of this technology, which integrates portable sensors, cell-phone technology and high performance computing at web-server's end. Portable sampler includes onboard (microcontroller) multiple optical sensors that record dust, CO, CO2, temperature, relative humidity, WiFi and storage card, and a cell-phone application that fetches data from sampler and transmit the data to our server in real time. The manufacturing cost of the instrument is < $500/unit and cell-phone application development is just one time investment. This is likely to pave the way for quantifying personal exposure to air pollution in real time, and monitoring and management of acute effects of air pollution.

There is strong positive association between dust from PRECISE and laser-based portable sensor, such as Aerocet 531, which is promising. Ten units of portable sensor will be deployed at several places at the University of Miami campus, classroom, dorms, library and student union. We plan to recruit students, who can install cell-phone application on their phones. The application will fetch data from the nearest sampler and warn student if at any place the concentration of CO and PM2.5 (converted using the dust, relative humidity and temperature from sampler) exceed the daily EPA's thresholds. Successful completion of this work is likely to have important implications for real-time risk surveillance and management of respiratory and related diseases.

6ST.4

Characterization of an Air-Microfluidic Direct-Reading MEMS PM Mass Sensor. IGOR PAPROTNY, Paul A. Solomon, Richard White, Lara Gundel, *University of California, Berkeley*

This work continues the development of a small portable particulate matter (PM) sensor that can be incorporated into lightweight, low-power devices with PM levels communicated through wireless networks for community-based monitoring of air pollution, as well as other aerosol instrumentation. The Microelectromechanical Systems (MEMS) - based PM sensor directly measures fine (< 2.5 micrometer aerodynamic diameter, AD) PM mass concentrations in real-time, with a limit of detection of a few microgram/m^3. Microfabrication techniques have reduced the area of the sensor to few cm^2 and about 27 g with its housing, enabling portable (perhaps wearable) real-time monitoring of airborne particles. The sensor consists of two main components: a virtual impactor (VI) that removes coarse (>2.5 micrometer AD) particles, and a deposition area where a film bulk acoustic resonator (FBAR) measures the mass of the particles that have been driven from the airstream to the surface of the resonator by thermophoresis. As the PM loading on the FBAR increases, the resonating frequency (600 MHz) decreases.

In this work, we show how the PM sensor performs in the field under ambient conditions as temperature and relative humidity change, affecting the sensitivity of the FBAR to the deposited PM mass. We also investigate the performance of the VI by comparing PM size cutpoints and size-dependent wall losses through its microfabricated channels. Several different designs of the microfabricated VI are investigated and discussed. The results are used to verify the numerical model used to design a nominal cutpoint of 2.5 micrometer AD at a flow-rate of 6 mL/min. Finally, we discuss improvements to key steps of the microfabrication process to improve the sensitivity of MEMS scale particle mass measurements.

6ST.5

Inexpensive Electrochemical Sensor Technology for Air Quality Monitoring. PRAVEEN KUMAR SEKHAR, Kumar Subramaniyam, *Washington State University*

Devices such as mobile phones, computers, and sensors are shrinking in size and cost. The air quality community is also experiencing this change as manufacturers of air quality instruments and sensors reduce the size and cost of their products. Low cost sensors have opened up a new vision for air quality control that includes the do-it-yourself (e.g., citizen science) community. In this talk, inexpensive electrochemical based sensor technology will be presented on air quality monitoring. Specifically, the talk will focus on the detection of gas phase pollutants.

Gases have been successfully sensed by gas phase induced polarization of metal/solid electrolyte/metal interfaces for many decades. The simplest operational mode occurs when the interfacial polarizations are fixed by a reversible reaction between the oxygen vacancies at the electrode-electrolyte interfaces and the partial pressure of oxygen gas at the interface. When the interfacial polarization is controlled by multiple triple-phase boundary reactions, the device is said to be a “mixed potential” sensor. The successful design of gas sensors of each of these types often requires different approaches to the engineering of the gas/electrode/electrolyte interface. Sensors that operate in mixed potential mode are particularly sensitive to electrode/electrolyte interfacial morphology as the devices rely on selective catalysis of desired reactions. Analysis of the requirements for mixed potential gas sensor design has led to the development of sensors with geometries that differ substantially from traditional solid electrolyte based sensors. Adopting commercial automotive manufacturing methods have led to the development of low cost mixed potential sensors

6ST.6

Spatiotemporal Modeling of Indoor Aerosol Mass Concentration. KIRSTEN KOEHLER, John Volckens, Kirk Lake, *Colorado State University*

Technological advancements in exposure assessment have recently increased the accuracy, reliability, and affordability of portable, direct-reading monitors. These monitors can rapidly assess exposures to occupational or other indoor hazards. By coupling an estimated exposure with a known location, contour plots of the hazard concentration over space, known as concentration maps, can be created. These maps are used to assess the spatial variability of hazards and show great potential to help identify and mitigate sources of exposure. Using direct-reading instruments, we generated a measurement dataset of aerosol mass concentration at high levels of spatial and temporal resolution at an engine testing facility. Instruments were deployed as static monitors (n=10), located both near and at a distance from known sources, and as a roving monitor (n=1) that traversed the facility along predetermined routes at 1 m spatial resolution. Data from this high-resolution measurement campaign were used to generate a reference concentration map. The reference map accounted for both spatial and temporal variation using spatiotemporal Kriging, which takes into account the correlation of measurements in both time and space. The reference concentration map provided a best estimation of the true spatiotemporal distribution of aerosol mass concentration in the facility and was used to evaluate simpler statistical approaches (i.e., Traditional and Bayesian Kriging) that do not account for temporal variation. We assessed the reliability of the roving monitor data, a method gaining popularity in occupational exposure assessment, to generate a time weighted average concentration map. We also considered the benefit of including static monitor data to improve time weighted average concentration map accuracy and representativeness. This work has resulted in recommendations for the occupational health community to generate concentration maps using direct-reading instrumentation.

6UA.1

The Spatial Characterization of Ultrafine Particles in Toronto (SCULPT) Study: The Winter Campaign. KELLY SABALIAUSKAS, Ezzat Jaroudi, Cheol-Heon Jeong, Jon M Wang, Natalia Mykhaylova, Krystal J. Godri-Pollitt, Jill Kearney, Amanda Wheeler, Ryan Kulka, Hongyu You, Greg J. Evans, *SOCAAR, University of Toronto*

The Spatial Characterization of ULtrafine Particles in Toronto (SCULPT) Study is an ongoing investigation focused on the spatiotemporal variation of traffic related air pollutants (ultrafine particles (UFPs), black carbon (BC), NO_2 and NO_x) in Canada's most populous city. A total of 22 residential field sites were selected based on their proximity to traffic and other geographical features such as parks, Lake Ontario, commercial areas, rail lines, and industrial areas. The 22 sites were dispersed between 4 and 45km away from a Central site.

The winter field deployment occurred between February 1st and March 10th 2013 and was divided into two phases each lasting two weeks (11 field sites operating simultaneously). Continuous measurements of UFPs with diameters >10nm and BC (measured by microaethalometer) were collected at each site. A variety of particle sizing and counting instruments were deployed to characterize UFP including a Fast Mobility Particle Sizer (Central Site), six Scanning Mobility Particle Sizers (various models), condensation particle counters and DiscMinis. Passive NO_2 and NO_x samples were collected at each residential field site and at the nearest major arterial roadway (44 sites).

A wide range of meteorological conditions were experienced in Toronto throughout the campaign including low temperatures, stagnant and fast moving air masses, and significant snowfall events. Preliminary results indicate that the residential field sites usually had lower particle number and BC concentrations than the downtown Central Site. However, BC concentrations exhibited less spatial variability than UFP (coefficient of divergence for UFP > BC). The diurnal behaviour observed at each residential site had different rush hour maximum times that varied due to their distance from the downtown core. UFP and BC concentrations were more homogeneous across the city during periods with stagnant air masses and when the city was impacted by long-range transport.

6UA.2

Particle Evolution near Major Roadways Based on Observed Ultrafine Particle Concentration Profiles under Stable Conditions. Wonsik Choi, SUZANNE PAULSON, *UCLA*

Ultrafine particles (UFP, < 100 nm), emitted from vehicular exhaust the dominant source in the urban areas, have been known to cause adverse health effects by recent epidemiological and toxicological studies as well as to affect visibility and climate indirectly. Most studies conducted during daytime found smaller nanoparticles emitted from traffic sources disappear within 300 m downwind, changing size distributions rapidly near major roadways. Particle evolution near roadways has been addressed primarily using modeling studies, but gaps between model results and observations still remain. The purpose of this study is to investigate how freshly-emitted UFP evolve in their characteristics during transport periods under stable conditions in near roadways, when transport times are much longer than during daytime.

We investigate the effects of particle dynamics on UFP plume decay rates based on size-segregated UFP concentration profiles measured with Mobile Monitoring Platform equipped with Fast Mobility Particle Sizer for stable pre-sunrise hours. Total 32 size bins were regrouped into 5 size groups based on observed size distributions for data analysis efficiency. Particle loss with distance for smaller size bins was larger than that only due to dilution/dispersion, implying particle dynamics likely affects observed UFP decay rates with distance. Brownian coagulation rates were not able to explain those gaps, and hence additional processes such as evaporation and coagulation enhancement due to van der Waals forces are needed. The upper limit of Hamaker constant for fleshly emitted UFP from vehicles, which is a key parameter to estimate enhanced coagulation rates due to van der Waals forces, is also presented.

6UA.3

Seasonal and Spatial Variability in Chemical Composition of Ambient Ultrafine Particles in the Megacity of Los Angeles.

NANCY DAHER, Sina Hasheminassab, Martin Shafer, James Schauer, Constantinos Sioutas, *University of Southern California*

Emerging toxicological research has shown that ultrafine particles (UFP, dp < 0.1–0.2 μm) may be more potent than coarse or fine particulate matter. To better characterize quasi-UFP ($PM_{0.25}$, dp < 0.25 μm), we conducted a year-long sampling campaign at 10 distinct areas in the megacity of Los Angeles, including source, near-freeway, semi-rural receptor and desert-like locations. Average $PM_{0.25}$ mass concentration ranged from 5.9 to 16.1 $\mu g\ m^{-3}$ across the basin and over different seasons. Wintertime levels were highest at the source site, while lowest at the desert-like site. Conversely, summertime concentrations peaked at the inland receptor locations. Chemical mass reconstruction revealed that quasi-UFP in the basin consisted of 49–64% organic matter, 3–6.4% elemental carbon, 9–15% secondary ions (SI), 0.7–1.3% trace ions, and 5.7–17% crustal material and trace elements, on a yearly average basis. Organic carbon (OC), a major constituent of $PM_{0.25}$, exhibited greatest concentrations in fall and winter at all sites, with the exception of the inland areas. Atmospheric stability conditions and particle formation favored by condensation of low-volatility organics contributed to these levels. Inland, OC concentrations peaked in summer due to increased $PM_{0.25}$ advection from upwind sources coupled with secondary organic aerosol formation. Among SI, nitrate peaked at semi-rural Riverside sites, located downwind of strong ammonia sources. Moreover, ionic balance indicated an overall neutral quasi-UFP aerosol, with somewhat lower degree of neutralization at near-freeway sites in winter. Lastly, coefficients of divergence analysis showed that while $PM_{0.25}$ mass is relatively spatially homogeneous in the basin, some of its components, mainly EC, nitrate and several toxic metals, are unevenly distributed. These results suggest that population exposure to quasi-UFP can substantially vary by season and over short spatial scales in the megacity of Los Angeles.

6UA.4

Diurnal and Seasonal Trends in the Apparent Density of Ambient Fine and Coarse Particles in Los Angeles.

SINA HASHEMINASSAB, Payam Pakbin, Ralph J. Delfino, Constantinos Sioutas, *University of Southern California*

Particle density, an important parameter in the transport and deposition of particles, depends on both physical characteristics of the particles and also their chemical composition. In this study, the day to day and diurnal variations in apparent density of ambient fine (dp< 2.5 micro-meter) and coarse (2.5 micro-meter< dp <10 micro-meter) particulate matter (PM) were investigated for a 7-month period in a location situated near downtown Los Angeles. The number size distribution of particles was measured by a Scanning Mobility Particle Sizer (SMPS) and an Optical Particle Sizer (OPS). Mass concentration of ambient fine and coarse PM were measured by a Beta Attenuation Monitor (BAM) and a Continuous Coarse Particulate Matter (CCPM) monitor, respectively. The hourly apparent density was calculated by the ratio of the mass concentration to volume concentration, calculated by converting the number size distribution to volume size distribution, with the assumption of spherical particles. Moreover, the impact of traffic emission was assessed by continuous measurement of black carbon, an indicator of diesel exhaust, using an Aethalometer. The results revealed that the daily averaged apparent density of CPM is greater than fine PM (1.9 ± 0.4 and 1.5 ± 0.3 g.cm-3, respectively). The apparent density also showed a strong daily variation in both size ranges. The minimum apparent density of fine PM was observed in the morning and afternoon rush hours (1.4 ± 0.2 g.cm-3), indicating the impact of traffic emitted agglomerate soot particles on PM2.5 density, while highest during early afternoon (1.7 ± 0.6 g.cm-3), mainly because of higher photochemical activity. Similarly to fine PM, lowest apparent density of CPM was found during the morning rush hours (1.5 ± 0.5 g.cm-3). However, after morning rush hours, CPM apparent density started increasing, as the wind speed peaks, and remained high until midnight (2.0 ± 0.2 g.cm-3).

6UA.5

Particulate Matter Exposure and Risk Assessment in Urban and Rural Areas of the San Joaquin Valley.

SURESH RAJA, Srikar Middala, Scott Nester, Neelesh Sule, Gary Casuccio, Traci Lersch, Roger R. West, *Providence Engineering and Environmental Group*

Accurate characterization and the relative influences of various sources that contribute to particulate matter (PM) mass is a prerequisite for studies on health effects, and to develop effective policies to mitigate health effects of urban air pollution. Spatial heterogeneity of PM chemical constituents is an important factor in studies of both short- and long-term effects. The primary goal of the present study is to better understand the spatial variability of fine-particle exposure, in terms of particle size and composition, in a range of urban and populated rural areas. An important secondary goal is to advance the understanding of emission source categories that contribute to particulate matter air pollution in the San Joaquin Valley. A winter campaign was conducted in the Fresno Metropolitan area to assess the spatial variability of fine particulate matter using passive samplers. Passive samplers were installed at forty one sites in Fresno and Clovis area. After collection, the PM samples were analyzed for chemical components, and particle size and morphology using a computer controlled scanning-electron microscope (CCSEM). Elemental composition of individual particles was then classified using an Adaptive Resonance Theory (ART) neural networks algorithm (Carpenter, 1991). Based on particle class memberships, inter-site and intra-Urban variability in PM exposure was analyzed in this work. In addition to this, speciation data is being used to assess differences in health risk across neighborhoods and between communities by empirical estimations. The results from this analysis will then be ranked based on the combination of mass and elemental composition to help conduct risk analysis. In this presentation, we will describe the methods used to determine spatial, and variability of PM composition and its sources. In addition to this, we will also document the intra-urban and inter-community variability in particle type exposures, and associated risk from PM exposures.

6UA.6

Exploring the Composition of Urban and Rural Organic Matter Found in Coarse Particles ($PM_{10-2.5}$) in Northeastern Colorado.

NICHOLAS CLEMENTS, Tiffany Duhl, Eunkyung Lee, Bounkheana Chhun, Fernando Rosario-Ortiz, Jana Milford, Shelly Miller, Michael Hannigan, *University of Colorado at Boulder*

Elevated concentrations of coarse particulate matter ($PM_{10-2.5}$) have been associated with negative health effects, such as an increased risk of mortality and respiratory disease. Despite many studies analyzing the inorganic fraction of $PM_{10-2.5}$, the organic fraction is currently poorly understood. To contribute to our general understanding of $PM_{10-2.5}$, the Colorado Coarse Rural-Urban Sources and Health (CCRUSH) study is investigating the composition and health impacts of $PM_{10-2.5}$ in urban and rural environments in Colorado. Twenty-four hour samples were collected on quartz filters every sixth day for a year using 50 lpm dichotomous samplers at four monitoring sites in the Colorado Front Range region. Two sites were located in Denver (urban) and two in Greeley (rural). Previous results from the CCRUSH study show that $PM_{10-2.5}$ in Colorado contains crustal materials, vehicle-wear particles, roadway deicing salt in winter, and biological particles (bacteria, fungi, and pollen). To understand the organic fraction of $PM_{10-2.5}$, we measured bulk elemental and organic carbon concentrations from quartz filter punches. Aqueous extractions of filter composite sets were performed at neutral and elevated pH and analyzed using a bulk dissolved organic carbon analyzer, UV-vis spectrometer, spectrofluorometer, and size-exclusion chromatography. Content of endotoxin, a lipopolysaccharide found in the cell wall of Gram-negative bacteria, was quantified with a limulus amebocyte lysate (LAL) assay. $PM_{2.5}$ and reference natural organic matter samples were analyzed with the same suite of instruments for comparison. Measurements of the organic fraction of $PM_{10-2.5}$ will be combined with total mass concentrations, elemental concentrations, biological particle concentrations, and meteorological observations to understand the seasonal variability of sources of $PM_{10-2.5}$ organic matter, and to explore how sources vary between urban and rural environments.

7AC.1

Evidence of the Secondary Origin of Nitrocatechols and Alkylated-Nitrocatechols in Atmospheric Aerosol Particles.

Alexandre Sylvestre, Sylvain Ravier, Anaïs Detournay, Emily Bruns, Brice Temime-Roussel, Dogushan Kilic, Jay Slowik, Imad El Haddad, Stephen Platt, Andre Prévôt, NICOLAS MARCHAND, *Aix Marseille Université, Laboratoire Chimie Environnement*

Biomass burning constitutes one major sources of aerosol particles, especially during winter. However, biomass burning aerosols studies mostly focus on the primary fraction, and little is known about Secondary Organic Aerosol (SOA) formation process. Recently, methylated nitrocatechol have been identified in atmospheric particles collected in winter. These compounds are strongly associated with biomass burning markers, such as levoglucosan or dihydroabietic acid. Furthermore, they are suspected to result from secondary sources. Actually, they can be formed through the oxidation of cresol, significantly present in biomass burning emissions. In the present study, a new analytical approach, based on Direct Analysis in Real Time (DART) mass spectrometry, has been adopted.

DART offers analysis of gases, liquids and solids on surfaces, avoiding material losses and significantly reducing the sample preparation time. DART source enables soft ionization and produces simple mass spectra suitable for analysis of complex matrices, like organic aerosol, in only a few seconds. For this study, the DART source was coupled to a Q-ToF mass spectrometer (Synapt G2 HDMS, Waters), with a mass resolution up to 40 000.

The analysis of atmospheric aerosol samples, collected in Marseille during winter 2011 (APICE project), revealed the abundance of nitrocatechols and alkylated nitrocatechols. Furthermore, temporal trends very similar to those of levoglucosan or dihydroabietic acid, were observed. If this point clearly confirm their biomass burning origin, their secondary origin remains not totally clear.

Biomass smoke aging experiments were then conducted at the PSI newly developed temperature controlled smog chamber to better characterize the origin of nitrocatechols. Sample collected were analysed by DART/Q-ToF and result confirms that nitrocatechols are associated with biomass smoke and are more importantly quasi exclusively of secondary origin. Considering the abundance of biomass burning primary aerosol, and the large fraction of unexplained SOA, this result is of prime importance.

7AC.2

The Acid-Dependent Hydrolysis of Organic Nitrates in the Aerosol Phase.

JOEL RINDELAUB, Kevin McAvey, Paul Shepson,*Purdue University*

The atmospheric production of organic nitrates under high NOx conditions can influence regional ozone concentrations and the oxidative capacity of the atmosphere by controlling the fate of nitric oxides through possible sink/reservoir processes. However, the degree of this effect is uncertain as photolysis, oxidation, and further reactions within the particle phase may dictate the fate of these compounds. Recent research has indicated that hydrolysis may be a significant reaction pathway for organic nitrates in the particle phase and could influence the equilibrium partitioning of the system. To further investigate the fate of organic nitrates in the aerosol phase, we conducted high NOx oxidation experiments of alpha–pinene in a photochemical reaction chamber focusing on the partitioning and particle phase stability of organic nitrates as a function of seed aerosol acidity, relative humidity, and aerosol composition. The total organic nitrate yield from these experiments was highly dependent on both seed aerosol acidity and chamber relative humidity, even at low RH. Here we will discuss our analysis of the aerosol phase composition, to attempt to decipher the nature of the aerosol phase chemistry that impacts organic nitrate partitioning. These experiments provide useful insight into the nature of some of the aerosol phase processes that might impact the fate of atmospheric organic nitrates, as well as the composition of SOA.

7AC.3

Formation and Gas-Particle Partitioning of Organic Nitrates: Influence on Ozone Production. LEA HILDEBRANDT RUIZ, Jeffrey Bean, Greg Yarwood, Bonyoung Koo, Uarporn Nopmongcol, *University of Texas at Austin*

In rural areas where emission rates of NOx (NO + NO2) are relatively low, ozone formation can be sensitive to secondary NOx sources such as decomposition of organic nitrates (R-ONO2). We present experimental evidence for NOx production when organic nitrates degrade by OH reaction and photolysis. Implementing NOx production from OH reaction with gas-phase organic nitrates in regional models causes ozone increases that are large enough to degrade model agreement with ozone observations. One potential explanation is that organic nitrates are less available to NOx recycling than gas-phase experiments suggest. We are investigating the hypothesis that uptake of organic nitrates into secondary organic aerosol (SOA) reduces the amount of NOx recycled by organic nitrate photolysis and OH reaction.

We added uptake of organic nitrates by SOA to the Comprehensive Air quality Model with extensions (CAMx). The conceptual model of Perraud et al. (PNAS 2012) was followed in which organic nitrate molecules stick to aerosol surfaces and become irreversibly buried by accretion of SOA. Initial modeling results were used to design laboratory chamber experiments in which organic nitrates were formed from the oxidation of VOCs in the presence of NOx and the distribution of organic nitrates between the gas and particle phases was measured. New chemical/physical mechanisms inferred from the experimental data were then tested by modeling the chamber experiments, and tested mechanisms were implemented in CAMx.

7AC.4

Reactivity of Water Soluble Organic Acids with Inorganic Particles Investigated by Micro-spectroscopy Analysis.BINGBING WANG, Steven Kelly, Rachel O'Brien, John Shilling, Alexei Tivanski, Ryan Moffet, Mary Gilles, Alexander Laskin, *Pacific Northwest National Laboratory*

Inorganic particles, such as sea salt and mineral dust, are main components in the atmosphere and undergo different aging processes which alter their physical and chemical properties. Depletion of chloride in sea salt particles was reported in previous field studies and was attributed to the acid displacement of chlorides with inorganic acids, such as nitric and sulfuric acids. Recently, we showed that NaCl can react with water soluble organic acids (WSOA) and release gaseous hydrochloric acid (HCl) resulting in formation of organic salts. A similar mechanism is also applicable to mixed WSOA/nitrate particles where multi-phase reactions are driven by the volatility of nitric acid. Furthermore, secondary organic material, which is a complex mixture of carboxylic acids, exhibits the same reactivity towards chlorides and nitrates. Here, we present a systematic study of reactions between atmospheric relevant WSOA/secondary organic materials and inorganic salts including NaCl, $NaNO_3$, and $Ca(NO_3)_2$ using complementary micro-spectroscopy analysis including computer controlled scanning electron microscopy with energy dispersive analysis of X-rays (CCSEM/EDX), scanning transmission X-ray microscopy with near edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS), and micro-Fourier transform infrared spectroscopy (micro-FTIR).

7AC.5

Model Evaluations of Heterogeneous Nitryl Chloride Production Sources during CalNex 2010. WAYNE CHANG, Nicole Riemer, *University of Illinois at Urbana-Champaign*

Recent ambient observations of nitryl chloride ($ClNO_2$), a nighttime precursor of the reactive chlorine radical, showed direct correlations with dinitrogen pentoxide (N_2O_5) levels. This points towards the N_2O_5 heterogeneous hydrolysis on chloride-containing aerosols as the main $ClNO_2$ production pathway. However, when state-of-the-art parameterizations for N_2O_5 heterogeneous reaction rates and $ClNO_2$ production yields were implemented in air quality models, simulation results always under-predicted ambient $ClNO_2$ concentrations. Sources of model uncertainty are both the parameterization of heterogeneous reaction rates as a function of meteorological conditions and aerosol compositions, and the emission inventory for gaseous chlorine species that can partition into the particle phase. In our work we incorporated a new hybrid N_2O_5 heterogeneous hydrolysis parameterization into the WRF/Chem model, taking into account both the uptake enhancement by the presence of particulate chloride and the uptake suppression by organic coating. Our modeling domain is the South Coast Air Basin of California and the modeled episode is the CalNex 2010 measurement campaign. We will present the sensitivity of $ClNO_2$ production to spatial and temporal variations in anthropogenic chlorine emission sources, as well as the resulting impact on criteria pollutants in the South Coast Air Basin of California.

7AC.6

Hydrogen Peroxide Enhances the Heterogeneous Oxidation of Oxygenated Volatile Organic Compounds on Mineral Dust. Yue Zhao, ZHONGMING CHEN, Dao Huang, *Peking University*

Heterogenous oxidation of oxygenated volatile organic compounds (OVOCs) serves as an important sink of OVOCs as well as a source of secondary organic aerosol. However, the oxidant sources and roles in these reactions are poorly understood. In this work, we present the first laboratory study of the heterogeneous reactions of methacrolein (MACR), an atmospherically important OVOC, on various mineral dust particles (i.e., kaolinite, alpha-Fe2O3, TiO2, and CaCO3) in the presence and absence of gaseous H2O2, with an emphasis on the role of H2O2 in the heterogeneous oxidation of MACR. It is found that the presence of gaseous H2O2 significantly promote both the uptake and chemical transformation of MACR on kaolinite, alpha-Fe2O3, and TiO2 but not on CaCO3. The organic acids were observed as the major low-molecular-weight products,and their yields increase several times in the presence of H2O2. Moreover, organic peroxides such as methyl hydroperoxide, peroxyformic acid, and peroxyacetic acid are only formed in the presence of H2O2, and the formation of methyl hydroperoxide indicates that the oxidation of MACR on the surface involves, at least in part, its reaction with OH radicals. A probing reaction verified the formaiton of OH radicals from H2O2 decomposition on kaolinite, alpha-Fe2O3, and TiO2, which is expected to account for the enhanced oxidation of MACR on kaolinite, alpha-Fe2O3, and TiO2. These results suggest that H2O2 would serve as a source of OH radicals on mineral dust particles and thus may favor the oxidation of co-existing organic compounds. Our findings would extend our understanding on the heterogeneous chemistry of organic compounds on mineral dust, and also highlight the need to investigate the heterogeneous chemistry involving multiple reactive gases.

7AC.7

Organic Aerosol Mixing Observed By Single Particle Mass Spectrometry. ELLIS SHIPLEY ROBINSON, Rawad Saleh, Neil Donahue, *Carnegie Mellon University*

Using single-particle mass spectra from the High-Resolution Time-of-Flight Aerosol Mass Spectrometer, direct measurements of vapor-driven mixing between organic aerosol populations are presented. Multiple-chamber mixing experiments between docosane and D46-docosane (22 C linear alkane, crystalline-solid at room temperature) showed no mixing at room temperature, while squalane (30 C branched alkane, liquid at room temperature) and D62-squalane mixed on the expected timescale from our condensational mixing model. Docosane and D46-docosane particles were driven to mix when the temperature of the mixing chamber was elevated above the melting point of docosane. In a mixing experiment at room temperature with populations of docosane and squalane, we show that docosane vapors were absorbed by squalane particles, but squalane vapors were not absorbed by docosane particles. We attribute these results to low-diffusivity in the crystalline docosane particles. Mixing experiments were also performed on surrogate systems for atmospheric primary and secondary organic aerosol (POA and SOA, respectively). SOA derived from D8-toluene oxidation (a surrogate for anthropogenic SOA (aSOA)) did not mix with squalane (a surrogate for hydrophobic POA (hPOA)), but does mix into SOA derived from alpha-pinene ozonolysis. Because aSOA/hPOA are not limited in volatility, we hypothesize that non-mixing in this system is due to immiscibility. In the aSOA/bSOA system, the presence of d8-toluene derived SOA molecules in the alpha-pinene derived SOA provides evidence that the diffusion coefficient in alpha-pinene derived SOA is high enough for mixing on the timescale of 1 minute. These observations are generally invisible to bulk aerosol measurements, which underscores the importance of single-particle composition data for understanding mixing processes.

7AE.1

Effect of Secondary Aspiration on Low Velocity Human Aspiration Efficiency Estimates: Computational Fluid Dynamics Investigation. KIMBERLY ANDERSON, T. Renee Anthony, *University of Iowa*

Background: Previous work using generic, uniformly applied non-zero coefficient of restitution (CoR) values on an inhaling humanoid found significant increases in low velocity aspiration as large as 90% compared to CoR=0. To improve modeling inputs, realistic CoRs for human facial skin were measured and applied to a CFD model used to examine the effect of particle bounce on human aspiration efficiency.

Objectives: The objective of this work was to examine the influence of human facial skin CoR estimates on secondary aspiration in human aspiration efficiency studies, using realistic values of CoR.

Methods: CFD simulations were conducted to examine airflow (standard k-epsilon turbulence) and particle transport (laminar) into a humanoid form, facing the wind (0.1 to 0.4 m/s), with constant mouth and nose inhalation. Values of CoR (0.55, 0.61 and 0.74) were applied to the forehead, nose and cheeks, respectively, corresponding to mean measurements obtained from 30 individuals using a ballistometer. Constant CoR measurements (1.0) and zero CoR were also evaluated. Aspiration efficiencies for particles ranging from 7-116 micrometers were computed for three freestream and two breathing velocities for three CoR schemes.

Results: Secondary aspiration using realistic CoR values were significantly greater than CoR=0 simulations ($p < 0.0001$) for both nose- and mouth-breathing, with differences ranging from 0 to 80%. Secondary aspiration was more important with increased particle sizes (>52 micrometer) and with decreasing freestream velocity and decreasing breathing rate. No difference was observed between using contant CoR and regionally varied CoR values ($p=0.06$).

Conclusions: Secondary aspiration contributes significantly to human aspiration estimates in low velocity environments. Realistic CoR values should be incorporated into models, although constant values applied to the face provided similar results to regionally specific CoRs. Ignoring this phenomenon could result in a significant underestimation of aspiration efficiency, particularly in the facing-the-wind orientation.

7AE.2
Characterization of the Exposure of Underground Miners to Mixed Aerosols. EMANUELE CAUDA, Luca Stabile, Giorgio Buonanno, Art Miller, *NIOSH*

The exposure to airborne aerosols in any occupational environment can lead over time to debilitating respiratory diseases that can affect the health of workers. In several environments, the workers are exposed not to a single aerosol but to a combination of particulate substances of different composition and size. Miners in countries where diesel-powered equipment are employed, are exposed to elevated concentration of respirable mine dust and ultrafine diesel-generated particles. It is common scientific practice to characterize and investigate the exposure to a single aerosol. Few studies have been conducted on the characterization of the exposure to a mixture of aerosols. This study investigated the characteristic of the exposure to mine dust and DPM simultaneously present in a calm air exposure chamber. Different levels and types of dust and DPM were introduced in the chamber in controlled conditions for steady state and decay testing: the conditions simulated the mass concentration levels for dust and Diesel Particulate Matter (DPM) typically present in underground mines. Real time spectrometers were used to monitor the characteristics of the mixed aerosol. The data from each test were then processed for the determination of exposure in terms of lung deposited mass, surface, and number of the particles for each condition. Specific attention was given to accurately convert the data into activity median thermodynamic diameter that is used in the lung deposited models. The potential interaction of the two aerosols was also investigated. Electron microscope analysis of collected particles indicated a substantial presence of DPM particles aggregates on the surface of respirable mine dust. This indicates phenomena of absorption and deposition between micrometric dust particles and sub-micrometric diesel aggregates and the formation of a new hybrid type of particle.

7AE.3
Measuring Commuter Exposure to Black Carbon in the Context of a Multi-Pollutant Study. NICHOLAS GOOD, Taylor Carpenter, Maggie Clark, Phil Clark, Ashleigh Kayne, Kirsten Koehler, Brianna Moore, Christian L'Orange, Amy L. Stuart, Jennifer Peel, John Volckens, *Colorado State University*

The Fort Collins Commuter Study aims to assess personal exposure to multiple airborne pollutants via extensive measurements and modelling approaches over a 5 year period. In particular the study aims to assess how choice of commuting mode (car, bicycle) and route (high vs. low traffic) affect air pollution intake, given that road traffic is the dominant source of pollution in the US. Black carbon exposure is of particular interest due to its association with potent cardiopulmonary health effects.

Personal exposures are assessed through space and time across 30 hour periods of continuous sampling using an instrumented backpack. Fifty participants complete a minimum of 8 sampling days commuting via car and bicycle resulting in a total of 400 participant days of data. Pollutants associated with road vehicle emissions are a particular focus of the study. Exposure to black carbon, carbon monoxide, particulate mass, particle number, volatile organic compounds, nitrogen dioxide and noise intensity are measured at 10 second resolution. The location of study participants is recorded via gps and apportioned into different microenvironments (home, work, commute) using a geospatial algorithm.

Initial results show culmulative daily personal black carbon exposure is generally dominated by the contribution from commuting. Results from the first 10 participants showed that on average 66% of daily black carbon exposure occurs during commuting compared to 25% for $PM_{2.5}$. Within-commute black carbon exposures are highly variable and dependent upon specific features of the route and transport mode. For example, the initial results show median black carbon exposures measured within 10 metres an intersection are 6 times higher than other on road exposures.

7AE.4

The Effect of Horse Bedding Type on Air Quality in an Equine Farm. YEVGEN NAZARENKO, Michael L. Westendorf, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

In New Jersey alone there are close to fifty thousand horses spread across several thousand farms. When horses are in their stalls, airborne particulate matter from their stall bedding materials is released, especially due to horses' activities. This aerosol can be inhaled by the horses and become a factor in their health and racing performance. The goal of this study was to assess the impact of different stall bedding materials on the potential for the horse inhalation exposure.
Four horse stall bedding materials were tested: wood shavings, straw, wood pellets Woody Pet™ (Woody Pet Products Inc., Surrey, BC, Canada) and wheat straw pellets STREUfex™ (Fex Straw Manufacturing Inc., Lumberton, NC).

We used a Grimm 1.108 optical particle counter (OPC) (0.30-20micro-meters, Grimm Technologies, Inc., Douglassville, GA) to measure various mass concentration fractions (PM2.5, PM10 and Total PM (<20micro-meters)) of airborne particles near the breathing zone of horses when those four stall bedding materials were in use. A control measurement session was conducted with no horses present. The measurements were performed at Rutgers Equine Science Center in New Brunswick, NJ.

During measurements, three adjacent stalls occupied by horses had the same bedding material and the OPC was placed in the middle stall. The measurements were conducted over 7 consecutive weeks during spring time between 4:20 pm and 8:00 am when the horses were turned in.

Total PM for Woody Pet™ (range 459-1126micro-grams/m^3) was significantly higher while Total PM for straw (110-253micro-grams/m^3) was significantly lower than control (305-385micro-grams/m^3). We also found significantly higher PM10 production from Woody Pet™ (127-373micro-grams/m^3) compared to straw bedding (63-126 micro-grams/m^3).

In conclusion, inhalation exposure of horses to airborne particulate matter at equine farms is likely to substantially depend on the stall bedding type, and can be minimized with its proper selection.

7AE.5

Personal and Community Coarse PM Mass Component Comparisons. RON WILLIAMS, Kasey Kolvacik, Ana Rappold, Robert Devlin, *US EPA*

The US EPA recently completed the Moderate and Severe Asthmatics and their Environment Study (MASAES). One goal of the MASAES was to determine the spatial and temporal variability of various particulate matter (PM) size fractions associated with the study cohort. This observational human exposure panel study involved a total of 16 ambulatory adults (mean age = 35.8; 60% male) having various levels of asthma symptom severity. The cohort consented to a repeated 24-hr based personal exposure monitoring regimen using the CPEM (Coarse Personal Environmental Monitor) sampler. The dual in-line impaction stages incorporate 25 and 37 mm teflon filters (coarse, fine, respectively) which provided the means for PM size-fractionated mass determination (gravimetric analysis) as well as eventual chemical component characterization (High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS)). A total of 65 participant days of time-matched (coincidental) personal and community (ambient) based PM monitoring was performed. The non-smoking participants were asked to follow their normal routine and electronic monitoring of protocol compliance (monitoring vest use) was performed to ensure data quality. Ambient (total) coarse PM mass concentrations were found to be highly consistent over the 13 month study period (January '08- March '09) averaging 3.7 ± 2.2 microgram/micrometer while total fine PM mass was significantly more variable (16.6 ± 12.0 microgram/micrometer). Of note was the highly variable nature of personal coarse PM mass concentrations which were typically multifold higher than matched ambient measures (11.6 ± 8.5 microgram/micrometer). The elements K, Zn, Cu, Fe, Mn, Ca, and S represented those in greatest abundance from the speciated personal coarse PM analysis with average daily mass concentrations ranging as high as 2.2 microgram/micrometer (K) for some participants.

7AE.6

Shifts in the Gas-Particle Partitioning of Ambient Organics with Transport into the Indoor Environment. NATASHA HODAS, Barbara Turpin, *Rutgers University*

$PM_{2.5}$ concentrations measured at central-site monitors are commonly used to estimate exposure to ambient $PM_{2.5}$ in epidemiologic analyses; however, people spend the majority of time indoors. Estimating indoor exposures to ambient organic aerosols (OA) is complicated by the fact that shifts in the gas-particle partitioning of ambient organics can occur with indoor transport due to indoor-outdoor differences in temperature and in the availability of organic particulate matter for sorption. The change in the gas-particle partitioning of ambient organics with indoor transport was calculated for 170 homes sampled during the Relationships, of Indoor, Outdoor, and Personal Air Study using measured indoor and outdoor temperatures, measured particulate organic carbon concentrations, and published ambient OA volatility basis sets. To evaluate the sensitivity of these calculations to uncertainty in the physiochemical properties of ambient OA, partitioning shifts were calculated assuming enthalpies of vaporization of 100 and 50 kJ/mol. Multiple linear regression (MLR) was used to determine the extent to which shifts in partitioning could be attributed to indoor-outdoor temperature differences and to differences in the availability of organic matter for sorption. Partitioning shifts were highly sensitive to enthalpy-of-vaporization assumptions. On average, the change in the fraction of organic matter in the particle phase was 39% and 17% for enthalpies of vaporization of 100 and 50 kJ/mol, respectively. The MLR models explained the majority of the variability in shifts in partitioning ($R^2 = 0.64 - 0.90$); however, whether partitioning shifts were driven by changes in temperature or OA concentrations varied with home location, season, and enthalpy-of-vaporization assumption. The MLR models developed in this work have the potential to provide simple parameterizations of shifts in the gas-particle partitioning of ambient organics with indoor transport. However, further work is needed to address uncertainty regarding the physiochemical properties and volatilities of ambient OA.

7AE.7

Potential Consumer Exposure to Airborne Ag and Zn Nanoparticles due to the Use of Nanotechnology-enabled Consumer Sprays. LEONARDO CALDERÓN, Taewon Han, Prasad Subramaniam, Yevgen Nazarenko, Kibum Lee, Jim Zhang, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

A variety of consumer products made with nanotechnology are commercialized worldwide. Studies had shown that nanomaterials have potential negative effects on human health. Despite these concerns, new spray products are released with little information on their aerodynamic size distribution, shape, concentration and other characteristics of particles to which consumers could be exposed.

The objective was to characterize size distributions, shape and agglomeration of particles released due to the use of nanotechnology-based silver and zinc sprays in order to understand their potential for inhalation exposure.

A total of 19 nanotechnology products, 13 containing silver and 6 with zinc, were characterized using three different aerosolization methods. C-Flow® and Collison® nebulizers were used to aerosolize the sprays. A test system was also built to analyze aerosol production using sprayers included with each product. Scanning Mobility Particle Sizer (SMPS) and Aerodynamic Particle Sizer (APS) were used to analyze particle size distribution and concentration of the aerosols generated from the products. A Transmission Electron Microscope (TEM) was utilized to examine the shape and agglomeration of particles captured from the airborne state using an electrostatic precipitator.

A production of nano-sized and micro-sized particles by the two nebulizing methods and by the product sprayer was found during experimentation with all products. The concentration in the nano-sized region ranged from 10^2 to 10^6 #/cm^3 for Ag and 10^2 to 10^5 #/cm^3 for Zn. Collison® nebulizer produced more number of nano particles per cubic centimeter than C-Flow® and sprayers. Images from the TEM analysis showed individual nano-sized particles and micro-sized agglomerates.

The results showed that the highest deposition by number of inhaled nanomaterial particles would be in the alveoli. Based on particle surface and volume considerable proportion of the inhaled particles would be found at the head airways as agglomerates. Some deposition would occur in tracheobronchial and alveolar region.

7BA.1

Inactivation of Bioaerosols by Nanoparticles from Consumer Products. JENNIFER THERKORN, Leonardo Calderón, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Better methods to inactivate microorganisms in the airborne state are urgently needed for applications like hospital ventilation systems and homeland security. Also, as the extent of antimicrobial resistance increases, there is an increasing need to find alternative cleaning products. Nanoparticles are of interest as they have been shown to offer antimicrobial properties through multiple modes of action ensuring less antimicrobial resistance to nanoparticle products. The antimicrobial effectiveness of silver nanoparticles has particularly been investigated and confirmed through surface applications. However, the efficacy of nanoparticles from consumer products against airborne biological particles is unknown. The goal of this research was to investigate the inactivation of bioaerosols by nanoparticles from consumer products. In a laboratory test chamber allowing about two seconds mixing time before sampling, bacterial bioaerosol (Escherichia coli) produced by three jet Collison Nebulizer (BGI Inc., Waltham, MA) was brought in contact with a separate stream of aerosol containing silver nanoparticles from a consumer product (0.001% weight in ethanol) generated by C-Flow PFA Concentric Nebulizer (Savillex, Eden Prairie, MN). Experimental controls included bioaerosol sampling with 1) no product mixing and 2) mixing with a stream of aerosol containing only 70% ethanol. Sampling via BioStage Impactor (SKC Inc, Eighty Four, PA), resultant colony forming unit (N_{CFU}) enumeration indicated ethanol control did not significantly influence N_{CFU} compared to sampling bioaerosol only (t(14)=-0.02, p=0.99) while the nanoparticle product significantly reduced N_{CFU} by 99% (t(12)=11.28, p<0.001). These results indicate that aerosols containing nanoparticles may be a highly effective means for protecting public health by inactivating airborne microorganisms thus reducing exposure to viable microbes. Furthermore, release of such nanoparticles could also have an impact on airborne microorganism ecology. Future research includes investigation of the airborne versus surface application of nanoparticles from consumer products, and testing of different types of nanoparticles and microbial species.

7BA.2

Differential Proteomic Analysis of Sphingomonas Aerolata Bioaerosols. Valdis Krumins, Sjef Boeren, Peter Schaap, Hauke Smidt, Gediminas Mainelis, Lee Kerkhof, DONNA FENNELL, *Rutgers, The State University of New Jersey*

The atmosphere contains substrates such as volatile organic compounds (VOCs) that could support metabolic activity of living bioaerosols. This study examined the proteomic response of bacterial aerosols during aerosolization in the presence of a VOC. Sphingomonas aerolata strain NW12 (AJ429240.1), a psychrotolerant bacterium isolated from ambient air and obtained from DSMZ-German Collection of Microorganisms and Cell Cultures, was used as a model atmospheric organism. The genome of Sphingomonas aerolata was sequenced using the Illumina HiSeq2000 platform. The genome was annotated and a theoretical proteome consisting of approximately 3000 proteins was obtained. Sph. aerolata cells were grown in minimal media with acetic acid as the sole substrate, and were aerosolized into rotating gas-phase bioreactors. The bacteria were incubated in the airborne state with either ethanol or no substrate. After two days, cells were collected using membrane filters (Supor, Pall, Port Washington, NY). Protein was extracted from the bacterial aerosol particles directly from the membrane. Peptides were obtained through in-gel digestion and analyzed by liquid chromatography-mass spectrometry. Putative proteins were identified and quantified in liquid controls, no-substrate aerosolized controls, and ethanol-fed aerosolized treatments. The gas-phase rotating reactors were able to maintain 20 to 80 x 10^6 cells airborne over several days, enough for adequate protein capture. Collection of cells via Supor membranes and extraction of proteins directly from the membranes did not interfere with downstream processing. Approximately 400 putative proteins were identified from the aerosolized cells, allowing comparison of different treatments. Preliminary results from one set of reactor experiments revealed that proteins involved in alcohol metabolism, central pathways in cellular metabolism and ribosome synthesis were more abundant in aerosolized cells fed ethanol than in aerosolized cells with no added substrate, suggesting metabolic activity of bacteria in the airborne state.

7BA.3

NanoPCR Detection of Bacterial Aerosols. Siyu Xu, MAOSHENG YAO, *Peking University*

Bioaerosol detection is of great importance in many fields, yet their low quantity in complex samples makes such an effort difficult. Here, we have investigated the use of nanoparticles (AgNPs, TiO2NPs and their combination) assisted PCR (nanoPCR) in enhancing the efficiency. Pure bacterial species E. coli and B. subtilis with serial dilutions were tested for obtaining optimal parameters such as nanoparticle concentration and the volume of the nanoparticle mixture. These optimal parameters were then applied to detecting indoor and outdoor bacterial aerosols collected using a liquid impinger. The PCR products were subsequently subjected to agarose gel electrophoresis and DNA stain.

The results showed that the enhancements varied with nanoparticle type, concentration level, and DNA template concentration. Data with E. coli and B. subtilis revealed that the optimal parameters were: 0.6 nM for TiO2NPs, 0.9 nM for AgNPs, 2 uL for the mixture, and diluted DNA templates. Our data also suggest that the mixture of AgNPs and TiO2NPs performed better compared to their individual ones especially for lower DNA levels when coupled with qPCR. BacLight DNA stain results showed that use of nanoparticles could form nanoparticle-DNA clusters, which led to concentrating local DNA and thus enhancing PCR detection. Our environmental bioaerosol monitoring data suggest that NanoPCR technique can be immediately applied to detecting 45 low quantity of airborne biological materials with up to 500 times enhancement. The developments in this work can further broaden qPCR applications in bioaerosol research fields.

7BA.4

Characterization of Aerosols Using an Electrodynamic Linear Quadrupole Trap. MATTHEW HART, Erin Davis, Jason Edmonds, Jay Eversole, *Naval Research Laboratory*

The physical characteristics of single, micron-sized particles are studied as they are confined along the axis of an electrodynamic quadrupole trap (ELQ) . Using an ELQ, single to several hundreds of particles simultaneously, can be studied in an atmospheric controlled, touch-less environment. The ELQ design is similar to both earlier 3-dimensional ring versions and linear ion traps used for mass spectrometry. One of the advantages of this approach over the ring version is its relative ease, or increased efficiency, of particle capture. The electrodynamic stability region of the ELQ is along the symmetry axis defined within four parallel, equally spaced rods where charged, micron-sized particles can be captured and confined at ambient atmospheric pressures. Captured particles can be transported along the axis using a controlled airflow along the length of the device or held stationary by applying an electric potential to a concentric ring that has the same polarity of the trapped particles creating a balance against the airflow and/or gravity. This trapping technique permits the study of particles over long time periods so that they may be subjected to challenging conditions of interest such as temperature, relative humidity, gas composition and EM radiation. Diagnostic measurements, such as particle size, can be obtained at points along the length of the ELQ using imaging and light scattering techniques. Particles may also be collected for additional diagnostic measurement outside the ELQ by depositing them onto a substrate through the end of the chamber controlled by the ring potential. Exploiting this collection capability, viability studies of aerosolized biological organisms are targeted for future study. As an initial example of the utility of this approach, we present data on evaporation rates of liquid droplets for specific neat materials and binary mixtures, and compare these data to predictive models using known bulk properties.

7BA.5

Fluorescence Characterization of Individual Bio-Aerosols and Ambient Air Measurements. VASANTHI SIVAPRAKASAM, John E. Tucker, Jay Eversole, *Naval Research Laboratory*

For more than a decade there has been a consistent effort at the US Naval Research Laboratory (NRL) to experimentally investigate the optical properties of aerosols particularly with regard to biological particle composition, for the purposes of developing bio-aerosol sensors. Throughout our history, we have pursued a guideline that the optimum environmental sensing capability will be achieved through on-the-fly, individual particle interrogation. We have previously developed a two-wavelength excitation (266 nm and 355 nm) based laser-induced fluorescence system to characterize individual micron-sized particles on-the-fly. This instrument has been extensively used to investigate the fluorescence properties of varying classes of biological agent simulants and potential ambient air interferents. Two-photon excited fluorescence from micron-sized aerosol particles was also explored using 270 nm, sub ps laser pulses for two common biological simulants. A version of the two-wavelength excitation system was developed along with an electro-static charging and collection capability in collaboration with Sarnoff Corp. (now SRI), which enables capture and collection of individual airborne particles in real time, based on their spectral emission signatures.

In April 2012, NRL inaugurated a new Laboratory for Autonomous Sensor Research, for developing and evaluating sensors under various environmental conditions. Included in this facility is a new Ambient Aerosol Test Facility (AATF) that draws in ambient air, enabling developmental sensors to sample local outdoor air continuously while remaining in a laboratory environment in order to achieve false positive testing over extended periods. The AATF includes an ability to mix various simulants and interferents in with ambient air for periodic true positive checks. Starting this summer, a long-term ambient data collection will commence with two sensor systems simultaneously: (1) two-wavelength fluorescence sensor and collector system mentioned above, and (2) a developmental single aerosol particle IR absorption spectral sensor. We will present a detailed description of the AATF system, as well as results of our latest outdoor data and sensor evaluations.

7BA.6

Study the Effects of Atmospheric Environmental Conditions on Fluorescence Spectra of Bioaerosols Using a Laboratory Reaction Chamber. YONG-LE PAN, Joshua Santarpia, Shanna Ratnesar-Shumate, Elizabeth Corson, Steven Hill, Mark Coleman, Chatt Williamson, Christopher Bare, Sean Kinahan, Jonathan Eshbaugh, *US Army Research Laboratory*

Real-time single bioaerosol particle detection and characterization technologies based on fluorescence spectra, elastic scattering patterns, and Raman spectra will be briefly reviewed. Mainly, the effects of atmospheric environment conditions (humidity, ozone etc) on the properties (size, concentration, viability, fluorescence intensity and spectral profile) of bioaerosols will be presented. Micron sized bioaerosol particles (mode size ~2 um) of Bacillus thuringiensis (Al Hakam) spores, MS2, and an octapeptide that contains one tryptophan and one tyrosine, are generated from their slurry solution and injected into a rotating drum reaction chamber. The chamber rotated at 1 rpm to keep particles aloft for several hours. Bioaerosols are sampled from the chamber hourly for the measurements of particle size distribution, concentration, total fluorescence via 355-nm excitation, and single particle fluorescence spectra via 266-nm and 351-nm excitation under different controlled relative humidity (20%, 50%, or 80%) and ozone concentration (0 or 150 ppb). Bioaerosols are also collected by all-glass impingers (AGI) for the analysis of viability (by culturing) and total (live+dead) organisms of the species generated using q-PCR. The results show the following. 1) Particle size, concentration, and 263-nm-excited fluorescence intensity decrease at different rates under different conditions. 2) 263-nm-excited fluorescence at 280-400 nm decreases faster than that at 400-600 nm. 3) The UV fluorescence peak near 340 nm has blue-shift with time in the chamber. 4) 351-nm-excited fluorescence does not change when ozone is absent, but increase when ozone is present, especially at high humidity. 5) Increases in 351-nm-excited fluorescence that occur with higher ozone concentration and humidity, along with decreases in 263-nm-excited tryptophan emission (more apparent in octapeptide) are consistent with the oxidation of tryptophan by ozone, and (in the presence of high humidities) conversion to kynurenine. Further analysis is in progress and will be presented.

Acknowledgements
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7BA.7

Using Spectral Analysis and Fluorescence Lifetime Imaging Microscopy (FLIM) to Discriminate between Grass and Non-grass Pollen. JOHN SODEAU, David O'Connor, David Healy, Daniela Iacopino, Pierre Lovera, *University College Cork*

A study has been performed that provides the first FLIM results for specific in situ biochemical components of individual pollen. The data obtained show that such measurements can, at least, provide a basis for discrimination between airborne grass and non-grass pollen. Relevant spectral data were obtained from the absorption, fluorescence and excited state lifetime measurements of three grass pollen and three non-grass pollen (Anthoxanthum odoratum (AO) Dactylis glomerata (DG) Fagus sylvatica (FS) plus Lolium perenne (LP), Quercus robur (QR), Quercus ilex (QI)).

Using excitation at 402 nm, the most striking differential FLIM spectral observation was found for the individual grass pollen, all of which featured a band with wavelength maxima at 675 nm and 725 nm. The feature is readily attributable to chlorophyll-a; these bands are absent from the non-grass counterpart spectra. The fluorescence lifetime experiments provided unambiguous evidence to show that the chlorophyll-a was located in a region that resembled a “free” solution environment. Furthermore the measurements are consistent with the fluorescence signals also originating from one further source: NAD(P)H bound to a protein. Such a result may be expected because of the photosynthetic origin of NAD(P)H but it has not been shown before for grass pollen. In contrast, the lifetime results obtained for the non-grass pollen can be interpreted purely in terms of the presence of the metabolite, flavin adenine dinucleotide (FAD), likely bound within a cell.

The work is relevant to the study of atmospheric dispersions of Primary Biological Aerosol Particles (PBAP) because the discriminatory lifetime fluorescence parameters obtained might be utilized for their real-time detection if suitable technical adaptions to current instrumentation can be made.

7CO.1

Morphology of Gas Turbine Particulate Matter. ADAM M BOIES, Jacob Swanson, Paul Williams, Amewu A. Mensah, Mark Johnson, Steven Rogak, Jason S. Olfert, Tyler Johnson, Ramin Dastanpour, Gregory Smallwood, Max L. Eggersdorfer, *University of Cambridge*

Black carbon (BC) emissions from gas turbines impact human health and radiative forcing, but the magnitude of these effects is dependent upon the morphology of the particulate matter (PM). BC characterization is available from a variety of instruments; however a complete analysis of the aerosol concentration, size and morphology only arises by complimentary analysis using in-situ and ex-situ measurement techniques. This work examines characteristics of BC that was generated by a General Electric CFM56-5B4-2P turbofan engine with staged combustion as a part of the SAMPLE III campaign. Gas turbine exhaust aerosol for a range of thrust settings was sampled, conditioned and delivered to a suite of instruments which included catalytic strippers (CS), scanning mobility particle sizers (SMPS), a laser induced incandescence (LII) instrument, a centrifugal particle mass analyzer (CPMA) and aerosol mass spectrometers (AMS). In addition, particles were collected on transmission electron microscopy (TEM) grids via thermophoretic and electrophoretic sampling of polydisperse and monodisperse (mobility selected) PM. In all cases the semi-volatile fraction of the aerosol was removed via a catalytic stripper, leaving the solid PM for in-line characterization or sampling. Measurements by complimentary instruments allow for characterization of distinct metrics of the PM, including particle number concentration and aggregate mobility diameter (SMPS); particle mass concentration and primary particle diameter (LII); aggregate mass (CPMA); and vacuum aerodynamic diameter (AMS). Other metrics, such as the mass-mobility exponent, primary-particle diameter and the aggregate dynamic shape factor are calculated from analytical and modeled relations. The in-situ characterization results are compared to primary particle size and aggregate morphology metrics determined from TEM studies. Key findings include the relation of primary particle diameter, aggregate shape factor and mass mobility exponent as a function of aggregate size and evidence of ash particles present within the soot aggregates.

7CO.2

In-situ Measurements of Aircraft Engine Exhaust at Cruise Conditions during the 2013 ACCESS Chase Plane Experiment.

RICHARD MOORE, Edward Winstead, Lee Thornhill, Andreas Beyersdorf, Suzanne Crumeyrolle, Luke Ziemba, Bruce Anderson,*NASA Langley Research Center*

Aircraft engine emissions constitute a negligible fraction of the global black carbon mass, but can have a disproportionate climatic impact because they are emitted high in the troposphere and in remote regions with otherwise low aerosol concentrations. Consequently, these particles are likely to strongly influence cirrus and contrail formation by acting as ice nuclei (IN). However, the ice nucleating properties of aircraft exhaust at relevant atmospheric conditions are not well known, and thus, the overall impact of aviation on cloud formation remains very uncertain.

To address this need, the NASA Alternative Fuel Effects on Contrails and Cruise Emissions (ACCESS) was conducted in February-March, 2013 to examine the aerosol emissions from the NASA DC-8 under a variety of different fuel types, engine power, and altitude/meteorological conditions. Two different fuel types were studied: a traditional JP-8 fuel and a 50:50 blend of JP-8 and a camelina-based hydro-treated renewable jet (HRJ) fuel. Emissions were sampled using a comprehensive suite of gas- and aerosol-phase instrumentation integrated on an HU-25 Falcon jet that was positioned in the DC-8 exhaust plume at approximately 100-500m distance behind the engines. Measurements of aerosol concentration, size distribution, soot mass, and hygroscopicity were carried out along with trace gas measurements of CO2, NO, NO2, O3, and water vapor. Contrail ice crystals were sampled with a DMT Cloud Droplet Probe mounted on the crest of the fuselage, as well as a Cloud Aerosol Spectrometer and a Cloud Imaging Probe on the starboard wing pylon. Emissions indices suggest that the cruise emissions are in line with past ground-based measurements, where similar particle numbers were emitted by burning pure JP-8 and the blended fuel. This indicates that blended fuels do not significantly affect particle emissions, and motivates future measurements of engines burning pure HRJ fuel.

7CO.3

Accurate Measurement of Particle Size and Number Concentration for Meeting Regulatory Limits on Vehicle Emissions: Inter-comparison of Three Particle Sizing Instruments.

NAOMI ZIMMERMAN, Krystal J. Godri-Pollitt, Cheol-Heon Jeong, Terry Jung, Josephine Cooper, James S. Wallace, Greg J. Evans, *SOCAAR, University of Toronto*

Upcoming Euro VI regulation limits diesel vehicle emissions by particle number concentration. Accurate characterization of particle number concentration requires sizing instruments capable of capturing transient events over a wide concentration range. The TSI Fast Mobility Particle Sizer (FMPS) and Engine Exhaust Particle Sizer (EEPS) are both able to provide these high-resolution size-distributed physical measurements. While these instruments share a common operation principle, differences exist between measurements. To understand these differences, we compared measurements of particulate matter (PM) with contrasting physicochemical characteristics (urban ambient, diesel exhaust, and laboratory-generated PM). The ambient PM was sampled at the intersection of two high-trafficked roads in downtown Toronto, Canada. Diesel PM was generated by a heavy-duty diesel engine under ISO8178 Mode 9 operation and diluted by a rotating disk thermodiluter (TSI 379020A). For a sub-25nm comparison, laboratory-generated measurements (TSI 3480 Electrospray Aerosol Generator) were conducted with two ionic solutions with particle diameter modes of 12.4 and 14.3nm, respectively. To determine the accuracy of the EEPS and FMPS, the diesel exhaust inter-comparison included a TSI Scanning Mobility Particle Sizer (SMPS).

In the diesel and ambient particle mixtures, EEPS number concentrations exceeded the FMPS in the sub-25nm (5-15% greater) and 93-220nm (11-32% greater) size ranges. For particles sized between 25-93nm, the measurements were within instrument error (<5%). The sub-25nm discrepancies were likely due to low total concentrations; comparisons using laboratory-generated PM reduced overestimation to <8%. From this we developed a new FMPS empirical correction for the EEPS when measuring diesel exhaust and ambient PM. Comparisons with the SMPS showed that for diesel exhaust PM a second empirical correction is required due to significant overestimation (25-38%) of particle concentrations by the EEPS and FMPS in the 29.4-107.5nm size range. The impact of particle morphology on the correction procedures required for the EEPS and FMPS will be discussed.

7CO.4

Dynamics of Light Absorption by Biomass Burning Organic Aerosol Photochemically Aged Using the Ambient Sunlight.

MIN ZHONG, Myoseon Jang, *University of Florida*

The light absorption of wood burning organic aerosol (WBOA) was measured as a function of photooxdiation time in a 104 m3 outdoor chamber with ambient sunlight. The experiments were conducted under different humidity and NOx conditions. The results showed that the light absorption of WBOA was dynamically changing during the aging process. The light absorption of WBOA increased in the morning and then decreased in the afternoon due to the competition among gas-particle partitioning, particle phase reaction, SOA formation and sunlight bleaching. More than 90% concentration reduction in PAH and levoglucosan indicated the progress of partitioning and particle phase reaction. WBOA enhanced up to 1.5 times caused by SOA formation. The light absorption of organic aerosol was found to be insensitive to NOx and RH, except high RH up to 85%. Under the high RH condition, the light absorption of WBOA kept decreasing. Such trend might be due to the more active particle phase reaction with higher water content. At RH of 85%, the water content of fresh particle was 40%, aged particles about 20%. The outdoor measurement was also compared with the ambient data obtained in a fire event. In the ambient, the light absorption of biomass burning organic aerosol continuously reduced from morning to afternoon. No color enhancement was observed. The difference between chamber observation and ambient data needs further investigation.

7CO.5

Particle Mass and Number Emissions, Size Distributions, and Composition from Commercial Charbroiling Operations - Are They Really Dangerous?

NICHOLAS GYSEL, Daniel Short, Poornima Dixit, Chia-Li Chen, William A. Welch, Keisha Williams, Ning Li, Akua Asa-Awuku, David R. Cocker III, Georgios Karavalakis, *University of California Riverside*

Commercial cooking is the leading source of PM2.5 emissions in Southern California. The South Coast Air Quality Management District (SCAQMD) projected that in 2014 and into 2023, PM2.5 emissions from cooking will surpass heavy-duty trucks and off-road vehicles. Large scale cooking has been identified to be an important contributor to organic carbon (OC) and elemental carbon (EC) in the urban environment including secondary organic aerosol formed by condensation of reaction products of gaseous organic emissions following photochemical processes.

This work attempts to gain insight into the physical, chemical, and biological nature of particle emissions from meat cooking from underfired charbroiled operations. Experiments were conducted upstream and downstream of different control technologies to determine their effect on PM emissions. Particle number emissions, particle size distributions, and black carbon concentrations were measured. Additionally, EPA Method 5 and SCAQMD Method 5.1 PM protocol methods for stationary sources were used to measure the removal efficiency of PM from the control devices and correlated with the real-time PM measurements. Chemical analysis, including EC/OC, metals, and inorganic ions was also performed on the PM samples collected upstream and downstream the control technologies. We further investigated whether PM could induce an inflammatory response in human bronchial epithelial cell line (BEAS-2B) and whether this effect is linked to the organic chemicals on these particles. BEAS-2B cells were exposed to different concentrations of water or methanol extract. Our data showed that while methanol extract induced a 30 percent cell death the water extract did not have any toxicity on BEAS-2B cells. At the same concentration, the methanol extract also increased IL-6 and IL-8 production. Taken together our results suggest that the organic chemical compounds on charbroiled-emitted PM may have a pro-inflammatory effect in the respiratory system.

7CO.6

Laboratory Characterization of Ultrafine Particle Number Size Distributions and Other Pollutants from Traditional and Improved Biomass Cookstoves. YUNGANG WANG, Daniel Wilson, Kathleen Lask, Ashok Gadgil, *Lawrence Berkeley National Laboratory*

Almost half of the world’s population still cooks on biomass cookstoves such as three stone fires (TSF) that exhibit poor efficiencies and primitive designs. Emissions from biomass cookstoves contribute to climate change and substantial morbidity and mortality. The smoke from biomass cooking fires has recently been found to be the largest environmental threat to human health and is associated with 4 million deaths each year. Ultrafine particles (UFP, $D_p < 100$ nm) are widely reported in biomass combustion smoke, and dominate the total airborne particle number concentrations. Size-resolved and high time resolution (1 Hz) measurements of UFP emissions from biomass cookstoves have not been documented in the current literature. During the past decade, a number of improved cookstoves with higher energy efficiency (and some with lower emissions), have been designed and promoted across the world. However, relatively limited UFP emission data from these stoves were reported. These data were in the format of total number of particles per volume unit of air with low time resolution (every two minutes). Furthermore, only a few number of replicate tests were conducted, commonly three, for each stove being evaluated. In this study, the Berkeley Darfur Stove and the TSF have been tested and compared for their performance and emissions characteristics with 15 replicates under well-controlled laboratory conditions at the stove testing facility of Lawrence Berkeley National Laboratory. UFP particle number size distributions are measured at 1 Hz using a Fast Mobility Particle Sizer Spectrometer (FMPS, model 3091, TSI, Inc.), together with $PM_{2.5}$, black carbon (BC) mass concentrations, and CO/CO_2 gases. Results of stove performance (time to boil, fuel consumption and energy efficiency) and real-time emissions of UFP and other co-pollutants are presented. Source apportionment by Positive Matrix Factorization (PMF) is also carried out to interpret different stages of the combustion process.

7CO.7

Establishing the Role of Sulfur in Coal in Aerosol (Sulfuric Acid, Sulfate and Organic) Formation during Pulverized Combustion in a Drop-tube Furnace. XIAOFEI WANG, Brent Williams, Pratim Biswas, *Washington University in St. Louis*

Pulverized coal combustion is widely used for electricity and heat generation. However, it results in the production of large quantities of air pollutants, including particulate matter. It is well known that sulfuric acid particles are formed in flue gas from coal combustion. However, there are very few (or no) studies establishing the pathway and role of transformation of the sulfur in coal. We report the presence of sulfuric acid on the surface of fly ash particles produced by PRB coal combustion in a drop-tube furnace, even those fly ash particles that are strongly basic. This probably indicates that the reaction of sulfuric acid and basic metal oxides in fly ash particles are slow, probably due to the low diffusion rate of sulfuric acid into particles. Using a high-resolution time-of-flight aerosol mass spectrometer, organic species were found to be internally mixed with sulfuric acid and sulfate. By varying the sulfur content, total concentrations of sulfuric acid and sulfate in flue gas particulate matter were changed. It was found that there was a strong correlation between organic and sulfuric acid/sulfate formation. The mechanism is investigated and proposed: sulfuric acid and sulfate may play an important role in covering and protecting organic species in particulate matter from oxidation in the environment with high temperature and high oxygen concentration. Organic composition of the aerosol was further characterized in detail using a thermal desorption aerosol gas chromatograph (TAG).

7IM.1

A Novel Multi-wavelength Photoacoustic-nephelometer Instrument Using a Supercontinuum Light Source for Aerosol Absorption and Scattering Measurements. NOOPUR SHARMA, Ian Arnold, Hans Moosmuller, W. Patrick Arnott, Claudio Mazzoleni, *Michigan Technological University*

Wavelength dependence of absorption and scattering by atmospheric particles has been studied for decades due to their relevance to climate, air quality and visibility. Absorption of particles like black and organic carbon and mineral dust exhibits different wavelength dependencies often with enhanced absorption toward shorter wavelengths. Methods used to measure the wavelength dependence of light absorption for atmospheric particles include: filter-based light attenuation measurements, photo-thermal interferometers, and photoacoustic spectrometers. While filter-based methods are very common, they present artifacts due to multiple scattering from the filter substrate. These artifacts become particularly difficult to deal with when measuring brown carbon aerosol, which typically exhibits stronger wavelength dependence and may change its morphology upon filter deposition. Therefore, new methods capable of measuring at multiple wavelengths are an active field of research, aiming to reduce uncertainties of atmospheric aerosol optical properties and their effect on radiative forcing and climate.

At Michigan Technological University and the Desert Research Institute (Reno, Nevada), we are developing a novel, multi-wavelength integrated photoacoustic-nephelometer spectrometer. This instrument combines a supercontinuum light source with photoacoustics and nephelometry to measure the absorption and scattering by aerosol particles, currently at five different wavelength bands (centered at 417, 475, 542, 607, and 675 nm). The wavelength bands of interest are selected from the continuous spectrum of the light source using a set of optical interference filters. Measurements on the aerosol sample are performed sequentially at each wavelength band and provide scattering and absorption coefficients simultaneously, allowing the direct calculation of the single scattering albedo at the given wavelength. We present the design and development of the instrument and discuss its performance. We review the results obtained from tests performed on laboratory-generated aerosols, including black carbon and sodium chloride particles.

7IM.2

Online Measurement of Aerosol Mass Optical Cross Sections. CHRISTOPHER ZANGMEISTER, James Radney, Michael Zachariah, *National Institute of Standards and Technology*

We demonstrate the measurement of mobility and mass selected absorption and extinction cross sections of laboratory generated aerosols. We utilize an aerosol particle mass analyzer after mobility selection to isolate aerosol with known size and mass (density). We measure the mass extinction and absorption cross sections, MEC and MAC, respectively, using cavity ringdown and photoacoustic spectroscopies. We demonstrate the utility of the technique for both absorbing and non-absorbing materials. Lastly, we demonstrate mass based particle separation and speciation in a multicomponent aerosol population.

7IM.3

The Captive Aerosol Growth and Evolution (CAGE) Chamber System. Don Collins, JILL MATUS, Nathan Taylor, Carlos Antonietti, Chance Spencer, Joshua Santarpia, Yong-Le Pan, Shanna Ratnesar-Shumate, Crystal Glen, *Texas A&M University*

The Captive Aerosol Growth and Evolution (CAGE) chamber system combines new and established design features to bridge some of the gaps in existing chamber research; informing our understanding of aerosol aging by subjecting an injected and retained population of particles to photolysis rates and gas phase composition that approach those of the immediate surroundings. Studies conducted with the chambers include assessment of bioaerosol viability, secondary organic aerosol (SOA) formation, and aqueous-phase processing. This work presents the unique design specifications and capabilities of the CAGE chamber system.

The cores of the CAGE system are two cylindrical, 1 m^3 aerosol retention/reactor volumes. Unconventionally, these volumes operate in equilibrium with a continuous air flow isolated behind gas-permeable expanded polytetrafluoroethylene (ePTFE) membranes which constitute the vertical, circular ends of the reactor cylinders. When the gas exchange flow consists of ambient air, the reactor gas phase will closely track ambient conditions. Further, the curved cylinder wall is comprised of UV-transmitting fluorinated ethyl-propylene (FEP) film and the chambers pivot to allow full sun exposure. Combined with temperature control, these features allow the CAGE reactor volumes to mimic the ambient photo-chemical environment. Alternatively, the gas exchange flow can be fully prescribed or spiked with trace gases. Typical CAGE operation resolves the sensitivity of the aerosol aging processes in the ambient environment to isolated factors (e.g., NO_x concentration) by spiking the gas exchange flow of one of two chambers otherwise mimicking ambient conditions. The retained aerosol injected during most experiments will be a mixture of monodisperse populations. Other CAGE features include portability to allow experiments in various ambient environments, adiabatic cloud formation, Goldberg chamber drum rotation to enhance particle and especially cloud droplet retention, equipment for generating tailored gas and aerosol samples, and analytical aerosol instrumentation including an Aerodyne HR-ToF-AMS, TDMA, SMPS and DMT-CCN.

7IM.4

Effect of Aerosol Volatility on the Sizing Accuracy of Differential Mobility Analyzers. ANDREY KHLYSTOV, *Research Triangle Institute*

Differential Mobility Analyzers (DMAs), also called electrostatic classifiers, are widely used to measure aerosol size distribution, aerosol hygroscopic growth and kinetics of particle evaporation and condensation, and to produce monodisperse aerosol for calibrating other instruments such as Aerosol Mass Spectrometers. The DMAs classify aerosol particles according to their mobility in an electric field. A well-defined relationship exists between the size of transmitted particles, their charge and the electrical field in the DMA. This relationship assumes that particles do not change their size during passage through the classifier. However, particles containing volatile or hygroscopic compounds could evaporate or grow inside the DMA, if there are differences in temperature, relative humidity and / or gaseous concentrations between the sampled air and the conditions in the DMA. The differences in the gaseous concentrations could also be induced by losses of the volatile species, such as nitric acid, to the walls of the DMA or in the tubing used to supply the sheath air to the DMA. Such particle changes inside the DMA could lead to sizing errors.

I will present a simple theoretical treatment of the processes occurring in the DMA when measuring semi-volatile particles. The predictions of the theory will be compared to measurements of laboratory-generated ammonium nitrate aerosol using TSI long DMAs. Ammonium nitrate is a major semi-volatile component of ambient aerosol, especially in industrialized areas. It is also the main component that is used for calibration of Aerosol Mass Spectrometers and Aerosol Chemical Speciation Monitors (ARI). One of its gaseous dissociation products - nitric acid - is a very reactive component and can be readily removed from the gas upon contact with the walls of the sampling tubing and the instrument itself. The magnitude of the sizing errors when measuring ammonium nitrate and other semi-volatile compounds will be discussed.

7IM.5

Introduction to Project "Dispersion of Air Pollution in the Boundary Layer – New Approach with Scanning Doppler Lidars". Anne Hirsikko, VILLE VAKKARI, Ewan J. O'Connor, Curtis R. Wood, *Finnish Meteorological Institute, Helsinki, Finland*

Air quality is much controlled by source rate of particulate and gaseous pollutants, as well as by their dispersion and dissipation within and from the atmospheric boundary layer, respectively. Similarly, a number of chemical and physical processes taken place in air and emissions from biosphere are greatly influenced by dynamical nature of atmosphere. In order to understand boundary layer and pollutant dispersion dynamics using scanning Doppler lidars we have launched a new project funded by Finnish Maj and Tor Nessling foundation (project number 2013006). During the project we utilise a scanning Doppler lidar (HALO Photonics) network of Finnish Meteorological Institute. The network was established during September 2011 – February 2013, and it consists of five meteorologically and environmentally different sites. Our aims are to:

1) Investigate capability and potential of scanning Doppler lidars as wind, turbulence and air quality investigation and monitoring tool.
2) Facilitate research of atmospheric and environment research disciplines.
3) Develop a product for area of industry where knowledge of wind and pollution dispersion is essential.

Project steps are as follows
4) We have implemented a number of scanning routines (vertical azimuth display and range height indicator with various azimuth and elevation setups) to monitor dispersion of aerosol particles and investigate effect of varying surface roughness on boundary layer wind and mixing in Helsinki and Utö island.
5) Currently we are developing data analysis methods for surface and boundary layer wind and turbulence. Status of our method development and subsequent results will be presented in the conference.
6) Next step will be investigation and subsequent data analysis method development for dispersion of aerosol particles within the boundary layer.

7IM.6

Data Analysis Procedures for a Novel Volatility and Polarity Separator (VAPS) Instrument for Atmospheric Organic Aerosol Chacterization. YAPING ZHANG, Raul Martinez, John Jayne, Manjula Canagaratna, Thorsten Hohaus, Douglas Worsnop, Brent Williams, *Washington University in St. Louis*

Two-dimensional chromatography has been applied to ambient aerosol in order to increase the molecular separation of complex samples. A significant challenge of analyzing multi-dimensional chromatograms is to identify and quantify the thousands of individual compounds found in ambient samples. The Volatility and Polarity Separator (VAPS) is an automated, field-portable instrument for in situ chemical characterization of organic aerosol as a function of volatility and polarity. The VAPS system sacrifices the molecular-level separation of multi-dimensional chromatography for improved mass throughput of oxidized and nonvolatile species. VAPS data consists of hourly volatility- and polarity-resolved bins of semivolatile and nonvolatile organic aerosol detected with high-resolution time-of-flight mass spectrometry. Analysis procedures, created with IGOR software (Wavemetrics Inc., Portland, OR), for novel VAPS data are presented here. The data analysis procedures include: auto retention time shifting, auto volatility and polarity binning of VAPS data, and auto internal standard mass calibration with interpolation of those calibrations across the entire VAPS data space. Lab and field (from SOAS 2013, Centreville, AL) VAPS data will be used to illustrate these auto data analysis procedures.

7IM.7

An Interactive Visual Analytics Framework for Multidimensional Data in a Geo-Spatial Context. ALLA ZELENYUK, Dan Imre, Zhiyuan Zhang, Jenny Hyunjung Lee, Klaus Mueller, Kevin McDonnell, *Pacific Northwest National Laboratory*

Single particle mass spectrometers (SPMS) by their very nature produce vast amounts of detailed data, the mining and analysis of which calls for unconventional methods that must draw on statistical methods, while preserving the wealth and depth of information. Success is critically dependent on a powerful data analysis and visualization software packages.

We have developed software packages called ClusterSculptor and SpectraMiner, with the former using statistical tools combined with the operator's scientific knowledge to steer the data classification process, while the latter is a unique data visualization and mining program that makes it possible to mine datasets of millions of particles using intuitive, visually driven tools.

Recently we showed that with our SPMS, SPLAT II and mini-SPLAT, in addition to single particle size and composition, we measure particle density, number concentrations, mass, asphericity, asymmetry, dynamic shape factor, morphology, phase, fractal dimension, rates of evaporation, and interaction of particles with water vapor (hygroscopic growth factor, activity as cloud condensation nuclei and ice nuclei).

To make use of this wealth of multidimensional information we implemented the parallel coordinates' interface that allows us to include the additional particle attributes measured by SPMS and other aerosol characterization instruments. The classification and mining process was extended to include, in addition to mass spectral peak intensities, all other observables measured by us or any other instrument, making it possible to quantify their relationships.

During airborne field deployment these data often have a geospatial reference and so it is of interest to show them within their geospatial context. Here we will present a new data visualization and analysis approach that uses Google Earth and is tightly linked to parallel coordinates display. Several other visual representations, such as pie and bar charts are integrated into the Google Earth display and can be interactively manipulated.

7UA.1

Understanding Spatial-temporal Variation and Sources of Black Carbon Using Stratified Mobile Monitoring. YI TAN, Eric Lipsky, Rawad Saleh, Albert A. Presto, Allen Robinson, *Carnegie Mellon University*

Pittsburgh's air quality is affected by a complex combination of local industrial and commercial sources, motor vehicles, terrain (e.g. river valleys) and regional transport. To better understand the spatial-temporal distribution of air pollution in Pittsburgh, we developed a mobile measurement platform to characterize a suite of air pollutants (black carbon (BC), particle-bound polycyclic aromatic hydrocarbons (PAH), benzene, and toluene). 42 sites were randomly selected based on stratification of elevation, influence of point sources and traffic. More than 270 hours of data were collected in winter (Nov 2011 – Feb 2012) and summer (Jun 2012 – Aug 2012). Mobile measurements were performed in 3 different sessions (afternoons/evenings, mornings, and midnights) in both seasons.

Pollutants displayed substantial spatial and temporal variation. Specifically, black carbon showed larger spatial variation than seasonal variation and diurnal variation in winter. Highest concentrations were observed in summer mornings due to the combination of meteorology and traffic. Black carbon concentrations were statistically different between valley sites and upland sites. Unlike other pollutants, the difference of black carbon between low and high traffic sites was insignificant. BC/PAH ratio was used to understand the sources of black carbon. BC/PAH ratios in winter and summer mornings resembled measurements in tunnels and near local point sources. However, higher BC/PAH ratios were observed at low traffic sites in summer afternoons and nights, suggesting additional sources and/or regional transport of black carbon.

7UA.2

Ambient Primary PM2.5 from Petroleum Refinery Operations.

LI DU, Jay Turner, *Washington University in St. Louis*

The Roxana Air Quality Study (RAQS), being conducted in Roxana (IL) at the fenceline of a petroleum refinery, will include three years of 24-hour integrated 1-in-6 day sampling for PM2.5 mass and speciation, volatile organic compounds (VOC), and gaseous carbonyl compounds. Routine operations at petroleum refineries are generally not considered to be a major source of primary fine particulate matter emissions. However, episodic releases from unit operations such as fluidized-bed catalytic cracking (FCC) can have considerable impacts. The Chellum group at the University of Houston has demonstrated a framework to track PM emissions from FCC operations using rare earth elements (REEs) as elemental tracers. We have analyzed RAQS PM2.5 samples from an 18-month period for REEs and interpreted the data using a two-source model assuming soil and FCC operations are the dominant sources of lanthanum (La) and cerium (Ce). On most days the La/Ce ratio is ~0.8 which is consistent with the bulk composition reported in the literature for soil. However, on some days the La concentration is much higher than predicted by the soil ratio. 20% of the 90 samples analyzed to date exhibit La/Ce > 1.6 (i.e. more than double the ratio expected for soil) and the 95th percentile of La/Ca ratio 4.6 (i.e. more than five time the ratio expected for soil). Nonparametric wind regression on the excess La, relative to soil, is generally consistent with the location of the FCC unit. This presentation summarizes the REEs patterns observed at this site including the two-source modeling results. PM2.5 major species reported for the Chemical Speciation Network (EC, OC, major ions, and elements by XRF) at the RAQS site are placed in a broader context by comparing to speciation network data at four other sites in the St. Louis metropolitan area.

7UA.3

Air quality during Landfill Fire in Iowa City, Summer 2012: Ambient Measurement and Plume Characterization.

ASHISH SINGH, Robert Bullard, Andrew Hesselink, Allaa Hassanein, Doug Beardsley, Michael D Wichman, Thomas Peters, Scott N. Spak, Elizabeth Stone, Charles Stanier, *University of Iowa*

The Iowa City Landfill experienced a fire in late May through early June of 2012, where approximately 1.3 million shredded tires caught fire, generating large amounts of smoke that impacted the surrounding cities and towns. A wide variety of measurements (particulate - mass, number/size, composition including molecular markers; gaseous pollutants- sulfur dioxide, carbon monoxide, carbon dioxide, and volatile organic compounds) were taken by public health and university researchers to characterize the smoke emitted from the fire and to determine the concentrations near the fire site and in nearby areas with higher population densities.

Excluding fenceline measurements at the fire site, peak recorded concentrations include benzene at ~10 ppb (grab sample), over 150 microgram per cubic meter $PM_{2.5}$ (~10 min averaging time) 1.6 km away from the fire, and impacts up to 40-70 microgram per cubic meter 4 to 9 km downwind away from the fire (1 hr avg.) were recorded. PAH concentrations up to 180x background were detected on one day at 3.9 km from the landfill (24 hr avg.).

A smoke forecast model (500 m horizontal resolution, 1 hour time resolution) based on the Weather Research and Forecasting (WRF) model and the AERMOD dispersion model was also employed during the incident. An overview of results will be presented in four categories: (1) ambient impacts of the smoke in terms of elevation above background levels; (2) chemical and physical emissions characterization of the smoke; (3) the WRF-AERMOD dispersion model results; and (4) lessons learned in terms of aerosol instrumentation and indicator-species selection for rapid screening of population risk.

7UA.4

Mass-Mobility Measurements of Urban and Background Aerosol – Measured with a DMA-TD-APM System.

ERIK, Z NORDIN, Jenny Rissler, Axel C. Eriksson, Emilie Hermansson, Adam Kristensson, Erik Swietlicki, Joakim Pagels, *Lund University, Sweden*

Soot particles emitted in urban environments are transformed to spherical-like particles through atmospheric aging during long range transport, this alters the climate and health affecting properties of the particles. The timescale of the aging and the composition of the aged aerosol are important parameters that need more investigation. For this purpose, mass-mobility measurements, using a Differential Mobility Analyzer-Aerosol Particle Mass analyzer (DMA-APM) system, were performed in consecutive winters in the city of Copenhagen, Denmark and at the rural background station Vavihill, 60 km northeast of Copenhagen.

A thermo denuder (TD, heated to 300 °C, residence time ~10 s) between the DMA and APM was used in selected experiments. Parallel measurements included a SMPS and a Soot-Particle-AMS were also performed. From the mass mobility relationship the effective density of the aerosol could be determined.

DMA-TD-APM measurements at Vavihill showed a dominant mode with almost size independent effective density mode at 1.3 - 1.4 g cm^{-3}, independent of wind direction, interpreted as long range transported aerosol particles. A size dependent mode at lower effective densities were detected for some measurement days predominantly at southern wind directions interpreted as freshly emitted or lightly aged soot.

The mode of fresh soot particles was essentially non-volatile in terms of mass when sampled through the thermo denuder. Most long range transported particles proved to have high volatile mass fractions in the thermo denuder experiments, there was a broad signal corresponding to very low masses, significantly lower than the soot mode. From this we conclude that the long range transport aerosol mainly consists of rather volatile material and that only a minor fraction of the mass can be interpreted as soot.

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7UA.5

Morphology and Mixing State of Atmospheric Aerosol in Mexico City.

SWARUP CHINA, Claudio Mazzoleni, Manvendra Dubey, Rajan K. Chakrabarty, Hans Moosmuller, W. Patrick Arnott, Timothy Onasch, Scott Herndon, *Michigan Technological University*

Morphology, mixing state, and size distribution of atmospheric aerosols influence their chemical and mechanical interactions with the environment, their physical properties, and radiative effects. We investigated the morphological and optical characteristics of atmospheric aerosols collected onboard the Aerodyne mobile laboratory during the MILAGRO (Megacity Initiative: Local and Global Research Observations) campaign that took place in Mexico City in March 2006. Aerosol samples were collected on nuclepore filters and individual particle were analyzed by scanning electron microscopy. Samples were collected at six sites with various atmospheric and geographical characteristics including urban, sub-urban, mountaintop, and industrial areas. Aerosol light absorption and scattering coefficients at 781nm were measured with an integrated photoacoustic nephelometer.

We show positive association between the relative abundance of soot particles and the aerosol co-albedo with some anomalies that are investigated using particle size distribution, morphology, and mixing state. Fractal dimension of aged soot is found to be more variable at the mountaintop and suburban areas than of fresh soot at the T0 site, close to the city center. Soot particles were found in different but distinct mixing states. We classified them into four categories based on their morphology and a visual classification: 1) bare (or thinly coated) 2) partly coated, 3) embedded, and 4) soot-inclusions, where soot is mixed with, but not uniformly coated by other material. Temporal variations of optical properties at T0 show that the minimum aerosol co-albedo was observed in the afternoon when the number fraction of soot was the lowest and the coated fraction of soot was the highest. On average,~70% higher number of soot-inclusion particles were found at the sub-urban area than at T0, suggesting that complex mixing and processing of soot particles can occur over a relatively short time.

7UA.6

Development of an Air Quality Model for Particle Formation from Sulfur Compounds and Amines. ANDREW MARTINEZ, Matt Dawson, Veronique Perraud, Barbara J. Finlayson-Pitts, Donald Dabdub, *University of California, Irvine*

Airborne particles are known for their wide-ranging effects on human health and climate, including their influence on cloud formation and ground-level solar radiation. The mechanisms and dynamic responses of particle formation are not well understood, contributing to International Panel of Climate Change's conclusion that this class of species provides the largest uncertainty in estimating the overall effect on radiative forcing and climate change. In particular, it has been shown that conventional air quality models cannot match observed atmospheric concentrations of airborne particles, particularly secondary organic aerosol (SOA) formed from oxidation of organic precursors. Discrepancies of a factor of ten or more have been reported. Recent experimental work has sought to provide greater accuracy to models' predictive capability via the identification of previously unrecognized reaction mechanisms. In this regard, the authors' efforts have focused primarily on the system consisting of combinations of amines, organosulfur compounds, sulfuric acid, and methanesulfonic acid. The authors are integrating reaction mechanisms for particle formation from these precursors into the previous-generation UCI-CIT air quality model. This three-dimensional, spatially resolved model is then utilized to investigate the potential for particle formation via these newly-included mechanisms. Of particular importance are the development of amine emission scenarios and investigation of oxidation chemistry that would compete with particle formation (via species such as OH and ozone). These considerations have been utilized as a tool for assessing the overall potential for particle formation from these reaction pathways in the South Coast Air Basin of California.

7UA.7

Simulating Particle Deposition on Urban Green Infrastructure. K. Max Zhang, Cliff Davidson, JONATHAN STEFFENS, Zheming Tong, *Cornell University*

Urban green infrastructure such as green roofs and green walls has the potential to reduce air pollutant concentrations due to enhanced deposition. In this talk, we will present our recent study in improving simulations of particle deposition on urban green infrastructure. The new method we developed is called Enhanced Resistance Network Approach (ERNA), in which the aerodynamic resistance term is derived from Large Eddy Simulation modeling of complex urban flows. We will compare the deposition velocity predicted by ERNA against those derived from traditional resistance network approach. ERNA has the potential to become a powerful tool in studying urban deposition.

8AC.1

Chemical Characterization of Secondary Organic Aerosol by Atmospheric Solid Analysis Probe Mass Spectrometry (ASAP-MS).

VERONIQUE PERRAUD, Carla Waring-Kidd, John Greaves, Barbara J. Finlayson-Pitts, *University of California, Irvine*

Secondary organic aerosol (SOA) is ubiquitous in the atmosphere and comprises a large fraction of the total aerosol budget. Although a lot of effort has been made over the years to develop specific analytical strategies, elucidation of SOA chemical composition and identification of key molecular species responsible for its formation and growth processes remains challenging. Understanding these processes is critical for assessing their impact on human health, visibility and climate. We report here the application of a relatively new technique, atmospheric solid analysis probe mass spectrometry (ASAP-MS), to laboratory-generated SOA. Ozonolysis of terpenes was studied using the unique UCI large volume slow flow aerosol flow tube under various relative humidity conditions (0 to >80%) in presence and absence of an OH-scavenger (i.e. cyclohexane). The particles were collected on 5 × 5 mm Si-wafers held on a commercial Sioutas impactor during sampling. Measurements were taken at different reaction times using two stages (stage C with a cut off diameter at 500 nm and, stage D with a cut off diameter at 250 nm) providing a size speciation of the particles. The Si-wafers were analyzed using a modified ASAP-MS probe that held the wafer in place without any need for transfer or modification of the sample prior to analysis, leading to a greater integrity of the sample and better reproducibility. Results include 1) the thermal desorption profile of the SOA by ramping the temperature from 20’C to 450’C; this provides insight into the volatility and thermal stability of the SOA and, 2) high resolution mass spectra, which provides accurate mass measurements and the identification of key species. Atmospheric implications of this study will be presented.

8AC.2

The Photolytic Processing of Organic Aerosols through Carbonyl Photochemistry.

SANDRA BLAIR, Scott Esptein, Sergey Nizkorodov, *University of California, Irvine*

Photochemistry is the primary driving force behind most chemical processes occurring in the atmosphere. Secondary organic aerosol (SOA) contains highly oxidized, multifunctional, organic compounds, many of which are photolabile, even under the near-UV excitation conditions representative of the lower atmosphere. Because of the high prevalence of carbonyl compounds in SOA, its photochemistry can be expected to be driven in part by the well-known photochemical reactions of carbonyls such as Norrish and Yang mechanisms. Therefore, investigating model carbonyls, such as linear chain aldehydes, provides valuable information on the mechanism and rate of photochemical processes occurring in SOA. Short chain aldehydes have been studied extensively over the last few decades in the gas-phase. The importance of condensed-phase photochemistry in the atmosphere has not been recognized until recently. The extent to which the photolysis quantum yield is suppressed in the condensed-phase is not well-known. There are many types of organic matrices that can be used to mimic the environment of SOA particles; the pure condensed-phase form of an aldehyde is a convenient representation of either a liquid or solid organic matrix (depending on the size of the aldehyde). A C-11 aldehyde, undecanal, provides a perfect model for this carbonyl photochemistry because it melts slightly below room temperature. The photochemistry of undecanal is investigated in several different environments: (1) liquid melt; (2) frozen solid; and (3) vapor phase. Products of condensed-phase experiments are analyzed with gas chromatography mass spectrometry, Fourier transform infrared spectroscopy, and ultraviolet-visible spectroscopy. Proton transfer reaction mass spectrometry is used for real time high resolution and sensitive gas-phase photochemical measurements. The main conclusion of this study is that condensed-phase photolysis of aldehydes is not significantly hindered relative to the gas-phase photolysis, suggesting that photochemistry of aldehydes in SOA should be just as important as photochemistry of gas-phase aldehydes.

8AC.3

SOA Yield from Ozonolysis of BVOC at Varying NO_2 Concentrations. Danielle C Draper, Delphine Farmer, Yury Desyaterik, JULIANE L. FRY, *Reed College*

Environmental chamber experiments were conducted studying SOA formation and growth from ozonolysis of alpha-pinene, beta-pinene, delta-carene, and limonene under varying concentrations of NO_2. Qualitatively different NO_2 dependences are observed for the different biogenic precursors. Analysis of SOA growth kinetics and aerosol chemical composition, as well as chemical kinetics box modeling, are used to identify mechanistic reasons for the observed behavior.

8AC.5

Reaction Pathways of Primary, Secondary and Tertiary Amines with Ozone, Hydroxyl Radical and Nitrate Radical. DEREK PRICE, Xiaochen Tang, David R. Cocker III, Kathleen Purvis-Roberts, Philip Silva, *University of California, Riverside*

The presence and importance of amines in the atmosphere continues to gain more attention. Common emission sources of aliphatic amines are agricultural facilities. Amine-based control technologies designed to capture NO_x and CO_2 from post fossil fuel combustion are a possible source of ammonia and amino alcohols. Determining the reactions of these amines with common atmospheric radicals is important to understanding both daytime and nighttime atmospheric chemistry. A series of well-characterized smog chamber experiments were conducted in which aliphatic and functionalized amines (primary, secondary, tertiary) were reacted with either ozone, hydroxyl radical (OH) or nitrate radical (NO_3). Chemical composition of the aerosol products was obtained with a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a Particle Into Liquid Sampler Time of Flight Mass Spectrometer (PILS-ToF-MS). The density and volatility of the aerosol were also measured. Chemical composition of the gas phase products was obtained with a Selected Ion Flow Tube Mass Spectrometer (SIFT-MS). Several reaction pathways were observed. These pathways will be discussed and include the formation of amine salts, the growth of higher mass oligomer-like compounds, as well as the production of nitrosamines and nitramines. The relative importance of each pathway to the overall production of aerosol is dependent on the type of amine and oxidant. For example, trimethylamine produced more organic aerosol compared to diethylamine, which produced more amine salts. Also, the secondary amines formed more nitramines than the tertiary amines when reacted with nitrate radical.

8AC.6

Quantification of the Carbonyl Group Contribution to Aqueous-Phase SOA Using Fourier Transform Infrared Spectroscopy. Kathryn George, Travis Ruthenburg, Jeremy Smith, Lu Yu, Cort Anastasio, Qi Zhang, ANN DILLNER, *University of California, Davis*

Reactions in the aqueous-phase play an important role in atmospheric secondary organic aerosol (SOA) production, yet many of the products remain poorly characterized. Phenols, water-soluble compounds released during biomass combustion, readily participate in aqueous-phase reactions to form low volatility SOA products. In this study, aqueous-phase SOA was produced from the oxidation of three phenolic compounds (phenol, guaiacol, and syringol) by OH and the triplet excited state of 3,4-dimethoxybenzaldehyde. Here, we analyze carbonyl-containing SOA products using a Fourier transform infrared spectroscopic (FTIR) technique.

Aqueous-phase SOA was atomized, collected on a Teflon filter, weighed, and scanned in transmission mode on an FTIR. In order to quantify the carbonyl functional group contribution, we calibrated using carbonyl-containing compounds that included carboxylic acids, a ketone, and an ester, all of which absorb in a wavenumber range similar to that found in our SOA samples. Our results indicate that carbonyl-containing compounds account for up to 11% of the total SOA mass in our samples. Carbonyls are generally present in the greatest amount in syringol SOA, followed by guaiacol and phenol SOA. Ion chromatography on the same samples indicates that only a small fraction of the carbonyls measured by FTIR are small acids. These results provide new insight on carbonyl production in aqueous-phase SOA.

8AC.7

Secondary Organic Aerosol Produced from Aqueous Reaction of Phenols with an Organic Excited Triplet State and Hydroxyl Radical. JEREMY SMITH, Haley Kinney, Lu Yu, Kathryn George, Travis Ruthenburg, Ann Dillner, Qi Zhang, Cort Anastasio, *University of California, Davis*

While reactions in atmospheric condensed phases can form and transform secondary organic aerosol (SOA), these reactions are not well represented in many air quality models. Many of the previous studies of aqueous SOA focused on small, non-aromatic compounds such as glyoxal and methyglyoxal, but here we are interested in benzene diols (aka diphenols or dihydroxybenzenes), which are emitted from biomass burning and formed from the oxidation of anthropogenic aromatics. These compounds possess significant water solubility, with Henry’s Law constants above 1000 M atm-1, and thus are good candidates for precursors of aqueous SOA.

In this study we examined aqueous SOA production from the oxidation of three benzene- diols (catechol, resorcinol, and 1,4-hydroquinone) by OH and the triplet excited state of 3,4-dimethoxybenzaldehyde (DMB). We chose DMB as a model atmospheric photosensitizer because it is released in significant quantities during wood and biomass combustion. We measured two components in our reaction systems: (1) the kinetics of benzene diol oxidation and (2) the SOA mass yield from these reactions. Our results indicate that aqueous oxidation of benzene diols via triplet excited states proceeds rapidly under atmospherically relevant conditions. SOA formation is very efficient with both of these oxidants, with SOA yields near or above 100%. The SOA products absorb significant amounts of UV-A light and appear to be highly oxidized. We will discuss these results and compare them to our recent studies of the oxidation of other biomass-burning phenols (phenol, guaiacol, syringol).

8AC.8

The Heterogeneous Oxidation of Internally Mixed Primary and Secondary Organic Aerosol: A Case for the Importance of Secondary Chemistry. KATHERYN KOLESAR, Chris Ruehl, Gabriel Isaacman, Gina Buffaloe, Theodora Nah, Allen H. Goldstein, Kevin Wilson, Christopher Cappa, *University of California, Davis*

Primary and secondary organic aerosol (POA and SOA) can exist as internally mixed particles in the atmosphere, yet laboratory studies tend to investigate the physical and chemical properties of each separately. Consequently, interactions between POA and SOA in the particle are largely unknown which could lead to errors in predicting particle hygroscopicity, light attenuation and lifetime. The heterogeneous oxidation of squalane, a C_{30} saturated, branched hydrocarbon found in diesel emissions, by hydroxyl radicals (in the presence of O_2) has been previously well-characterized, and the effective uptake coefficient at [OH] ~ 10^{10} molecules cm^{-3} was $gamma_{eff,Sq}$ = 0.30 ± 0.07. Here, the influence of internal mixing of squalane with two different complex mixtures, SOA from alpha-pinene + O_3 and motor oil, on $gamma_{eff,Sq}$ is investigated. Particle composition was measured with a vacuum ultraviolet aerosol mass spectrometer that uses soft ionization (10.5 eV photons), allowing for the unique characterization of squalane reactivity separate from the additional components. We found that as the SOA coating thickness increases (or squalane volume fraction decreases) the γeff,Sq also increases. Similarly, when squalane was doped into motor oil the $gamma_{eff,Sq}$ was increased over that of pure squalane. The largest increase of the effective uptake coefficient observed in both the motor oil + squalane and squalane + SOA systems is ~5 times that of pure squalane. Under typical 24-hour average [OH] (1 x 10^6 molecules cm^{-3}) the atmospheric lifetime of pure particulate squalane (D_p = 180 nm) with respect to OH oxidation is ~13 days, whereas a particle of mixed composition has an oxidation lifetime of ~3 days.

8AC.9

Simulation of Isoprene SOA Formation Using UNIPAR: A Lumping Model Integrated with Explicit Gas Phase Kinetic Mechanisms and Aerosol Phase Reactions. ROSS BEARDSLEY, Yunseok Im, Myoseon Jang, *University of Florida*

The Unified Partitioning-Aerosol phase Reaction (UNIPAR) model, which was developed to predict the secondary organic aerosol (SOA) formation through multiphase reactions, has been applied to the photooxidation of isoprene/NO_x in the presence and the absence of SO_2. UNIPAR utilizes an explicit kinetic model to predict the gas phase oxidation of volatile organic compounds (VOC) whose products are then lumped by volatility (6 levels) and reactivity (5 levels) throughout the cycles of gas phase oxidation. In UNIPAR, organic matter (OM) formation is predicted as the sum of the OM formed by partitioning (OM_P), via the module used in CMAQ 5.0.1, and the OM formed by aerosol phase reactions (OM_{AR}), including oligomerization, acid-catalyzed reactions and organosulfate (OS) formation. Model performance was tested using SOA data produced using a large outdoor chamber (UF-APHOR). Day long experiments were performed for various VOC/NOx conditions in the presence and absence of SO_2 under the diurnal patterns of ambient temperature and humidity. The updated UNIPAR model was found to reasonably predict isoprene SOA formation and OMAR was found to dominate the overall isoprene OM formation in the presence of SO_2. The effect of both gas phase aging and organosulfate formation on isoprene SOA yields were evaluated using the model.

8AC.10

Secondary Organic Aerosol Formation from Glyoxal: Salting Behavior and Kinetics of SOA Formation and its Dependence on Aerosol Seed Composition. ELEANOR WAXMAN, Jay Slowik, Christopher Kampf, Rupert Holzinger, Josef Dommen, Andre Prévôt, Urs Baltensperger, Rainer Volkamer, *University of Colorado*

Glyoxal forms secondary organic aerosol (SOA) by partitioning to the aerosol aqueous phase according to Henry's law. Our recent simulation chamber experiments suggest that electrical forces, rather than vapor pressure, drive glyoxal partitioning to ammonium sulfate seed aerosols. The Henry's law partitioning coefficient increases exponentially with salt concentration. A single "salting in" constant is found to bridge between dilute cloud water and concentrated aerosol water, providing a unifying concept for these very different chemical regimes. Through a series of experiments performed at the Paul Scherrer Institut in April/May 2011 and May/June 2013, we have studied the effect of these electrical forces on glyoxal partitioning by using a variety of aerosol seed chemical compositions, including ammonium sulfate, ammonium nitrate, and sodium nitrate. We have also varied the aerosol pH by including gas-phase ammonium. In this work, we present preliminary analyses of these experiments. We also briefly investigate the formation of irreversibly-formed and reversibly-formed SOA from glyoxal and the effect of seed chemical composition, and identify species that contribute to each of these SOA fractions.

8AC.11

Measurement of the Sensitivity of Biogenic SOA Formation under Ambient Conditions to Anthropogenic Factors Using a New Captive Aerosol Growth and Evolution Chamber System during the Southern Oxidant and Aerosol Study. Don Collins, NATHAN TAYLOR, Jill Matus, Carlos Antonietti, Chance Spencer, Robert Griffin, Yu Jun Leong, Basak Karakurt Cevik, *Texas A&M University*

We present first results from a new portable Captive Aerosol Growth and Evolution (CAGE) chamber system deployed in the summer of 2013 during the Southern Oxidant and Aerosol Study (SOAS). Experiments were designed to isolate the sensitivity under ambient conditions of aerosol processes to anthropogenic factors--investigation for which the CAGE system is well suited.

The gas phase of aerosol retention/reactor volumes in each of the dual CAGE chambers are maintained in equilibrium with a continuous air flow isolated behind gas permeable ePTFE membranes. An ambient air exchange flow causes the reactor gas phase to closely follow ambient conditions. Coupled with temperature control and UV-transparency, the CAGE chambers can thus mimic the ambient photo-chemical milieu. This gas exchange stream can also be spiked (with trace gases or water vapor) or fully prescribed. Additional CAGE features include adiabatic cloud formation, equipment for generating tailored gas and aerosol samples, and analytical aerosol instrumentation including an Aerodyne HR-ToF-AMS, TDMA, SMPS and DMT-CCN.

Typical experiments contrasted the evolution of aerosol properties between a control and a perturbed chamber. The control chamber was operated to mimic ambient conditions; the perturbed chamber gas exchange flow was identical, but spiked with an anthropogenic factor such as NO_x or ozone. In both chambers the initial aerosol was a mixture of three monodisperse aerosol with the following diameters: ~10 nm, to capture impacts on initial aerosol growth; ~100 nm, for impacts on CCN activity; and ~350 nm, to suppress nucleation. The contrast in the aged aerosol was summarized as the sensitivity of aerosol process characteristics (O:C ratio, size, hygroscopicity) to the trace gas concentration under ambient conditions. These experiments were repeated at different ambient conditions and occasionally included cloud cycles. Other primary experiments included perturbations of aerosol mass and number loading, light and dark conditions, and cloud condition perturbations.

8AC.12

Temperature Effects on Secondary Organic Aerosol Formation and its Properties. MARY KACARAB, Ping Tang, Lijie Li, Derek Price, David R. Cocker III, *University of California, Riverside*

Temperature has a profound effect on secondary organic aerosol (SOA) formed from various aromatic hydrocarbon species. A series of temperature-controlled atmospheric chamber experiments were carried out to revisit the effects of temperature on aerosol formation, volatility, hygroscopicity, and chemical composition. The temperature of the environmental chamber system was cycled through various patterns of 5, 27, and 40^{o}C in order to examine the reproducibility and hysteresis of the SOA formed during aromatic photooxidation. It is consistently seen that a larger volume of SOA than would be expected is formed at the lower temperature (5^{o}C) than is formed at room (27^{o}C) and higher (40^{o}C) temperatures. Significant mass is lost when the system is heated up, not all of which is gained back once the system is cooled down again, indicating the formation of thermally labile compounds. The chemical composition of the aerosol is monitored with an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS), while volatility and hygroscopicity are each measured with a Tandem Differential Mobility Analyzer (V-TDMA and H-TDMA, respectively). Furthermore, online gas phase chemical composition is observed with the SYFT Technologies Voice200 Selected Ion Flow Tube Mass Spectrometer (SIFT-MS). The multiple physical and chemical properties studied also show clear impacts due to both current system temperature and temperature at which the aerosol is formed. Properties of aerosol formed at 40^{o}C then cooled to 5^{o}C do not match the properties of aerosol formed at 5^{o}C, showing a clear hysteresis effect. Due to the wide range of temperatures encountered in our troposphere, it is imperative that we understand temperature’s effect on aerosol formation in order to implement it in current SOA formation models.

8AC.13

Understanding Secondary Organic Aerosol Formation from Aqueous-phase Reactions of Phenolic Compounds. LU YU, Jeremy Smith, Alexander Laskin, Julia Laskin, Kathryn George, Cort Anastasio, Ann Dillner, Qi Zhang, *University of California, Davis*

Phenolic compounds, which are emitted in significant amounts from wood combustion and wild fires, potentially make a significant contribution to atmospheric secondary organic aerosol (SOA) via aqueous-phase reactions. In this study, we investigate the aqueous-phase reactions of three types of phenols (phenol, guaiacol and syringol) with two oxidants-hydroxyl radical (OH) and the excited triplet state (3C*) of an aromatic carbonyl. We thoroughly characterize the chemical compositions of the low volatility reaction products using an Aerosol Mass Spectrometer with mass resolution of ~6000 m/delta m and a Nanospray-Desorption Electrospray Ionization-High Resolution (100,000 m/delta m) Mass Spectrometer (Nano-DESI MS). Our goal is to understand the chemical mechanisms responsible for aqueous phenolic SOA formation.

Our results indicate that the aqueous oxidation of phenols forms a large number of compounds, including phenolic oligomers (up to hexamers) and their derivatives with varying numbers of carbonyl, carboxyl, and hydroxyl functional groups, and a number of ring-opening species including small organic acids (e.g., oxalate, formate, and acetate). While the identities of the product molecules are similar between the two oxidants, reactions initiated by OH produce more small organic acids while oxidation by 3C* enhances the formation of higher molecular weight species, including phenolic oligomers and hydroxylated products. In addition, the low-volatility reaction products of phenol with OH are dominated by monomer and monomeric derivatives, while dimer and dimeric derivatives are the dominant products of 3C* reactions of phenol. Dimers are the dominant species in syringol and guaiacol SOA, both for oxidation by OH and 3C*. The results indicate that the formation of low volatility products via aqueous-phase reactions of phenols mainly involves polymerization, hydroxylation, carbonylation, esterification, and various fragmentation processes including aromatic ring opening and loss of methoxy groups.

8AC.14

Instantaneous Secondary Organic Aerosol Formation from M-xylene Photooxidation: Quantification of NOx and NO3 Radical Effects on SOA Yield. LIJIE LI, Ping Tang, Chia-Li Chen, Mary Kacarab, David R. Cocker III, *University of California, Riverside*

Observations from recent field studies indicate that the formation of secondary organic aerosol (SOA) from anthropogenic sources is considerably underestimated in current models. Aromatic hydrocarbons have been recognized as a major anthropogenic SOA precursor gases. Further, it has been widely reported that SOA formation from aromatic hydrocarbon photooxidation is highly sensitive to the NO_x level. In this study, instantaneous aerosol yield (IAY) and a modified SOA growth curve are introduced and applied during data mining of 89 classic m-xylene photooxidation experiments with HC/NO_x ratios ranging from 1.3 to 71.6. It is observed that IAY trend is categorized into two types. For low NOx experiments (initial NO_x lower that 100 ppb), NO_2/NO ratio higher than 70 could serve as a threshold to the substantial formation of SOA. When the initial NO_x concentration is higher than 100 ppb, the IAY of SOA formation is lower even though NO_2/NO ratio is higher than 70. For these high initial NO_x experiments, the product of NO_2 and O_3 is comparatively high indicating the potential effects of NO_3 radical when using black lights as a light source for photooxidation. Next, radical experiments are carried out to study the effect of NO_3 radical. NO_3 radical experiments are realized by injecting N_2O_5 in the middle of photooxidation experiment. m-Xylene, H_2O_2 and O_3 are injected into the chamber to initialize the SOA formation and black lights are still used as light sources. The effect of NO_3 radical on SOA yield, volatility and density will be reported. Mz43 ($C_2H_3O^+$)/mz44 (CO_2^+) ratio determined by ToF-HR-AMS is used to demonstrate the difference in SOA chemical composition. This study facilitates the understanding of potential mechanism that is critical to the SOA formation from aromatics.

8AC.15

OH Initiated Heterogeneous Degradation of Organophosphorus Compounds. LIU YONGCHUN, Liggio John, Harner Tom, Jantunen Liisa, Shoeib Mahiba, Shao-Meng Li, *Environment Canada*

Organophosphorus compounds (OPs) have been extensively used worldwide as flame retardants, plasticizers, antifoaming agents, and additives because of their favorable physicochemical characteristics. In 2004, the global consumption of OPs used as flame retardants was 209,000 tons [Möller et al., 2012]. However, the global consumption of OPs may increase greatly due to the phasing out of bromine-containing flame retardants (BFRs) and OPs are identified as possible substitutes. In most applications, OPs easily leach out of the material into the environment via volatilization, abrasion, and dissolution. OPs have been observed widely in atmospheric particles even in polar regions [Möller et al., 2012]. However, little is known about their atmospheric fate. The Canadian Chemicals Management Plan (CMP) has targeted OP FRs for risk assessment, including assessing stability and atmospheric transport potential of OP FRs and other priority chemicals that are associated primarily with particles.

In the current study, OH initiated heterogeneous reaction kinetics of tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris-2-ethylhexyl-phosphate (TEHP), tris-2-butoxyethyl-phosphate (TBEP), and tri-phenyl phosphate (TPhP) coated on (NH4)2SO4 were investigated using a photo-chemical flow tube which was coupled to an Aerosol Mass Spectrometer (AMS) and Proton Transfer Reaction Mass Spectrometer (PTR-MS). The second order rate constants (k2) for these compounds with OH were measured at 298 K. The k2 of TDCPP was measured to be (1.30±0.42)×10-11 cm3 molecule-1 s-1. Based on 12 h-average OH concentration (1.5×106 molecule cm-3), its life-time is estimated to be (1.3±0.4) days in the troposphere. This relatively short atmospheric life-time represents a lower limit for persistence in air. Future work will evaluate atmospheric lifetimes of OP FRs using more complex and realistic particles, which is expected to increase their persistence.

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8AC.16

The Influence of Molecular Structure and Chemical Functionality on the Heterogeneous OH-initiated Oxidation of Unsaturated Organic Particles. THEODORA NAH, Sean Kessler, Kelly Daumit, Jesse Kroll, Stephen R. Leone, Kevin Wilson,*University of California, Berkeley*

Recent studies on the oxidation of organic particles suggest that the heterogeneous oxidation rate and reaction mechanism depend heavily on the molecular structure of the hydrocarbons in the particle. In this work, two model reaction systems (OH + squalene ($C_{30}H_{50}$) and OH + unsaturated fatty acid (oleic acid ($C_{18}H_{34}O_2$), linoleic acid ($C_{18}H_{32}O_2$) and linolenic acid ($C_{18}H_{30}O_2$)) are analyzed to investigate the effect of molecular structure and chemical functionality on the reaction rates and mechanism in the heterogeneous OH-initiated oxidation of unsaturated organic particles. Squalene is a branched alkene with six C=C double bonds, while oleic acid, linoleic acid and linolenic acid are linear acids with one, two and three C=C double bonds, respectively.

The effective uptake coefficient for squalene measured at 10 % [O_2] is 2.34 ± 0.07, while the effective uptake coefficients measured for oleic acid, linoleic acid and linolenic acid at 10 % [O_2] are 1.72 ± 0.08, 3.75 ± 0.18 and 5.73 ± 0.14, respectively. The effective uptake coefficients are larger than unity, providing clear evidence for particle-phase secondary chain chemistry. The effective uptake coefficient for squalene is smaller than that measured for linoleic acid and linolenic acid when O_2 is present in reaction. Additionally, the effective uptake coefficient for squalene increases with the [O_2] in the reactor, whereas the effective uptake coefficients for the unsaturated fatty acids decrease with increasing [O_2]. This suggests that the chain propagation chemistry in squalene oxidation is different from the unsaturated fatty acids. Elemental composition analysis of squalene particles shows that the average particle mass and particulate carbon content decreases immediately when oxidation is initiated at 10 % [O_2]. In contrast, elemental composition analysis of linoleic acid particles shows that O_2 does not influence the rate of particle volatilization in the OH + linoleic acid reaction. This suggest that while fragmentation reactions becomes more important when O_2 is present in the OH oxidation of branched unsaturated organic aerosol, O_2 does not alter the relative importance of fragmentation reactions in the OH oxidation of linear unsaturated organic aerosol.

8AC.17

Aqueous Reaction Rates of Hydroxyacetone with Ammonium Sulfate and Amines Measured by NMR as a Function of pH.MICHAEL SYMONS, Alyssa Rodriguez, Melissa Galloway, David De Haan, *University of San Diego*

Hydroxyacetone is a common tropospheric ketone because it is formed by oxidation of isoprene and biomass combustion. Reactions of hydroxyacetone in aqueous droplets and aerosol particles that contain ammonium salts and amines may be significant sources of secondary organic aerosol and brown carbon material. We report reaction rates of common atmospheric amines (glycine and methylamine) and ammonium sulfate with hydroxyacetone in D_2O at room temperature over the pH range 3-7. Reaction mixtures of amines and hydroxyacetone were monitored by ^1H NMR over 12 or more hours. Data was normalized using internal standards acetonitrile (ACN) or dimethyl sulfoxide (DMSO). Hydroxyacetone + methylamine reaction rates increase with pH. Hydroxyacetone’s methyl group (2.13 ppm) reacts 2.5 times faster than the methylene group where OH is attached (4.36 ppm), indicating that aldol condensation occurs mainly via the methyl group. However, at pH 3.9 reaction the methyl and methylene groups occur at similar rates, within 10.0 percent. Additionally, we observed the formation of aromatic products.

8AC.18

Infrared Spectra of Individual Wavelength-Scale Particles: Spectral Challenges and Novel Techniques. ARUNA RAVI, Antriksh Luthra, James Coe, *The Ohio State University*

The characterization of infrared (IR) extinction and absorption spectra of single particles of mixed composition has wide use in astronomy, geology, atmospheric sciences, and nanotechnology. To quantify the amount of a material in a bulk model, one might employ the Beer–Lambert law, whereas with single particles one might have a specific orientation and require a nonlinear, Mie-like particle theory. A "scatter-free" infrared library of 63 previously airborne dust particles of 3-5μm size was obtained with an imaging infrared microscope by trapping the particles in the holes of plasmonic metal mesh, providing a qualitative analysis of the occurrence of common materials in our lab air [K.E. Cilwa et al, J. Phys. Chem. C. 115, 16910 (2011)]. A recent study by our group [D.B. Lioi et al, J. Phys. Chem. A. (2013), under review] presents a quantitative analysis of inhalable dust using IR spectra of 94 individual dust particles of known composition. Single particle spectra present a unique set of challenges, for instance, spectral lineshapes of wavelength scale particles can be distorted by shape, phase, and orientation. Another recent study by our group [A. Ravi et al, Phys. Chem. Chem. Phys., 2013, 15, 10307-10315] uses three dimensional finite difference time domain (3D-FDTD) calculations on single particles to illustrate some of the challenges – in particular the distortion of lineshapes by strong phonon vibrations that lie within a range of strong scattering. It is observed that at small sizes relative to the wavelength, particles exhibit Beer-Lambert-like behavior. However, as the particle size increases to about the wavelength, this behavior begins to diverge from Beer-Lambert. A Mie–Bruggeman model for single particle spectra is presented to isolate the effects of strong phonon vibrations on lineshapes which has utility for analyzing the spectra of single, mixed-composition particles. This model enables the determination of volume fractions of components in single particles that are mixtures of many materials with strong phonons, as are the dust particles breathed into people's lungs.

8AC.19

Kinetics and pH Dependence of Aqueous-phase Reactions of Glycolaldehyde with Glycine, Ammonium Sulfate, and Methylamine. ALYSSA RODRIGUEZ, Michael Symons, Alexia De Loera, Melissa Galloway, David De Haan, *University of San Diego*

Glycolaldehyde is produced by biomass burning and isoprene oxidation, and is a common atmospheric aldehyde. Its photooxidation in aqueous droplets and aerosol has been identified as a potentially important SOA source. Its aqueous phase reactions with atmospheric amino acids and amines may also be a source of SOA and brown carbon material. These reaction rates can be measured by proton NMR in 0.5 M D2O solutions. Aqueous reactions of glycolaldehyde with glycine, ammonium sulfate, or methylamine were studied over the pH range 3-7. After 11 hour reactions in a 400 MHz NMR spectrometer, signals were converted to concentrations using MestReNOVA software and reaction rates were extracted from both reactant signals. Reaction rates (and browning) increased with pH, as expected. Glycolaldehyde loss rates were typically far in excess of amine loss rates, consistent with amine-catalyzed aldol condensations being the dominant reaction pathway. Aromatic products were observed in the NMR spectrum.

8AC.20

Glyoxal in the Po Valley, Italy as a Tracer for Aqueous Aerosol Processing. KATE SKOG, Yong Lim, Amy P. Sullivan, Natasha Hodas, Barbara Turpin, Jeffrey L. Collett, Jr., Frank Keutsch, *University of Wisconsin - Madison*

Even though most aerosol in the atmosphere interacts with water, aqueous chemical processes are not well understood. Glyoxal, a secondary organic compound produced photochemically, has a high Henry’s law constant and has been shown to partition into aerosol. This makes glyoxal an ideal tracer for aqueous secondary organic aerosol formation. In June and July of 2012, the Madison Laser-Induced Phosphorescence instrument (Mad-LIP) was deployed to the San Pietro Capofiume, Italy field site for the Pan-European Gas-AeroSOls-climate interaction Study (PEGASOS) to measure gas phase glyoxal concentrations. Using these measurements, gas phase HOx measurements, modeled liquid water content, and the Lim et al. aqueous chemistry mechanism, the contribution of glyoxal to aqueous SOA was modeled and compared to measured aerosol composition. Contribution of glyoxal to oxalate, a compound prevalent in (aqueous) aerosol, will be discussed.

8AC.21

Determination of Setschenow Constants of Organic Compounds in Ammonium Sulfate Solutions and the Salt Effect on Air-Water Partitioning. CHEN WANG, Ying Duan Lei, Frank Wania, *University of Toronto*

The presence of salts significantly influences the partitioning behavior of organic compounds between the gas phase and environmentally relevant aqueous phases such as sea water and aqueous aerosol. The change in the activity of organic chemicals in aqueous solutions caused by inorganic salts is quantified with empirical Setschenow constants. Atmospheric water (cloud, fog and aqueous aerosol) contains a mixture of various inorganic salts, of which ammonium sulfate is often the most abundant. As a result, Setschenow constants for ammonium sulfate are required for accurate atmospheric phase distribution assessments of organic compounds, including those implicated in secondary organic aerosol (SOA) formation. However, Setschenow constants for ammonium sulfate are available only for a very limited number of chemicals. One reason for this lack of data might be that their determination traditionally requires highly precise measurements of aqueous solubility at different ionic strength. In the present study, the suitability of three methods for determining Setschenow constants in a relatively simple, reliable and inexpensive way is explored. They are a shared headspace passive dosing method, a negligible-depletion solid phase micro-extraction (SPME) technique, and a headspace gas chromatography method. The objective of this project is to make measurements of the Setschenow coefficients for diverse organic compounds (especially SOA relevant substances) in ammonium sulfate solutions and then develop a predictive model for estimating Setschenow coefficients from chemical structure.

8AC.22

React or Evaporate? Atmospheric Aldehydes in Aqueous Droplets Containing Amines or Ammonium Sulfate. MICHELLE POWELSON, Melissa Galloway, David De Haan, *University of San Diego*

Approximately half the mass of typical aerosol particles consists of organic compounds, which change the radiative properties of aerosol and so contribute to global climate change. Oligomer formation in atmospheric aqueous aerosol is an important formation mechanism for low-volatility organic material. There are several aldehydes present in clouds droplets, including methylglyoxal, glycolaldehyde, hydroxyacetone, glyoxal, and acetaldehyde. These aldehydes have the potential to oligomerize and/or create “brown carbon” products when reacted with ammonium sulfate or primary amines (methylamine and glycine). Physical properties of oligomers, such as mass and volatility, can be determined using Thermogravimetric Analysis (TGA). The change in mass of solutions containing amine and aldehyde compounds was measured as a function of temperature to determine the quantity and stability of compounds that remain in the condensed phase. The mass loss profile after water evaporation varied depending on the aldehyde + amine solution. Aldehyde + glycine mixtures produced the most condensed-phase material with glyoxal and methylglyoxal, as observed by other techniques where aerosol evaporation occurs at room temperature. Aldehyde + methylamine and ammonium sulfate mixtures, however, unexpectedly produced the most condensed-phase material with the smallest aldehydes, formaldehyde and acetaldehyde. . These reactions were likely greatly accelerated by the 105 °C temperature used to evaporate water in this TGA method. Further analysis on room-temperature-evaporated materials by TGA will be reported.

8AE.1

Intake Fraction for Urban Emissions of Semivolatile Organic Compounds from Vehicles. JOSHUA APTE, Julian Marshall, William Nazaroff, *University of California, Berkeley*

We model the inhalation intake fraction (iF) for semivolatile organic emissions from urban vehicles. Population exposure to organic vehicle emissions is strongly affected by photochemical oxidation (“aging”), dilution, and other processes that alter gas-particle partitioning. Accordingly, the overall magnitude and spatial distribution of inhalation intake of semivolatile emissions may differ substantially from that of non-reactive emissions. In this investigation, we compare and contrast patterns of iF for semivolatile vehicle emissions with those of primary, conserved (“inert”) pollutants.

We use the volatility basis set framework to account for the dynamic phase partitioning of primary organic emissions owing to dilution and aging. We develop a nested multi-compartment model to simulate exposures at three spatial scales: urban core (length 25 km), periurban (100 km), and regional (400 km). Results are reported separately for particle and vapor-phase exposures as a function of the volatility of emitted material.

For urban emissions of inert pollutants, ~70% of domain-wide population intake occurs in the same compartment as emissions. In contrast, for semivolatile emissions, spatial patterns and gas-particle partitioning of intake depend substantially on emissions volatility. Low volatility organic emissions in urban areas produce predominantly intraurban, particle-phase exposures (similar to inert pollutants). As volatility of material emitted in urban areas increases, three key trends emerge that reduce particle-phase iF: (1) the overall proportion of population exposure that takes place in the particle phase decreases and the proportion of exposure in the gas phase increases, (2) photochemically aged material accounts for a larger fraction of particle-phase population intake, and (3) regional-scale exposures account for the predominant fraction of organic aerosol exposure attributable to urban precursor emissions. Since higher volatility compounds account for a large fraction of motor vehicle emissions, the overall iF for organic particles attributable to urban semivolatile organic emissions is lower than for inert pollutants.

8AE.2

Development of a Human Lung Co-Culture Model System for Hazard Identification of Aerosolized Particles.

CHRISTIE SAYES, Seung-Hyun Cho, Quentin Malloy, Christopher West, Madhuri Singal, Danielle Vitale, *RTI International*

There is a growing need for lung cell culture model systems to assess potential hazards associated with airborne particulate matter of various sizes and compositions. In vivo models for safety testing are being phased out due to increased social, financial, and time pressures. In vitro cell cultures have shown promise as surrogates in screening assays when multiple substances require preliminary information on toxicity. We present an exposure apparatus composed two of critical parts. The first part is an aerosol generator that delivers liquid and/or solid aerosols in the size range of 1–3 microns in diameter. The second part is a co-culture exposure system of upper respiratory tract mammalian cells including epithelial, macrophage, and dendritic cells. The aerosols used in the development of this apparatus include trimellitic anhydride (i.e. solid powder) and toluene-2,4-diisocyanate (i.e. liquid droplet). Both aerosols have been shown to induce inflammation and/or cause irritation in the respiratory tract. This study focuses on comparing the cellular effects before and after aerosol exposure. Specific cytokine expressions of exposed cells compared to control cell populations are as follows: MIP-1 (increase by 50%), TNF-alpha (increase by 75%), and IL-1β (increase by 20%). The overarching goal is to develop a high-throughput co-culture screening system that could be used in conjunction with current in vivo test models.

8AE.3

From Rural to Personal Level PM2.5 Concentrations and Their Linkages to Biological Sample Metal Concentrations.

QUENTIN MALLOY, Cortina Johnson, Jocelin Deese-Spruill, James Raymer, Jonathan Thornburg, Elizabeth Frey, Richard Perkins, Larry Michael, *RTI International*

The southern Delaware area surrounding the town of Millsboro has been previously designated as a cancer cluster because of the elevated lung and bladder cancer rates. In order to study the potential linkage between the local coal-fired power plant, a two part study was developed to examine regional, residential, and personal $PM_{2.5}$ samples along with biological samples. Thirty-two participants were recruited during for two sampling seasons in order to monitor outdoor residential, indoor residential, personal level $PM_{2.5}$ as well as four ambient and one semi-rural background site. Results indicate that the primary driver for ambient $PM_{2.5}$ within the region is due to long-range transport from the nearby metropolitan areas of Baltimore, Washington D.C. and New York City even with a major coal-fired power plant coming on-line during season 2. Evidence for this includes the geometric mean $PM_{2.5}$ concentrations from background samples showing no statistical difference between sampling seasons (P-value 0.06). Ambient monitors located closer to the power plant did show statistically different (alpha=0.01) PM concentrations; however these were reduced during operation of power plant. Despite this, the majority of participant exposure to $PM_{2.5}$ occurred while residents were indoors. These elevated exposures were captured through use of the RTI MicroPEM. Personal level $PM_{2.5}$ concentrations of 20.3 micrograms per cubic meter, 119% higher than the ambient monitors, were recorded. In addition to elevated PM, optical absorbance and XRF analysis of the samples indicated strong correlations with environmental tobacco smoke. These secondary filter analyses along with blood and urine metals analysis will be presented in order to provide a picture of a population exposure in order to evaluate one possible exposure pathway which may be linked to documented elevated cancer incidences.

8AE.4

Estimating Population Exposure to Fine Particulate Matter (PM2.5) during Extreme Air Pollution Events in the Pacific Northwest. ABDULLAH MAHMUD, Kelley C. Barsanti, *Portland State University*

Particulate matter with diameter less than 2.5 µm (PM2.5) is known to cause adverse health effects, particularly among susceptible population groups including children and elderly. EPA (2008) estimated that approximately 158 million people in the United States live in regions where the National Ambient Air Quality Standard (NAAQS) for PM2.5 is violated. The objective of the current study is to estimate population exposure to PM2.5 during extreme air pollution events in the Pacific Northwest. In this study, air quality model data will be obtained from the Air Information Report for Public Access and Community Tracking version 3 (AIRPACT-3) (http://lar.wsu.edu/airpact/index.html) data warehouse. AIRPACT-3 is a regional air quality forecasting system that generates daily total PM2.5 mass concentrations for the Pacific Northwest, namely for Washington, Idaho and Oregon. The modeling system is based on the WRF-CMAQ modeling pair, and has a spatial resolution of 12-km bounded by a 95 x 95 x 21 (XYZ) modeling domain. Daily average PM2.5 for the 2008-2012 period will be obtained and analyzed for identification of extreme pollution events. The extreme events will be categorized based on the 99th percentile value of the domain-wide daily average PM2.5 mass concentrations for the entire 2008-2012 period. Population exposure will be calculated for only those days with 99th percentile and above the domain-wide PM2.5 daily average concentrations using the EPA's Environmental Benefits Mapping and Analysis Program (BenMAP) modeling software. The base-case BenMAP runs will generate spatial distributions of source apportioned PM2.5 exposure throughout the entire modeling domain. These results will then be utilized to build 'what-if' scenarios to understand the effects of emissions from various sources on population exposure during extreme pollution events in the Pacific Northwest.

Keyword: population exposure, fine particulate matter, extreme air quality events, Pacific Northwest

8AE.6

Characteristics of Personal Exposure to PM2.5 in Public Transportations in Beijing, China. CAIQING YAN, Mei Zheng, Qiaoyun Yang, Qunfang Zhang, Xinghua Qiu, Tong Zhu, Yifang Zhu, *Peking University*

People living in megacities in China such as Beijing are exposed to higher levels of air pollutants due to large and dense population, diversified transportation modes, and longer exposure to roadway and railway emissions. This study examined pedestrians and commuters' exposure to fine particulate matter (PM2.5) and polycyclic aromatic hydrocarbons (PAHs) in different transportation modes including walking, taking subway and riding bus during two weeks of December 2011 in Beijing. Concentrations of PM2.5, particle number as well as PAHs were measured by DustTrak, CPC, and offline GC-MS, respectively. The results revealed particulate matter exposure level, including mass concentration and particle number, in Beijing subway was the highest. PM2.5 exposure levels in roadway transportation (including walking and riding bus) exhibited clear diurnal variation with higher level during commuting rush hours and lower at noon. However, particle number concentrations showed an opposite trend, peaking at noon but lower at rush hours. Particulate PAHs concentrations were about 2.5 times higher in roadway environment than subway system, and up to 17 times higher in polluted days with high ambient PM2.5 concentration compared to clean days. The results indicated that walking pedestrians were more susceptible to higher risks (about 1.3-3.4 times) than people using other commuting methods based on calculated benzo[a]pyrene toxic equivalents (BaP TEQs). Although subway commuters were exposed to the highest particulate matter exposure level, their BaP TEQs levels were lower than waling pedestrians. Some characteristic sources in China, such as roadside restaurants and barbecuing as well as smoking, were also strong sources for sudden and significant increase of particle number experienced by pedestrians.

Keywords: fine particulate matter, PAHs, transportation exposure, subway, bus, walking.

8AE.7

Passive Deposition Following Reaerosolization of Bacillus Spores from Urban and Operationally Relevant Surfaces.

KAREN PONGRANCE, Jana Kesavan, Jason Edmonds, Deborah Schepers, Jerold Bottiger, Donna Carlile, Dan Vanreenen, *US ARMY ECBC*

The potential for Bacillus in outdoor environments to resuspend or reaerosolize following an initial biological agent release is of concern because of its stability and potential for use as a biological weapon. A quantitative understanding of reaerosolization off of different surfaces is needed in order to make an assessment of the associated public health risks to secondarily exposed individuals if an event were to occur. The purpose of this study was to assess the potential biological hazard associated with wind driven reaerosolization off of contaminated surfaces commonly found in urban and military environments. The surfaces used in this study were vinyl floor tiles, brick, sod, concrete, gravel and CARC. In our study, we seeded Bacillus thuringiensis var. kurstaki dry spores onto these six surfaces in an ambient breeze tunnel, and then reaerosolized the organisms using a bank of fans which created a wind speed of 3.8 m/s over the seeded surface. Reaerosolized spores were recovered from floor tiles placed every ten feet up to a total distance of 100 feet from the initial point of deposition and were analyzed by culturing. Our results show that the settling deposition of reaerosolized Bacillus spores is dependent on the surface that the spores are reaerosolized off of, and that the quantity of Bacillus spores recovered down the length of the breeze tunnel was inversely correlated with distance from the seeded surfaces for all materials tested.

8AE.8

Assessment of Lead Particle and Acidic Gas Exposure During Gun Firing.

JUN WANG, Lin Shou, Chang-Yu Wu, *University of Oklahoma Health Sciences Center*

Modern ammunition used in gun shooting consists of lead (Pb) bullet, gun powder, and primer. Gunpowder is a mixture of sulfur, charcoal, and potassium nitrate, while primers are compounds such as lead styphnate, nitrate, chloride, and sulfide. The firing process creates gas and particles from primer ignition and powder burning, which may have adverse health effects to the shooters. The knowledge about the shooting fume’s composition is currently scarce. The objective of this study is to assess the shooter’s exposure to the lead aerosol and acidic gas when firing different types of gun, in both indoor and outdoor shooting ranges. In this study, silica-gel type personal samplers were worn by the shooters while firing. The indoor range was well-ventilated with low relative humidity, while the outdoor range was a more open area with high relative humidity. Since pistols and rifles have distinct barrel lengths and hence different combustion conditions, only one type of gun was fired during each sampling period to investigate the effect of each type. The gas and particles collected by the silica gel were extracted according to NIOSH method 7903, and analyzed by an ion chromatograph (IC) for acidic gas concentration. The results showed the shooter’s averaging exposure to the sulfuric acid were 1.76 (±0.35) milligram per cubic meter for pistol and 0.76 ((±0.27) milligram per cubic meter for rifle over 2 hours sampling period, while the Occupational Safety and Health Administration permissible exposure limits (PEL) for sulfuric acid is 1 milligram per cubic meter for 8-hour time weighted average. Nitric acid in the samples was below PEL, while hydrochloric acid was below the detection limit. There was no statistical difference between the samples collected from indoor and outdoor shooting range. The partitioning of acidic gas in gas and particle phase will be evaluated using a newly developed denuder-type personal sampler. The lead particles will be analyzed by an inductively coupled plasma atomic emission spectroscopy. Furthermore, a scanning mobility particle sizer will be used to examine the particle size distribution in the shooting fume.

8BA.1

Living Microorganisms in Clouds. Mickaël Vaitilingom, Muriel Joly, Pierre Amato, Nicolas Gaiani, Laurent Deguillaume, Eleonore Attard, Martine Sancelme, ANNE-MARIE DELORT, *Clermont Université, Institut de Chimie de Clermont-Ferrand*

Despite the enormous volume they represent and the importance they have for Earth’s climate, clouds remain aquatic ecosystems where the microbiological features are still obscure. Between 2003 and 2010, 38 independent samples of cloud water were collected at the summit of the Puy de Dome mountain (1465 m asl, France) in order to study the microbial community with its qualitative and quantitative variability.

On average, 105 bacteria and 103 fungi per mL of cloud water are detected by DAPI labeling and microscopy. Less than 1% of the bacterial cells collected in cloud water are cultivated on a medium for drinking water (R2A) in aerobic conditions and absence of light. Concentrations of ADP / ATP measured in cloud water and their ratio are consistent with the existence of metabolic activity in the cloud droplets.

More than 500 strains of bacteria or yeasts were isolated and identified by 16S or 26S rRNA genes sequencing. Most frequent genera include Pseudomonas, Sphingomonas and Frigoribacterium for bacteria and Udeniomyces, Dioszegia and Cryptococcus for yeasts. These strains present high similarities to those isolated from the vegetation, soils or other aquatic environments. Interestingly, most of the Sphingomonas strains isolated from cloud water are located within a small and specific phylogenetic cluster that gathered species isolated from the atmosphere.

Vaïtilingom M. et al. (2012) Long-term features of cloud microbiology at the Puy de Dôme (France). Atmospheric Environment 56, 88-100.

8BA.2

Survival of Microorganisms to the Main Stress Factors Encountered in Clouds. Muriel Joly, Pierre Amato, Martine Sancelme, Mickaël Vaitilingom, Virginie Vinatier, Laurent Deguillaume, ANNE-MARIE DELORT, *Clermont Université, Institut de Chimie de Clermont-Ferrand*

Microorganisms are present in low altitude clouds at concentrations of ~104 bacteria per mL and ~103 fungi per mL. The microbiological monitoring of cloud water since 2003 at the puy de Dôme station (1465 m a.s.l., France) revealed the presence of recurrent microorganisms among the cultivable bacterial community: Pseudomonas spp. and Sphingomonas spp. notably were present in 55% and 45% of the samples collected respectively, and they represented 30% of the total heterotrophic bacteria cultivable at 17°C.

Clouds represent nearly obligate ways to the redeposition of micrometer-sized aerosols such as microorganisms onto the ground. Even though they are believed to be less aggressive environments than dry air, clouds likely remain harsh and probably operate as environmental filters to airborne microorganisms through various selection factors: solar radiation, oxidants, low temperature, acidity, osmotic shocks… etc…

In order to test this hypothesis, we selected five bacterial or yeast strains isolated from cloud water (Arthrobacter sp. AJ551167 ; Pseudomonas syringae AB001440 and HQ256872 ; Sphingomonas sp. HQ256831 ; Bullera armenica JF706549). These strains were chosen to offer a good representation of the particularities of the culture collection (Gram-positive and Gram-negative bacteria, pigmented or not, ice nucleation active or not). In parallel, an Escherichia coli strain (ATCC10798) was chosen as reference as none was found viable among our cloud samples.

The survival rates of each of these strains to four factors of stress consistent with the conditions encountered in clouds were investigated: osmotic shock, which occurrs when water vapour condenses or evaporates around airborne microorganisms, freeze-thaw cycles, presence of toxic compounds such as hydrogen peroxide, and solar radiation. The first results demonstrated that the strains isolated from clouds as well as E. coli were resistant to these treatments. Hence those selective factors are not sufficient to explain the composition of the viable community in clouds.

8BA.3

The On-line Detection of Biological Particle Emissions from Selected Agricultural Materials Using the WIBS-4 (Waveband Integrated Bioaerosol Sensor) Technique. DAVID O'CONNOR, David Healy, John Sodeau, *University College Cork*

Agricultural activities, including crop harvesting, have for been linked for some time to adverse health effects such as Farmers' lung, hypersensitivity pneumonitis, aspergillosis and chronic obstructive pulmonary disease (COPD). This connection is known to be, at least in part, due to the numerous microbiological organisms that live and grow on materials found in occupational settings such as barns, animal shelters, stables and composting sites.

In the study reported here, fluorescence and light scattering signals obtained from primary biological aerosol particles (PBAP) were analysed in conjunction with the traditional impaction/optical microscopy technique to provide near real-time data for spore types released from hay and silage. On-line particle emissions were characterised by a Waveband Integrated Biological Sensor (WIBS-4) according to their numbers, size distributions, asymmetry values and fluorescence characteristics. The variables obtained were subsequently plotted to provide potential "fingerprint" signatures for PBAP emissions emanating from both hay and silage. Comparisons between the data acquired by the WIBS-4 bioaerosol sensor, our optical microscopy findings and also previous literature suggest the likely identification of Aspergillus/Penicillium and Actinomycetes spp.

8BA.4

Ubiquity and Persistence of Streptococcus Suis Bioaerosols in Swine Confinement Buildings. LAETITIA BONIFAIT, Marc Veillette, Daniel Grenier, Caroline Duchaine, *Université Laval, Canada*

Streptococcus suis is a swine pathogen causing septicaemia, meningitis, endocarditis and pneumonia. Also recognized as an important emerging agent of zoonosis, S. suis is the main cause of human meningitis in Vietnam. Among the 35 serotypes of S. suis, serotype 2 is the predominant isolate from diseased animals and humans. In order to better understand the transmission route of S. suis and the potential risks of infection for pig farmers, we developed tools to study the aerosolization and persistence of S. suis in the air of swine confinement buildings (SCB). We investigated the presence of this pathogen in bioaerosols from finishing SCB as well as in SCB with noticed cases of these bacteria. Air was sampled on gelatin membranes mounted in IOM cassettes or by a Coriolis cyclone sampler. Using a PCR-based method, one out of two finishing SCB showed the presence of serotype 2 in the air while S. suis serotype 2 was present in the air of all SCB with noticed S. suis cases. In the latter situation, the presence and the concentration of total bacteria, total S. suis and S. suis serotype 2 were monitored during five weeks and showed the persistence of S. suis serotype 2. Our results provide a better understanding of the aerosolization, ubiquity and persistence of S. suis and will had to the knowledge required to improve prevention and protection of swine cattle and swine producers in North America.

8BA.5

A Field-deployable Electrostatic Collector for Bioaerosols with High Concentration Rate. TAEWON HAN, Donna Fennell, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

In our earlier research, we developed and optimized an electrostatic precipitator with superhydrophobic surface (EPSS) for bioaerosols, including selection of housing and electrode materials and ionizer configuration. Its latest version shows an overall collection efficiency of up to 84% when sampling Escherichia coli bacteria at 10 L/min and accumulating the bacteria in rolling water droplets as small as 20 micro-liters thus achieving a very high sample concentration rate (up to 4.2 × 10^5/min). However, these results were achieved with bench scale components, such as large power supplies, liquid injection via pipetting and use of external pumps. For the application and testing of this technology in the field, the sampler's components must be integrated into a field-deployable instrument. The objective of the next project phase is to integrate all component parts, e.g., charger, sampler, fan, batteries, DC-to-DC converters, peristaltic pump, liquid reservoir, and collection vial into a field-deployable novel bioaerosol sampler.

In the integrated sampler, bioaerosol particles are collected onto a narrow electrode and a collecting droplet is injected automatically using a small peristaltic pump attached to the sampler. The collection liquid is provided by an attached reservoir. The size and frequency of the droplets are controlled by adjusting the diameter of the injection needle and the operating time of the peristaltic pump. Due to the inclination of the collection chamber, the liquid droplet rolls down the electrode picking up the deposited biological particles and is collected in a vial located at the end of the collection chamber. The collection air flow is provided by an integrated battery-operated fan. The charging and collection voltages are supplied via battery-operated miniature DC-to-DC converters. Once the integration is completed, the bioaerosol sampler will be tested in the field against several commercial bioaerosol samplers.

8BA.6

Quantifying the Effect of Relative Humidity and Ozone on the Viability of Aged Bacillus Thuringiensis Al Hakam and MS-2 Bacteriophage Biological Aerosols. SEAN KINAHAN, Elizabeth Corson, Shanna Ratnesar-Shumate, Yong-Le Pan, Jonathan Eshbaugh, Christopher Bare, Joshua Santarpia, *Johns Hopkins University Applied Physics Laboratory*

The viability of primary biological aerosols (PBA) is a complex function of the particle properties and atmospheric conditions surrounding their release. The type of organism, aerosolization method, relative humidity, oxidation, irradiation, and the presence of secondary organic aerosol forming constituents may each or cumulatively alter an organism's survivability and fate as an aerosol particle. To isolate and better understand the effects of any individual variable over time, it is essential to contain these particles in a controlled environment. JHU/APL developed a rotating drum system (RDS) to simulate an increased residence time of biological aerosols in the atmosphere, in order to observe changes due to controlled levels of relative humidity and ozone concentration. The viability of two biological aerosols, Bacillus thuringiensis Al Hakam (Bt) and the bacteriophage MS-2, was investigated. A Sono-tek ultrasonic nozzle generated each biological particle of interest into the RDS until a target concentration of 200 particles cc^{-1} was achieved, as monitored by a TSI Inc. Ultraviolet Aerodynamic Particle Sizer (UV-APS) spectrometer. All glass impingers (AGI) sampled the biological aerosol immediately after reaching the target concentration and after four hours of aging. Experiments consisted of three humidity targets (~20%, 50%, and 85% RH) to which the drum was preconditioned before aerosolization of the biologicals in HEPA-filtered laboratory air. Each relative humidity condition was coupled with trials at background (<5 ppb) and high ozone concentrations (~150 ppb), introduced after the initial time-zero sample was collected. Viability was quantified using culture for the Bt and an E. Coli plaquing assay for MS-2. These culture numbers were normalized to total sampled genomic content, using quantitative polymerase chain reaction (qPCR), to account for losses in particles over time and improve percent viability correlations.

8BA.7

Understanding Aerosolized Viral Particles Behaviour in a Mechanically Ventilated Agricultural Building Using Nebulized Bacteriophages.

MARTYNE AUDET, Matthieu Girard, Martin Belzile, Stéphane Godbout, Caroline Duchaine, *Centre de recherche de l'IUCPQ, Université Laval*

Dissemination of viral pathogens via airborne particles is a known phenomenon. In agriculture, indoor air of livestock confinement buildings holds a high concentration of bioaerosols that may be dispersed to neighbouring sites through ventilation systems. Control of pathogenic viruses remains to this day a major concern for the health of agricultural workers and animals, as well as for the great negative economic impact epidemics inflict on the industries. The development of methods for virus detection in the air of agricultural buildings that are fast, simple, reliable, ecologically sound and without risk for animal health is urgent. As aerovirologists, our laboratory has collaborated with a group of agricultural engineers to tackle this problem. A 55 m3 mechanically ventilated experimental confinement building was used to develop a tool to improve air sampling strategies by assessing the spatial concentration variations of an artificially nebulized virus and a fluorescent marker. Firstly, air displacements were visualized by video recorded smoke tests. Potential dead zones leading to longer particle residence time were assessed by 10 blinded individuals. Secondly, bacteriophages in a fluorescent solution (NSF60) were nebulized as animal virus surrogates and air was sampled in 12 different locations in the room. Thirdly, analyses of representative air samples by fluorescence microscopy and molecular biology were performed. So far, we have determined a critical area of 3,5 ± 1,5 m3 where the viral particles are more likely to stay in suspension and be detected. The next step of this investigation is to co-nebulize the fluorescent bacteriophage suspension with standardized ISO test dusts in elevated concentrations to imitate the agricultural context. In the near future, molecular diagnostic tests will be available to the agricultural industry. Simply nebulizing a fluorescent bacteriophage solution in a real setting might lead to the determination of the most suitable area for surveillance air sampling.

8BA.8

Measurement of Ribosomal RNA in Airborne Escherichia Coli: Sample Collection Methods Produce Bias in 16S rRNA-based Analysis Methods.

HUAJUN ZHEN, Valdis Krumins, Taewon Han, Donna Fennell, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Enumeration and characterization of ribosomal RNA (rRNA) is widely used in microbiology when analyzing metabolically active species within microbial communities, but there is little information on rRNA measurement in bioaerosols. Because airborne bacteria experience various mechanical and/or desiccation stress during sampling, which may affect rRNA production, it raises a question whether the rRNA concentration in collected bioaerosol samples could be used to analyze the concentration and composition of airborne bacteria.

We collected fresh Escherichia coli bioaerosol with sampling devices that utilize different collection mechanisms: filtration, impingement and electrostatic precipitation. The 16S rRNA content in collected samples was reported as an amount relative to the amount of 16S rRNA genes detected in the same sample: i.e., rRNA/rRNA gene ratio.

As a baseline measurement, when E. coli bacteria were inoculated in Tryptic Soy Broth (TSB) at 37 °C, the rRNA/rRNA gene ratio increased rapidly to ~1900 during the initial 3 hours of exponential growth phase, and then gradually decreased and finally leveled off to around 600 after 16 hours. This confirmed that actively growing cells had a higher relative rRNA content than more slowly growing cells. To simulate stress during sampling by filtration, aerosolized E. coli were collected on filters and particle-free air was then passed through the samples for 0, 2, 4 and 6 hours. To our surprise we found that the ratio rapidly increased 8-fold from ~650 to ~5200 within 4 hours, and then decreased to ~3800 after 6 hours. The bacteria suspended in air for similar durations before collection exhibited much lower ratios. The tests with other samplers are ongoing.

Our results suggested that when analyzing the airborne microbial community based on 16S rRNA, special attention should be paid to selection of appropriate sampling techniques as they may bias the amount of detected rRNA, and thus the study results.

8BA.9

Comparison of Airborne Bacterial Compositions in Bioaerosols Collected at 3,000m, 1,000m, 10m over Japan.

TERUYA MAKI, Fumihisa Kobayashi, Kakikawa Makiko, Maromu Yamada, Atsushi Matsuki, Yasunobu Iwasaka, *Kanazawa University*

Tropospheric transport of airborne microorganisms plays an important role in microbial dispersal and has significant impacts on biological ecosystems, human life, and atmospheric processes in downwind areas. However, microbial communities in the troposphere have rarely been investigated because the direct collection of microbial cells at high altitude requires sophisticated sampling techniques. In this study, air samples at 800m and 3000 m over the Noto Peninsula in Japan were collected using a balloon and an aircraft, respectively, and that at 10m was also collected on the building of Suzu City located at north edge of he Noto Peninsula. During the sampling period at March 1, 2013, the tropospheric air mass came from Gobi desert area by westerly wind. The air samples collected at 3000m included aerosol particles significantly suggesting that winds carry aerosol particles from continental areas. After bacterial compositions were determined using 16S rDNA clone library techniques and pyrosequence analysis, bacterial communities were compared among different altitudes of 10 m, 1000 m and 3000 m. The 16S rDNA clone libraries revealed that bacterial communities at upper altitudes was mainly composed of marine species such as Cyanobacteria and Alpha-proteobacterium members, while that at lower altitudes consisted primarily of terrestrial bacterial species belonging to the phylum Firmicutes. Moreover, one phylotype of B. subtilis occupied lagers numbers of clones in the air sample at 3000 m than those at 1000m and 10m, suggesting that B. subtilis was possibly transported from continental areas. Pyrosequence analysis provided more than 8,000 sequences from each air samples. Bacterial compositions of pyrosequencing showed similar vertical-distributions of the clone libraries and included large number of minor bacterial species that have not detected from atmosphere. In summary, tropospheric air mass would contribute to the vertical dynamics of airborne bacterial communities in atmospheric column.

8BA.10

Seasonal Cycles of Fluorescent Biological Particles in Finland and Colorado Forests.

Carolyn J. Schumacher, Christopher Pöhlker, Pasi Aalto, Markku Kulmala, Ulrich Pöschl, J. ALEX HUFFMAN, *University of Denver*

Biogenic aerosols are ubiquitous in the Earth’s atmosphere, influencing atmospheric chemistry and physics, the biosphere, climate, and public health. They play an important role in the spread of biological organisms, can cause diseases, and may form nuclei which initiate water (CCN) and ice (IN) cloud formation.

The ultraviolet aerodynamic particle sizer (UV-APS) measures the concentration and aerodynamic diameter of particles in the size range of 1–20 micro-meter by light scattering and time-of-flight measurement, complemented by the measurement of fluorescence emission. The instrument provides real-time detection of fluorescent biological aerosol particles (FBAP) as a lower-limit proxy of coarse-mode primary biological aerosol particles (PBAP) with relatively high time and size resolution.

The UV-APS was operated in a European boreal forest (Hyytiälä, Finland) and a semi-arid, North American pine forest (Manitou Forest, Colorado) continuously for 18-months and 11-months, respectively, to monitor the seasonal cycles of coarse aerosol. FBAP concentrations peaked during summer and were lowest in winter at both locations and showed strong contrast to non-fluorescent aerosol seasonality. Additionally, we observed differences in the relationship between FBAP and temperature, relative humidity, and rainfall as a function of season suggesting that factors influencing bioaerosol emission change through the course of the year.

8BA.11

Hidden Biological Aerosol Exposure Risks from Vehicle Air Conditioner Filter. Jing Li, MINGZHEN LI, Fangxia Shen, Zhuanglei Zou, Maosheng Yao, Chang-Yu Wu, *Peking University*

Although use of automobile air conditioning (AC) was shown to reduce in-vehicle particle levels, its microbial aerosol exposure risk is not adequately characterized. Here, both AC and engine filter dust samples were collected from 30 automobiles in four different geographical locations in China. Biological contents (bacteria, fungi and endotoxin) were studied using culturing, high throughput gene sequence as well as Limulus amebocyte lysate (LAL) methods. In-vehicle viable bioaerosol concentrations were directly monitored using an ultraviolet aerodynamic particle sizer (UVAPS) before and after use of AC for 5, 10 and 15 mins.

Regardless of locations, the vehicle AC filter dusts were shown to be laden with high levels of bacteria (up to 26150 CFU/mg), fungi (up to 1287 CFU/mg) and endotoxin (up to 5527 EU/mg). More than 1000 bacterial species including human pathogens were detected in the filter dusts. In addition, pathogenic fungal species were also found abundant. Here, we observed unexpected fluorescent peaks around 2.5 µm during the first 5 minutes use of AC, which can be attributed to the re-aerosolization of those filter-borne microbial agents. This work presented evidence that use of automobile AC, if not cleaned or disinfected properly, would predispose the in- vehicle people to respiratory infections.

8BA.12

Temporal Distribution of Gram-negative (G-) and Gram-positive (G+) Bacterial Aerosols with Different Charge Polarity and Level. KAI WEI, Maosheng Yao, *Peking University*

Here, we investigated the temporal distribution of Gram-negative (G-) and Gram-positive (G+) bacterial aerosols with different charge polarity and level in both indoor and outdoor environments using an electrostatic sampling system (Aerobiologia, 27, 135-145). The bacterial aerosols with different charge polarity were collected separately using the electrostatic sampler with two square agar plates for morning, noon and afternoon. Selective media were used for culturing G+ and G- respectively, and obtained CFUs were further confirmed by Gram stain method.

Our preliminary data showed that for indoor bacterial aerosols the G+ prevailed over G- regardless of the charge polarity, while G- dominated for outdoor environment. The temporal distributions of G+ and G- with different charge polarity were shown to vary greatly with time and location, and no consistent trends were observed, which might be due to climatic conditions such as temperature, humidity, wind and differences in bioaerosol emission sources. It appears that outdoor aerosol charge levels turned to be more normally-distributed, while indoor aerosol charge levels seemed to be more skewed. Results from selective medium and Gram stain generally agreed well. Bacterial Gram types as well as their charge levels are important in terms with their lung inhalation and subsequent health effects. Information developed here not only described the temporal distribution of G+ and G- aerosols in different environments, but also yielded information that can help design better electrostatic sampling device.

Key words: Bacterial aerosols, Positive charge, Negative charge, Charge Polarity

8BA.13

Real-time Measurements Of Airborne Fungal Spores Biomarkers Using PILS-LC-MS/MS. ROLAND SARDA-ESTEVE, Nicolas Bonnaire, Marie-Helene Nadal, Lorna Foliot, Jean Sciare, *LSCE*

In recent years, the impact of primary biological aerosol particles on atmospheric processes and their ability to act as ice nuclei or cloud condensation nuclei has been studied with increasing intensity. Airborne fungal spores are considered as the dominant fraction of bioaerosols in the size range 2–10 micrometer. Recent studies have shown that the concentration of these fungal spores could be quantified using specific biomarkers (mannitol and arabitol) (Bauer et al., Atmos. Environ., 2008).

A new technique is presented here to investigate real-time concentrations of these two biomarkers (mannitol and arabitol) in ambient conditions. This technique is based on the coupling between a Particle-into-liquid-sampler (PILS), a liquid chromatography (LC) and an Electro Spray Ionisation source – tandem mass spectrometer (ESI-MS/MS, AB SCIEX model 3200 QTRAP). Ambient aerosols are collected at 15 LPM in the PILS and send into a 100µl loop of the LC at a flowrate of 50µl/min. Injection is performed every 12 min and separation is achieved using an Hypercarb column (Thermo Environment). Quantification of mannitol and arabitol is achieved in negative mode by ESI using a specific m/z transition in Multiple Reaction Monitoring (MRM) mode. Four additional specific transitions are also monitored for each compound for confirmation purposes. A limit of quantification (LOQ) below 0.3 ng/m3 is calculated here for each compound.

Based on these settings, unattended measurements of mannitol and arabitol by PILS-LC-MS/MS have been performed every 12 min in the region of Paris (France) for a period of 2 weeks during summer (July 2013). Comparisons were performed using off-line (filter sampling) technique and an alternative analytical protocol using IC-PAD detection. Comparison with parallel measurements performed using Hirst collector and individual fungal spore counting were also performed showing the capability of our technique to document in a quantitative way real-time concentrations of airborne fungal spores.

8BA.14

Investigation on the Vertical Distribution of Japanese Cedar Pollen and its Potential Impact on Ice Cloud Formation.IWATA AYUMI, Hara Kazutaka, Atsushi Matsuki, Iwamoto Yoko, Teruya Maki, Kakikawa Makiko, *Kanazawa University*

The Japanese cedar is widely distributed over Japan and emits large amount of pollen into the atmosphere. The cedar pollen is causing the pollinosis that is most common in Japan. The bioaerosols (bacteria, pollen, spores, etc.) have been shown to have significant impacts both on human health and on climate. However, ice nucleation activity of pollen has been investigated only by a few experiments. The purpose of this study is to investigate the climate impact of the cedar pollen, a species characteristically found in Japan. In order to probe the vertical distribution of the pollen grains as well as their derivative substances in atmosphere, samples were collected at altitudes of 10m, 500m, 1000m and 2500m, over Noto peninsula onboard a helicopter in spring 2013. In addition to the pollen grains themselves, the distributions of the allergens specific to Japanese cedar (namely, Cry j1 and Cry j2) were also investigated as the proxies for the pollen derived substances. These derivatives were measured in order to test the suspected release of allergens from the pollen grains for example following rainfall. In one case, we detected Cry j2 even at altitudes as high as 2500m, with maximum concentration found at 1000m. In addition, the ice nucleation activity of the pollen was investigated in the laboratory by cooling the grain suspension in pure water. We chose Arizona Test Dust (ATD) as reference ice nuclei. The result showed that numbers of ice nuclei per mg of the pollen (or its extracts) were lower than that of ATD. Thus, it was suggested that Japanese cedar could potentially inject significant amount of pollen and related derivatives into the altitudes relevant for aerosol-cloud interactions. At the same time however, their impact on ice cloud formation could be considered modest as compared mineral dust aerosol.

8CA.1

Wavelength-dependent Complex Refractive Indices of Different Types of Secondary Organic Materials. PENGFEI LIU, Yue Zhang, Scot Martin, *Harvard University*

For accurate quantifying aerosol optical properties, recent studies have emphasized the importance of obtaining improved knowledge of the complex refractive indices of the secondary organic materials (SOM). However, measurements of the complex refractive indices of SOM were typically limited to a few wavelengths, and the wavelength dependence is still not well understood. In this laboratory study, spectroscopic data of complex refractive indices of different types of SOM were obtained using a variable angle spectroscopic ellipsometer at wavelengths between UV (220 nm) and Near-IR (1200 nm). The SOM were generated from ozonolysis of monoterpene precursors alpha-pinene and d-limonene, and aromatic precursor catechol (Benzene-1,2-diol) using an aerosol flow tube reactor. The results show that both real and imaginary parts of different types of SOM decrease with increasing wavelength. The wavelength dependence is especially strong in the UV range. The real parts of the complex refractive index of catechol-derived SOM are slightly higher than that of monoterpene-derived SOM; the values are in the range from 1.53-1.58, 1.49-1.52 and 1.48-1.50 at the wavelengths 300, 550 and 1000 nm, respectively. Catechol-derived SOM has moderate light absorption in the UV range; the imaginary parts of complex refractive index are 0.017 ± 0.001 and 0.002 ± 0.0015 at the wavelengths 300 and 400 nm, respectively. By comparison, UV absorption of SOM derived from alpha-pinene and d-limonene is about an order of magnitude lower than that of catechol-derived SOM. Light absorption of studied SOM in visible and near-IR range is negligible. The new spectroscopic information about SOM complex refractive index is helpful for updating aerosol optical database for aerosol and gas satellite retrievals and atmospheric chemical modeling.

8CA.2

Characterizing the Efficiency of the SP-AMS for Measuring Black Carbon in Organic Coated Particles. MEGAN D. WILLIS, Alex K. Y. Lee, Jonathan Abbatt, *University of Toronto*

Black carbon (BC) containing aerosol affects air quality, impacts human health, and can have a significant effect on regional and global climate. Freshly emitted BC particles tend to be small (aggregates of ~10-50 nm BC spherules), but quickly grow and become mixed with other species through condensation and coagulation. The Soot-Particle Aerosol Mass Spectrometer (SP-AMS) is a new instrument that combines the operating principles of the Single Particle Soot Photometer with the Aerodyne High-Resolution Time-of-Flight AMS, making quantification of BC and its non-refractory coating materials possible. The goal of this work is to assess the ability of the SP-AMS to accurately quantify BC inclusions of atmospherically relevant sizes in organic coated particles. This issue is addressed in two ways. First, we examine whether small BC inclusions (e.g. down to 50 nm) in organic-rich particles are being detected with the same efficiency as larger, bare BC particles (e.g. 300-400 nm). Secondly, we examine whether BC and its associated coating materials are being quantified accurately relative to each other. The ionization efficiency for BC relative to nitrate was measured for small cores in organic rich particles (0.40 ± 0.10) and for larger, bare BC particles (0.25 ± 0.05), yielding an average value of 0.35 ± 0.10. The difference in sensitivity may be due to a combination of factors, including differences in particle collection and transmission efficiency. These measurements demonstrate that the SP-AMS is capable of detecting small BC inclusions with the same efficiency as larger BC particles previously used for instrument calibration. In addition, the SP-AMS can accurately quantify the fraction of BC in organic rich particles down to 3% BC by mass.

8CA.3

The Role of Organic Condensation on Ultrafine Particle Growth during Nucleation Events. DAVID PATOULIAS, Ilona Riipinen, Spyros Pandis, *University of Patras, Greece*

The ultrafine particles can grow to larger sizes and become cloud condensation nuclei (CCN) affecting cloud reflectivity and lifetime. This indirect effect is thus perturbing the energy balance of the planet. We applied an updated box model version of the Dynamic Model for Aerosol Nucleation in order to simulate the nucleation and subsequent growth in a remote continental location, Hyytiala, Finland. The individual effects of various processes and parameters on aerosol growth were quantified. DMAN uses the Two-Moment Aerosol Sectional algorithm to track both aerosol number and mass concentration using a sectional approach and describes both coagulation and condensation (sulfate, ammonium, organics). Our approach combines the SAPRC-99 mechanism for gas-phase chemistry and the 1-D the volatility basis set framework (VBS) for secondary organic aerosol formation and OA chemical aging.

The surface energy of the condensing organics has as a significant effect on the ultrafine particle rate. For a typical spring nucleation episode, an increase of the assumed surface energy results in a decrease of the particle number concentration above 3 nm (N3) but it increases the number concentration above 100 nm (N100). On the other hand the different parameterizations of the secondary OA chemical aging have a small effect on N3 but can have a major effect on N100.

The model reproduces the observed onset of nucleation and the qualitative features of the event. The particle growth is reproduced well by comparison with measurements.The simulation suggests that while sulfuric acid plays an important role of nucleation of new particles, it is not responsible for most of their growth, a finding consistent with the analysis of field observations in the site. The semivolatile-SOA produced upon oxidation of biogenic volatile organic compounds (BVOCs) is a key player for the later stages of growth.

8CA.4

Microphysical Simulation of Biomass-Burning Aerosol Size Distributions from BORTAS 2011. KIMIKO SAKAMOTO, James Allan, Hugh Coe, Jonathan Taylor, Thomas Duck, Jeffrey Pierce, *Colorado State University*

Biomass-burning aerosol size distributions are a function of combustion characteristics (e.g. fuel type, combustion efficiency) as well as near-source processing in the plume (e.g. coagulation, SOA formation and nucleation) that is not resolved by regional and global models. Thus, emitted size distributions vary in time in space, and emissions inventories of aerosol mass do not constrain aerosol and CCN number. These uncertainties in emissions number and size in global climate models leads to uncertainties in aerosol radiative forcings. We use aircraft-measured size distributions of biomass burning aerosol from the BORTAS field campaign to train a model of aerosol microphysics in biomass burning plumes. The microphysical simulations account for the aerosol processes occurring in a dense biomass-burning plume as it ages (coagulation, SOA formation/condensation, nucleation, entrainment, diffusion and plume dispersion). The model is initialized with emissions taken from GFED3 for July 19th, 2011 over Western Ontario (52.25 N, 90.75 W). We use the measurements to estimate the size distributions, SOA formation and nucleation rates by optimizing the model inputs to provide matching size distributions to the measurements. Future work will involve applying these techniques to other datasets of biomass-burning aerosol and creating parameterizations of biomass-burning number and size for regional and global models.

8CA.5

Evaporation Kinetics of Engine Lubricating Oil Aerosols at Near Ambient Conditions. Sara Jaber, Rawad Saleh, ALAN SHIHADEH, *American University of Beirut*

Unburned engine lubricating oil (LO) accounts for a major fraction of the primary organic aerosol (POA) emissions of internal combustion engines. Because LO spans a wide volatility range, its gas-particle partitioning behavior is of interest both for determining engine emission factors and for estimating gas precursor inventories when predicting secondary aerosol formation in the atmosphere. While some investigators have used chambers to study POA under thermodynamic equilibrium conditions, using thermodenuders to study aerosol volatility under non-equilibrium conditions is of practical importance. In these circumstances, data must be fitted to kinetic models of POA evaporation. Models in turn require knowledge of the evaporation coefficient, for which there are currently no reliable estimates. In this study we sought to determine the effective evaporation coefficient of LO aerosols over a range of particle concentrations (25-250 ug/m3) relevant to atmospheric pollution. The approach involved perturbing an aerosol system from its initial equilibrium state by isothermal dilution, and tracking particle volume versus time as the aerosol returned to phase equilibrium in an inert flow tube. The resulting normalized volume change versus time curve was fitted for evaporation coefficient using a numerical model. The studied aerosols were generated by condensing vapors produced by bubbling nitrogen through a 150 C column of LO, and total particle volume was simultaneously measured by two electrical mobility spectrometers (TSI SMPS 3936 equivalent) upstream and at various axial distances along the flow tube. The aerosols were also analyzed by GC-MS. In contrast to our previous work with representative SOA compounds, we found the observed phase equilibration kinetics were well described by effective evaporation coefficients approaching unity. We also found that the effective vapor pressure of the LO aerosol was well correlated to particle concentration, with higher concentrations yielding higher effective vapor pressures, as predicted by equilibrium partitioning theory.

8CA.6

Validation of Long-term Observations Using Sample-air Dilution with Particle Soot Absorption Photometer. JOHN BACKMAN, Aki Virkkula, Ville Vakkari, Johan Paul Beukes, Pieter G. van Zyl, Miroslav Josipovic, Stuart Piketh, Petri Tiitta, Kgaugelo Chiloane, Gerhard Fourie, Alfred Wiedensohler, Thomas Tuch, Tuukka Petäjä, Markku Kulmala, Lauri Laakso,*University of Helsinki*

There is an increase in scientific interest with respect to the climatic effects of black carbon (BC), which is an absorber of insolation. Research suggests that BC is the second most prominent radiative forcing agent. Atmospheric BC absorbs solar radiation in the atmosphere, reduces insolation at the surface, and redistributes energy vertically in the atmosphere with climatic implications.

A variety of challenges in the remote sensing of BC aerosols promotes the importance of in-situ measurements. Filter-based absorption measurements techniques are an economical and widely used method to determine atmospheric BC concentrations. Primarily, the deposition of light-absorbing species onto a filter-matrix will reduce the amount of light transmitted through the filter. Light-absorption coefficients can then be calculated by measuring the attenuation of light through the filter-matrix. Eventually, the aerosol-laden filter need to be changed to a pristine one, therefore, the method relies on filter changes. There are commercially available instruments capable of changing filters automatically; the Radiance Research Particle Soot Absorption Photometer (PSAP) require manual filter changes.

The interval, by which the filter needs to be changed, can be extended by diluting the sample air. This decreases the amount of manual labour required for long-term observations. Thus, the applicability of the instrument can be improved. The comparison between a diluted sample measured with a particle soot absorption photometer (PSAP) and a non-diluted sample measured with a multi-angle absorption photometer (MAAP) provides a means of assessing this sampling method. The method, however, requires non-standard post-processing of the of the PSAP data. The post-processing of the data lowers the detection limit, which is necessary due to the low concentrations of the diluted sample. The data analysed comprise of 23 months of measurements conducted on the Mpumalanga Highveld in South Africa, ending in January 2011. Initial results show a correlating slope of 0.981.

8CA.7

Examining Evolution of Biogenic Organic Aerosols Using a Theoretical Carbon Number Functionality Grid. JUDITH PERLINGER, Tanvir Khan, Bo Zhang, Hans P. Arp, *Michigan Technological University*

According to the Abraham solvation model, non-ionic intermolecular interactions in aerosols as in other condensed phases can be characterized according to non-specific interactions (van der Waals and cavity formation) and three types of specific interactions (dipolarity/polarizability, hydrogen bond donor, and hydrogen bond acceptor interactions). The magnitude of these interactions is altered as aerosols are transformed through oxidation in the atmosphere. Interaction of organic aerosol species with atmospheric water, which affects aerosol optical properties, cloud condensation nuclei activation, and removal by precipitation, is expected to increase as hydrogen bond donor-acceptor (HDA) character and ionization increase. Using this model, a retention index diagram of a hypothetical, multidimensional gas chromatographic (GCx2GC) analysis of a mixture of non-ionic biogenic precursors and oxidation products can be created and used to quantify changes in organic aerosol. In GCx2GC analysis, separation of complex mixtures is achieved by diverting the modulated effluent from a polar or non-polar primary column, which separates species according to non-specific and specific interactions, into two polar secondary columns having different stationary phases that provide further separation of species. In previous simulations it was shown that, when derivatization was employed, and using 50%-trifluoropropyl-methylpolysiloxane as primary column and secondary columns 90%-cyanopropyl polysilphenylene-siloxane and polyethylene glycol, none of which undergo HDA interaction, the primary column was able to separate species by carbon number, and the polar secondary columns provided additional separation according to functionality. Here, we examine use of ionic liquid stationary phases, which undergo HDA interactions and as such provide enhanced separation of underivatized compounds. Using a combination of published measurements and computational chemistry, we examine theoretical retention in GCx2GC, including ionic liquid stationary phases, for hypothetical, complex mixtures of biogenic precursors and oxidation products.

8CA.8

Direct Determination of Soot Mass Absorption and Mass Extinction Coefficients at Multiple Wavelengths. JAMES RADNEY, Christopher Zangmeister, Michael Zachariah, *National Institute of Standards and Technology*

The in-situ measurement of mass absorption and mass extinction coefficients – MAC and MEC, respectively – of laboratory generated soot aerosol at multiple visible wavelengths will be presented. A tandem differential mobility analyzer, aerosol particle mass analyzer, photoacoustic spectrometer, cavity ring-down spectrometer and condensation particle counter was used for these measurements. We observe that the MAC is a direct function of mass while the MEC demonstrates both mass and mobility diameter dependencies. Potential implications of MEC complexity in deriving SSA for soot will also be discussed.

8CA.9

Measurements of Organic Haze Particles Formed from UV Irradiation of Acetylene by High-Resolution Soot-Particle Aerosol Mass Spectrometry. JONATHAN FRANKLIN, Eleanor Browne, Manjula Canagaratna, Timothy Onasch, Paola Massoli, Douglas Worsnop, Hiroshi Imanaka, Kevin Wilson, Jesse Kroll, *Massachusetts Institute of Technology*

The atmospheres of some planetary bodies (such as Saturn's moon Titan) are characterized by the presence of organic haze particles, formed by irradiation of simple organic species in the absence of oxygen. In this study, simple organic haze particles were generated in the laboratory and chemically characterized using an Aerodyne High-Resolution Time-of-Flight Soot-Particle Aerosol Mass Spectrometer (SP-AMS) operated with only the laser vaporizer (CW nd:YAG 1064 nm). Particles were formed by irradiating acetylene diluted in nitrogen with short wavelength UV light. Haze particles were measured by the SP-AMS using both the standard electron impact (70 eV) ionization mode as well as a vacuum ultraviolet light (VUV) photoionization mode which uses tunable VUV light (from the Chemical Dynamics Beamline at the Advanced Light Source of the Lawrence Berkeley National Laboratory). The vaporization and detection of these particles by SP-AMS indicate they can absorb in the infrared (1064 nm). Mass spectra show a range of carbon clusters and hydrocarbon components, including major peaks at m/z 91 ($C_7H_7^+$) and m/z 78 ($C_6H_6^+$), as well as clear signals at m/z 720 (C_{60}) and m/z 840 (C_{70}). Elemental analysis of the haze particles showed roughly a 1:1 hydrogen-to-carbon ratio, the same as that of the C_2H_2 precursor. The degree of nitrogen and oxygen incorporation into the particles, and mass spectrometric signatures as a function of ionization wavelengths is also discussed.

8CA.10

Plant Stress in a Changing Environment and its Impacts on Future Climate: The Effects of Simulated Herbivory on Biogenic Secondary Organic Aerosol. CELIA FAIOLA, Graham VanderSchelden, Miao Wen, B. Thomas Jobson, Timothy M. VanReken, *Washington State University*

The largest global source of volatile organic compounds (VOCs) in the atmosphere is from biogenic emissions. These VOCs are one of the principal factors influencing the oxidative capacity of the atmosphere in forested regions, and impact both ozone concentration and secondary organic aerosol (SOA) formation. Emission rates of biogenic VOCs are predominantly controlled by temperature. However, plant stressors associated with a changing environment can alter both the quantity and composition of the compounds that are emitted. Alterations to the biogenic VOC profile could impact the characteristics of the SOA formed from those emissions. This study investigated the effects of one global change stressor, increased herbivory, on the characteristics of SOA derived from real plant emissions. Plants were housed in the laboratory within a 0.3 cubic meter biogenic chamber. Herbivory was simulated via exogenous application of methyl jasmonate, an herbivory proxy. Plant emissions were transported from the biogenic chamber to a 7 cubic meter FEP Teflon aerosol growth chamber, where they were oxidized with ozone in the absence of light. The evolution of gas-phase species and particle characteristics were monitored over the following eight hours. Experiments were repeated under baseline and stressed conditions for a variety of species including, but not limited to, ponderosa pine, Douglas-fir, blue spruce, and bur oak. Gas-phase species were measured with a gas chromatograph coupled to a mass spectrometer and flame ionization detector (GC-MS-FID). Particle size distribution, chemical composition, and hygroscopic properties were measured with a scanning mobility particle sizer (SMPS), high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS), and cloud condensation nuclei counter (CCNc) respectively. A comparison of the BVOC emissions and resultant SOA characteristics under baseline and stressed conditions will be presented.

8CA.11

Experimental Studies of Particle Bounce: Comparison of Secondary Organic Material (SOM) from Harvard Environmental Chamber and Field Studies in Amazonia. ADAM BATEMAN, Pengfei Liu, Scot Martin, *Harvard University*

The effect of relative humidity (RH) on the extent of semisolidity was investigated through the use of particle bounce (or lack thereof) during impaction. The physics governing particle bounce can be attributed to particle surface properties, specifically the coefficient of restitution and surface adhesion forces. It has been suggested that aerosols can form disordered amorphous solids (glasses) due to the complex organic composition, with larger and more hydrophobic organic molecules more likely to form glasses. The amorphous organic phases can form from a variety of organic compounds upon drying of an aqueous solution and can undergo transitions during the course of hydration and dehydration. By varying the particulate matter water content and observing particle bounce as a function of RH, the phase state of the organic material under investigation can be determined. Custom made impactors were employed to study the effects of RH on the phase state of organic particles, up to an RH of 99%. Particles were produced in the Harvard environmental chamber from a variety of precursors and oxidants, including isoprene, alpha-pinene, and toluene. In addition, two field campaigns were conducted in the wet and dry season in Amazonia using the custom impactors. Comparison with the particle bounce experiments from the laboratory give insights into the phase state of atmospheric SOM as a function of RH.

8CA.12

Changes in Soot Aggregate Morphology Due to Coatings of Secondary Organic Aerosol from Anthropogenic and Biogenic Precursors. ELIJAH G. SCHNITZLER, Ashneil Dutt, Jason S. Olfert, Wolfgang Jaeger, *University of Alberta*

The optical properties and climatic effects of soot aggregates depend on their size and shape, which can change during the atmospheric lifetime of the aggregates. For example, vapours can condense onto the surface of aggregates and cause them to collapse, presumably due to surface tension effects. Changes in morphology have previously been observed for aggregates exposed to saturated vapours of sulfuric acid, oleic acid, and a number of other species. Changes in morphology have also been reported for aggregates exposed to oxidation products of alpha-pinene, toluene, and isoprene in smog chamber experiments, in which secondary organic aerosol (SOA) coats the aggregates. We investigated changes in soot aggregate morphology due to coatings of SOA from five precursors (benzene, toluene, ethyl benzene, p-xylene, and limonene) in a series of smog chamber experiments designed to determine if the extent of aggregate collapse depends on precursor species. Soot generated using a McKenna burner was dried, denuded, neutralized, size-selected, and passed into a smog chamber. Once the soot particle concentration reached at least 1000 per cubic centimeter, a given SOA precursor was injected. Hydrogen peroxide was photolyzed to generate hydroxyl radical. During photo-oxidation, coated and denuded particles were alternately sampled by a differential mobility analyzer. The denuded particles decreased in diameter until a final collapsed soot core formed. The difference between the initial and final diameters for 100, 150, 200, and 250 nanometer soot aggregates exposed to SOA from all precursors was measured. As expected, the extent of collapse increases with increasing initial soot aggregate size; however, the extent of collapse does not depend on the identity of the SOA precursor.

8CA.13

Impact of Hygroscopicity and Refractive Index of Black Carbon Coatings on Absorption Enhancement. LAURA FIERCE, Francisco Mena, Tami Bond, Nicole Riemer, *University of Illinois at Urbana-Champaign*

Absorption by black carbon (BC) is enhanced when BC is mixed with non-absorbing aerosol components. Modeled absorption by a BC-containing particle depends on the volume of the BC core, the volume and composition of the coating material, and the assumed particle configuration. The size and composition of fresh BC-containing particles vary between emission sources and are modified after emission by condensation of semi-volatile substances and coagulation with other particles, so absorption by atmospheric BC depends on the characteristics of fresh BC-containing particles and the processes that affect them after emission.

In this study, we simulated the evolution of aerosol emissions in an urban area with the particle-resolved model PartMC-MOSAIC and evaluated the sensitivity of absorption enhancement by BC-containing particles to the hygroscopicity and refractive index of non-BC components. We evaluated BC absorption as a function of relative humidity and wavelength, considering two assumed particle configurations: the core-shell approximation and the dynamic effective medium approximation. For both optical configurations, we show that the sensitivity of BC absorption to particle composition depends strongly on the ambient relative humidity. At high relative humidity, absorption by black carbon is highly sensitive to the hygroscopicity of the dry aerosol coating and is insensitive to the coating refractive index. At low relative humidity, absorption is insensitive to particle hygroscopicity but sensitive to the refractive index of the dry coating.

8CA.14

Carbonaceous Nanoparticle Toxicity as a Function of Ferrous Iron Content. DAN HINZ, Hsiang Teng, Hoi Ting, Anne Johansen, *Central Washington University*

Experiments on mitochondria indicate that toxicity of inhalable atmospheric nanoparticles that are emitted from fossil fuel combustion correlates with both ferrous iron (Fe(II)) and anthracene concentrations in collected ultrafine particles (UFP). To further understand underlying chemical mechanisms responsible for this detrimental effect, UFPs and carbonaceous nanoparticles are investigated under near physiological conditions while analyzing Fe(II) and the representative oxidative species hydrogen peroxide (H2O2). Realistic concentrations of Fe(II) at sub-nanomolar and H2O2 at nanomolar levels are quantified using flow injection analysis (FIA) with chemiluminescence. Results show that biological electron donors play a significant role when exposed to black carbon particles that are used as UFP proxy material. Furthermore, preliminary results show that black carbon (Printex 90) in the presence of ascorbate generated H2O2. Fe(II) did not show a significant increase in H2O2 under the conditions tested. This study will shed light on the chemical processes and significance of the chemical species Fe(II) and anthracene-like molecules that seem to be responsible for the toxicity of inhalable carbonaceous particles that are emitted from the incomplete combustion of fossil fuel.

8CC.1

Chemical Composition of Rain Water Collected from 2009 to 2010 at Queretaro City and a Rural Mining Site of San Joaquín, Querétaro, México. ROCIO GARCIA, Sara Solís, Carolina Muñoz, Gilberto Hernández, Ma. Elena Calderón, Armando Báez, *Centro de Ciencias de la Atmósfera, UNAM*

Our study aims to understand the chemical composition of rainwater although all ions were analyzed SO_4^{-2}, NO_3^-, Cl^-, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+ and H^+ were performed in rainwater samples collected in Queretaro City and San Joaquin, a suburban area nearby the city. At a north site of Queretaro City during the rainy seasons of 2009 and 2010. The correlation analysis shows a positive and high correlation among them, indicating that the most important source was anthropogenic. Ammonium presented the higher volume weighted mean concentrations (VWMC), followed by SO_4^{-2}, NO_3^-, HCO_3^-, Ca^{2+}, Cl^-, H^+, Na^+, K^+ and Mg^{2+}. Air mass back trajectories were associated to the concentrations of trace metals and of SO_4^{-2}, Ca^{2+}, Mg^{2+}, NH_4^+ and H^+ observed during each rainy day. Three factors have been used in this analysis, giving each variable a loading within each factor. Loadings greater than 0.5 are considered to be significant components of the factor. The four factors explain 67.19% of the total variance of all the data for San Joaquin. The third factor associates NH_4^+, NO_3^-, SO_4^{-2}, Ca^{2+} and K^+ (10.4% of the total variance). This factor 3 expresses the control of the terrestrial source that could influence the alkalinity of the atmospheric water due to carbonate dissolution. Many studies pointed out the role of meteorological factors in determining the chemical features of precipitations.

8CC.2

Contact Freezing Efficiency of Mineral Dust Particles Determined via Optical Tweezers. RYAN SULLIVAN, Hassan Beydoun, Kyle Gorkowski, Benjamin Dennis-Smithers, Toni Carruthers, Jonathan P. Reid, *Carnegie Mellon University*

Contact freezing is believed to be the most efficient heterogeneous ice nucleation mechanism that catalyzes the freezing of supercooled cloud droplets. This process is notoriously difficult to study experimentally as it requires knowledge of how many particles have collided with the water droplet before it nucleates an ice crystal. Here we report the first use of optical tweezers to study contact freezing. A supercooled cloud droplet is tweezed in the temperature-controlled optical trap. The droplet is then bombarded with size-selected mineral dust particles. The tweezed droplet’s Raman spectrum that is retrieved in real-time provides a precise measure of the number of dust particles that have coagulated with the droplet. The occurrence of droplet freezing is also readily observed from the Raman spectrum and visual imaging. Together, this enables the precise determination of the freezing efficiency of various types of atmospherically-relevant mineral dust particles, by measuring the number of particle-droplet contact events required before ice nucleation occurs. The validity of the notion that contact freezing is the most efficient ice nucleation method has been explicitly interrogated for a variety of mineral dust samples. This new method helps to address fundamental deficiencies in our understanding of the ice nucleation properties of atmospheric particles.

8CC.4

Complex Refractive Index of Hematite in the Visible and Near Visible: A Review. HANS MOOSMULLER, Johann Engelbrecht,*Desert Research Institute*

Hematite (alpha-Fe_2O_3) is an iron oxide that generally dominates ambient light absorption by entrained mineral dust in the visible and near-visible spectral region. Therefore, knowledge of its complex refractive index spectrum is critical for calculating mineral dust absorption, scattering, and extinction coefficients and single scattering albedo as needed for determination of sign and magnitude of its direct radiative forcing. Unfortunately, literature values for the complex refractive index as function of wavelength vary greatly, often by more than an order of magnitude for the imaginary part. Here, we review published values in the visible and near-visible spectral region together with methods of determination and attempt to give a recommendation for values that should be used.

8CC.5

Aerosol-Vertical Velocity Coupling Effects on Stratus Cloud Microphycs. STEPHEN NOBLE, James Hudson, *Desert Research Institute*

It is well known that increasing atmospheric aerosol leads to greater cloud albedo and longer cloud lifetimes, the indirect aerosol effect (IAE), which increases cloud droplet concentration (N_c) and decreases cloud droplet mean diameters (MD). In large areas of marine stratocumuli, IAE produces cooling that offsets greenhouse warming. However, changes in N_c and MD can lead to feedbacks that further change cloud microphysics and even IAE. Observations of cloud microphysics, dynamics, and below cloud CCN from two marine stratocumulus field campaigns are analyzed. Results show limited evidence of feedbacks involving vertical velocity (W) and possibly latent heat exchanges.

Cloud supersaturation (S) can be measured two ways. Because aerosol below stratocumuli often have bimodal particle size distributions, which is said to be from cloud processing, the size between the two modes of the distributions can be related to cloud S through assumptions of aerosol composition. A comparison between N_c and the CCN spectra produces another cloud S estimate that is usually higher. Droplets with small MD are not as likely to be involved with the cloud processing because when dry air is mixed into the cloud from above they more readily evaporate, which makes latent heat exchange. This evaporative cooling then increases W (sigma_W) perturbations.

Furthermore, smaller MD due to increased CCN suppresses drizzle. Less drizzle decreases evaporative cooling below cloud, which reduces the stability of the boundary layer (Ackerman et al. 2004) and thus increases buoyancy and turbulence i.e., greater sigma_W. Also, sigma_W can be increased with latent heat release from condensation on smaller more numerous droplets with more surface area that produce more rapid condensation. These feedbacks can reduce IAE.

Ackerman, A.A., M.P. Kirkpatrick, D.E. Stevens, and O.B. Toon, 2004: Nature, 432, 1014-1017.

8CC.6

Development of a Source Oriented Version of the WRF/Chem Model and Its Application to the California Regional PM10/PM2.5 Air Quality Study. HONGLIANG ZHANG, Steven DeNero, David Joe, Hsiang-He Lee, Shu-Hua Chen, Michael Kleeman, *UC Davis*

A source-oriented representation of airborne particulate matter was added to the Weather Research & Forecasting (WRF) model with chemistry (WRF-CHEM). The source-oriented aerosol separately tracks primary particles with different hygroscopic and light absorption properties rather than instantaneously combining them into an internal mixture. The source-oriented approach avoids artificially mixing light absorbing black+brown carbon particles with hygroscopic material such as sulfate that would encourage the formation of additional coatings. Source-oriented particles undergo coagulation and gas-particle conversion, but these processes are considered in a dynamic framework that realistically “ages” primary particles over hours and days in the atmosphere. The source-oriented WRF-CHEM model more accurately predicts radiative feedbacks from anthropogenic aerosols compared to models that make internal mixing or other artificial mixing assumptions.

A three-week stagnation episode (December 15, 2000 to January 7, 2001) during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) was chosen for the initial application of the new modeling system. Emissions were obtained from the California Air Resources Board. Gas-phase reactions were modeled with the SAPRC90 photochemical mechanism. Gas-particle conversion was modeled as a dynamic process with semi-volatile vapor pressures at the particle surface calculated using ISORROPIA. Source oriented calculations were performed for 8 particle size fractions ranging from 0.01–10 µm particle diameters with a spatial resolution of 4km and hourly time resolution. Primary particles emitted from diesel engines, wood smoke, high sulfate combustion, food cooking, and other anthropogenic sources were tracked separately throughout the simulation as they aged in the atmosphere. Results show that the source-oriented representation of particles with meteorological feedbacks in WRF-CHEM affects the aerosol extinction coefficients, downward shortwave, and primary and secondary particulate matter concentrations. Downward shortwave radiation predicted by source-oriented model is enhanced by 1%. The extinction coefficient predicted by the source-oriented model is reduced by an average of about 5-10% in the central valley and a maximum of 20%. Particulate matter concentrations predicted by the source-oriented model are all 5-10% lower than the internally mixed version of the same model. All of these results stem from the mixing state of black carbon. The source-oriented model predicts that hydrophobic diesel engine particles remain largely uncoated during the simulation, while the internal mixture model predicts significant accumulation of secondary nitrate and water on diesel engine particles. More substantial differences in predicted concentrations generated by the source-oriented model and the internally mixed version are expected when predicted concentrations of secondary particulate matter increase to higher levels.

8CC.7

Mixing State of Size-selected Submicrometer Particles in the Arctic (Ny-Ålesund, Svalbard) in the Spring and Fall of 2012. Kihong Park, GIBAEK KIM, Jae-Seok Kim, Young Jun Yoon, Hee-joo Cho, *Gwangju Institute of Science and Technology*

Measurements of hygroscopicity, volatility, and mixing state of size-selected Aitkin and accumulation mode particles were conducted by hygroscopicity and volatility tandem differential mobility analyzer (HVTDMA) in the Arctic (Ny-Alesund, Svalbard) in May and September of 2012. In May, the accumulation mode particles were dominant with occasional observation of the Aitken mode particles. Appearance of the Aitken mode particles happened almost simultaneously at two locations which are ~2 km away from each other with different heights 61 m and 474 m above sea level, respectively, suggesting that they were produced regionally by nucleation. In September, the accumulation mode particles were suppressed, while the Aitken mode particles still exist. The less number of submicrometer particles in September might occur because the strength of the long-range transported aerosols became weak with the change of air mass flow pattern and more mixing happened. During the period of enhanced concentration of the Aitken mode particles, the average hygroscopic growth factor (HGF) and shrinkage factor (SF) of the Aitken mode particles were 1.46 and 0.88, respectively, without significant external mixing of different hygroscopic or volatile species, suggesting that the Aitken mode particles mostly consist of sulfates with some volatile organic species secondarily formed from biogenic marine sources. The accumulation mode particles displayed a significant external mixing of long-range transport aerosols and marine aerosols significantly, which were affected by the air mass transport pattern. Mixing structure of the accumulation mode particles was further examined by gradually increasing heater temperature up to 200 oC. The “more-volatile” particles were completely evaporated at 200 oC, and they had some volatile species at 100 oC, suggesting that the “more-volatile” particles should be an internal mixture of sulfate and volatile organics. On the other hand, the “less-volatile” particles are not completely evaporated at 200 oC, suggesting that they had some non-volatile species.

8CC.8

Properties of Carbonaceous Aerosols during CARDEX 2012: An Instrument Intercomparison. NICHOLAS BERES, Ian Arnold, Rajan K. Chakrabarty, Hans Moosmuller, P.S. Praveen, Ramanathan Veerabhadran, W. Patrick Arnott, James Schauer, Orjan Gustafsson, *Desert Research Institute*

In this study, we present comparisons of in-situ and filter-based measurements of aerosol light absorption, black carbon (BC) concentration, elemental carbon (EC), and organic carbon (OC) from the 2012 CARDEX (Clouds, Aerosol, Radiative forcing, and Dynamics EXperiment) campaign based on the island of Hanimaadhoo in the Republic of Maldives. The instruments used for this comparison study include two photoacoustic spectrometers (PAS, lambda = 870 and 405 nm), a 7-wavelength aethalometer (lambda = 370, 430, 470, 520, 590, 700, and 880 nanometers), and independent 12- and 24-hour integrated filter samples, analyzed for EC - OC using the NIOSH thermal evolution protocol. During the dry monsoon season (December to April), anthropogenic aerosols from India and Southeast Asia are characteristically transported to the Maldives at surface level. Data shown here were collected between February and April of 2012 at the Maldives Climate Observatory-Hanimaadhoo (MCOH). Using correction factors adopted from Corrigan et al., (2006), we show reasonable agreement between absorption coefficients obtained with the aethalometer and the photoacoustic spectrometer and between BC mass concentrations obtained with the aethalometer and EC mass concentrations obtained with NIOSH analysis of filter samples. Additionally, we attempt to further develop site-specific correction methods by altering the mass-absorption efficiency values used in the Corrigan et al. (2006) study.

REFERENCE:
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8CC.9

Evaluating Simulated Profiles of Aerosol Optical Properties Using Measurements Collected during the Two Column Aerosol Project (TCAP). JEROME FAST, Larry Berg, Jerome Barnard, Duli Chand, Richard Ferrare, Connor Flynn, Chris Hostetler, Arthur J. Sedlacek, John Shilling, Jason Tomlinson, Alla Zelenyuk, *Pacific Northwest National Laboratory*

Relatively large uncertainties remain in climate model predictions of aerosol radiative forcing. Climate models are usually evaluated using column-integrated measurements collected by instruments at the surface or from satellites because measured profiles of aerosol optical properties are limited. Adequately simulating the vertical distribution of aerosols and their effect on the radiation budget is also important since it affects how the meteorological conditions respond to aerosol radiative effects. In this study, we compare simulated profiles of aerosol optical properties obtained from the WRF-Chem model with those obtained from both in situ and remote sensing measurements during the Department of Energy’s (DOE) Two-Column Aerosol Project (TCAP). TCAP was designed to investigate changes in aerosol mixing state, CCN concentration, aerosol radiative forcing, and cloud-aerosol interactions in two atmospheric columns: one over Cape Cod, Massachusetts and another located approximately 200 km to the east. TCAP was the first science mission for the Sky-Scanning, Sun-Tracking Atmospheric Research (4STAR) spectrometer and the second generation downward looking High Spectral Resolution Lidar (HSRL-2). Two types of simulations are performed, the first with predicted aerosols and the second in which aerosol mass, composition, and size distribution measurements are used to drive the aerosol optical property module. Differences in scattering and absorption are quantified between the second simulation and the measurements will arise from assumptions employed by the aerosol optical property module (e.g. mixing rule, refractive indices, internal versus external mixing state). By comparing the results of the two types of simulations, we can identify the factors that contribute to errors in simulated optical depth, single scattering albedo, and angstrom exponent that are used by radiation modules. The model is also used to investigate reasons for changes in aerosol properties between the two columns, as aging alters aerosol optical properties as they are transported over the ocean.

8CC.10

Photooxidation of Polycyclic Aromatic Hydrocarbons in Clouds and Fog – Laboratory and Model Studies. JERSHON EAGAR, Pierre Herckes, Barbara Ervens, *Arizona State University*

Cloud and fog droplets are an atmospheric medium for aqueous phase photochemical reactions. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere and are among products formed during the incomplete pyrolysis of organic matter. Higher molecular weight PAHs bound to particulate matter may dissolve in the aqueous phase during cloud and fog droplet nucleation. The reactivity of these higher molecular weight PAH (four, five, and six ring) has not received much attention from the atmospheric chemistry community. This work will present laboratory studies on the photodegradation of chrysene under atmospherically relevant conditions. In a first step, reaction kinetics and product formation will be discussed.

In a second step, the significance of cloud and fog droplets as a sink for the photodegradation of four, five, and six ring PAHs will be explored as compared to the sink strength of gas and particle phase reactions. Parameter spaces will be mapped out by means of a box model using literature data and new experimentally-determined values of photochemical kinetic data. The partitioning between gas and aqueous phases will be described using literature Henry’s law constants. Photooxidation in the aqueous phase will be calculated for several droplet formation and evaporation cycles.

8CC.11

Impact of Biomass Burning Aerosols on Regional Climate over Southeast USA. PENG LIU, Yongtao Hu, Athanasios Nenes, Armistead Russell, *Georgia Institute of Technology*

Great interest has been aroused in how important aerosols may play a role in the cooling of the southeastern USA. A major contributor to the particulate matters over this region is biomass burning, which is rich in black carbon and organic compounds, and may have significant feedbacks to regional climate through the direct and indirect effects.

In this study, the cloud droplet activation parameterization of Kumar et al.(2009), which considers the competition between soluble and insoluble aerosols for water vapor during cloud droplet formation in ascending air parcels, is implemented in coupled WRF-CMAQ. The water uptake properties of the biomass burning aerosol (required for predicting optical depth for direct radiative forcing, and CCN activity for indirect effects) are constrained using observations of fresh and aged biomass burning aerosol sampled during the 2008 ARctas campaign (Jacob et al., 2010). In order to isolate the direct and indirect effects, we first couple the aerosol module only with radiation module to estimate direct effect, and then with microphysics module for the indirect effect.

References:

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8CC.12

Assessing the Relative Contribution of Emissions to Cloud Droplet Formation with Sectoral and Spatial Specificity.

SHANNON CAPPS, Vlassis Karydis, Daven Henze, Armistead Russell, Athanasios Nenes, *US EPA*

The radiative balance of the earth system is strongly dependent on the reflectivity of clouds, which arises from the cloud droplet number concentration (CDNC). Aerosol acting as cloud condensation nuclei (CCN) can modulate CDNC by providing additional sites for droplet formation; thus, the aerosol concentration from precursor gas or primary emissions can indirectly perturb climate. Many global climate models include a representation of this microphysical process, but the assessment of the relative influence of specific emissions sources remains a significant computational challenge. In recent years, this information has proven valuable enough to warrant expensive investigations including traditional sensitivity analysis (e.g., emissions toggling) and more sophisticated approaches, such as building model emulators. We present an operationally efficient alternative.

The adjoint of a model allows expedient and accurate determination of the sensitivity of the CDNC of a specific region with respect to each aerosol and precursor emissions simultaneously. For the first time, a global chemical transport model adjoint (Henze et al., 2007) fully coupled with the adjoint of a droplet activation parameterization (Karydis et al., 2012) determines the relative influence of aerosol and precursor gas emissions on CDNC. The now widely used GEOS-Chem adjoint is equipped with ANISORROPIA (Capps et al., 2012) to ensure that the sensitivities of inorganic precursor gases and aerosol are modeled with the same accuracy as the forward GEOS-Chem model. The adjoint of a droplet activation parameterization that models absorption of water on soluble aerosol and adsorption of it on insoluble dust (Kumar et al., 2009) is fully integrated into the GEOS-Chem adjoint framework with a set of prescribed size distributions. This novel system is used to assess the relative influence of global emissions on regions where stratocumulus cloud decks persist.

8CC.13

New Particle Formation and Growth Events Observed under Clear-sky and Cloudy Conditions at Gosan Climate Observatory.

SOON-CHANG YOON, Yumi Kim, Sang-Woo Kim, *Seoul National University*

New particle formation and growth events at Gosan Climate Observatory (GCO), Jeju Island, south of the Korea Peninsula were analyzed according to cloud amount during May 2008 – April 2012. Two cases show possibility for occurrence of strong new particle formation and growth under low-level cloud (30 January 2012) and mid-level cloud (28 January 2012) conditions in spite of decrease of global down-welling shortwave radiation. In addition, new particle formation and growth events occurred under not only cloudy condition but also elevated dust layer at 20-21 March, 2012. For 4-year data seasonal occurrences of total new particle formation and growth events were 85 (spring), 31 (summer), 88 (fall), and 76 (winter) days out of a total 805 days. Only 13% of days for total events were observed under clear sky. 85% of strong event also observed under cloudy condition. The mean event start time was delayed according to increasing cloud amount. On average, formation rate of strong new particle formation and growth under between clear skies and cloudy conditions were similar. However, mean growth rate and condensation sink of strong events were decreased according to increasing cloud amount. Those imply that other factors (e.g., enough condensable gases, low condensation sink) rather than radiation are satisfied for occurred events at GCO.

8CC.14

Forty-Seven Years of MSA Concentrations in the Finnish Arctic. JAMES R. LAING, Philip K. Hopke, Eleanor F. Hopke, Liaquat Husain, Vincent A. Dutkiewicz, Jussi Paatero, Yro Viisinen, *Clarkson University*

MSA (Methane Sulfonate) is a unique organosulfur species that can be used as a marker for these biogenic oceanic sulfur sources. MSA is the oxidation product of DMS (dimethylsulfide), which is excreted by marine planktonic algae and subsequently transported to the air (Bates, 1992). Week-long historical filter samples collected at Kevo, Finland from 1964-2010 have been analyzed for methane sulfonate (MSA) as well as various other species. MSA has a distinct summer maximum during the months of May, June and July associated with warmer waters and increased primary productivity in the surrounding oceans. PSCF (potential source contribution function) analysis was performed using HYSPLIT4 5-day back-trajectories. Results show that source regions for MSA in the summer are primarily in the North Atlantic Ocean, and the Norwegian and Barents Seas. For the peak summer months, the average MSA concentrations decreased from 1964 to the early-1980s, increased from the early 1980s till 2000, and have decreased in the 2000's. It has been proposed by Charlson et al. (1987, Nature 326, 655-661) that biogenic sulfate is part of a negative feedback mechanism that moderates the climate, where biogenic sulfate form cloud condensation nuclei (CCN). Increased CCN alters the radiative balance of the atmosphere by increasing shortwave radiation albedo, affecting sea surface temperature and the production of DMS by algae. Sea surface temperatures in the northern hemisphere have risen since the early 1970s, most dramatically in the North Atlantic (Thompson, 2010). Using the HadSST2 Dataset (Rayner, 2006, Journal of Climate 19, 446-469), a significant correlation was found between average yearly MSA concentrations for the months of peak concentration (May, June, and July) and yearly SST anomalies in the region from 30W to 80E and 40N to 90N.

8CC.15

Long-term Trend Analysis of 47 Years of Finnish Arctic Aerosol Composition. JAMES R. LAING, Philip K. Hopke, Eleanor F. Hopke, Liaquat Husain, Vincent A. Dutkiewicz, Jussi Paatero, Yro Viisinen, *Clarkson University*

Long-term datasets of aerosol chemical composition are very useful for understanding past events. Significant changes have occurred in the Arctic over the past half century. Black carbon and sulfate concentrations in particular can help assess aerosol-driven climate forcing that has taken place and lead to a better understanding of changes in the Arctic atmosphere. Week-long historical filter samples collected at Kevo, Finland from 1964-2010 have been analyzed for various chemical species. Major ions and methane sulfonate (MSA) have been analyzed by ion chromatography (IC), trace elements by inductively coupled plasma - mass spectrometry (ICP-MS), and BC by light transmission. Black carbon and non-sea salt sulfate (nss-SO42-) have decreased dramatically over the past 5 decades, most significantly in the early 1990's coinciding with the collapse of the Soviet Union. This decline correlates with published global emissions inventories (Bond, 2007, Global Biogeochemical Cycles 21, GB2018; Smith, 2011, Atmos. Chem. Phys. 11, 1101–1116). Most heavy metals of interest (V, Ni, Cu, Cd, Sb, Pb) have decreased over this time period as well. The decrease in Pb in the Arctic atmosphere is attributable to the restricted use and ban of leaded gasoline in Europe. The 47-year complete data set will be analyzed by Positive Matrix Factorization (PMF). The receptor modeling results will be connected with back trajectory data in a Potential Source Contribution Function (PSCF) analysis to determine possible source areas. The combination of PMF and PSCF will identify sources and their geographic locations.

8CC.16

Effect of Pressures and Temperatures on Ion-induced Nucleation Rate Measurement in SO2/H2O/N2 Gas Mixture by Soft X-ray Ionization. TAKASHI OGI, Asep Suhendi, Kikuo Okuyama, Muhammad Miftahul Munir, Ferry Iskandar, *Hiroshima University*

The importance of the role of ions in the production of aerosols in the atmosphere has been discussed for a long time, but the precise mechanism is still not known and more research is required to understand and quantify the effect. Recently, the observation of nucleation and subsequent growth in the real atmosphere has been done in a wide variety of altitude locations corresponding to different pressures, temperatures, and atmospheric conditions. However, recent basic experiments in exploring the role of ion-induced nucleation (IIN) in the production of aerosols have been only conducted under standard temperature and pressure or only in some specific conditions; this is insufficient for understanding the role of IIN in the realistic atmospheric conditions that have variations in pressure and temperature. This study reports the systematic investigation of IIN rate measurement in a SO2/H2O/N2 gas mixture, employing soft X-ray at different pressure and temperature levels. Experiments were conducted using a modified continuous flow gas-generation system, employing a soft X-ray ionizer and a particle counter with an improved integrated online temperature, pressure, and a relative humidity (RH) control system. Nucleation rates were measured as a function of SO2 concentration at different levels of RH, pressure (600–970hPa) and temperature (5–25ºC). The results showed that the nucleation rate dependence on SO2 concentration followed a power law, and the slope varied slightly in a range from 1 to 1.26 at different RH levels (15–60%). A positive pressure effect was generally found and a power law was followed with varied scaling for different SO2 concentrations. The trend of an increase in nucleation rate with temper-ature was consistent with observations in homogenous nucleation experiments, and with the behavior predicted by classical binary nucleation theory. These experimental results will be useful to explain the contribution of IIN in differ-ent locations and atmospheric conditions.

8CC.17

Can Meteorology Obfuscate Aerosol Indirect Effects in Stratocumulus? Jonathan Petters, Hongli Jiang, Graham Feingold, Dione Rossiter, Djamal Khelif, Lisa Sloan, PATRICK CHUANG, *University of California, Santa Cruz*

The impact of changes in aerosol and cloud droplet concentration on the radiative forcing of stratocumulus-topped boundary layers has been widely studied. However, how these impacts compare to those due to variations in meteorological context has not been investigated in a systematic fashion for non-drizzling overcast stratocumulus. In this study we examine the impact of observed variations in meteorological context and aerosol state on daytime, non-drizzling overcast stratiform evolution, and determine how resulting changes in cloud properties compare. Using large-eddy simulation we create a model base case of daytime southeast Pacific coastal stratocumulus, spanning a portion of the diurnal cycle (early morning to near noon) that is constrained by observations taken during the VOCALS (VAMOS Ocean-Atmosphere-Land Study) field campaign. We perturb aerosol and meteorological properties around this base case to investigate the stratocumulus response, specifically changes in cloud liquid water path, bulk optical depth and cloud radiative forcing (CRF). We find that realistic variations in meteorological context can elicit responses in radiative forcing that are on the same order of magnitude as, and at times larger than, the responses due to factor of two changes in drop concentration. We estimate that cloud top jumps of potential temperature and total water must be constrained to within 0.1 to 1 K and 0.1 to 1 g/kg, respectively, for accurate observation of aerosol radiative impacts on stratocumulus, depending on time of day. These constraints suggest that accurately observing aerosol radiative impacts in stratocumulus may be challenging as co-variation of meteorological properties may obfuscate aerosol-cloud interactions.

8CC.18

The Impact of Future Meteorology on Air Quality in the Eastern United States. MELISSA DAY, Benjamin Murphy, Spyros Pandis, *Carnegie Mellon University*, *University of Patras*

Future changes in climate will affect regional air quality, but the behavior of some species is uncertain. To examine the effect of climate change on ozone and fine (under 2.5 micrometers) particulate matter (PM), we use the Global-REgional Climate-Air Pollution modeling System (GRE-CAPS). GRE-CAPS couples the Goddard Institute for Space Studies (GISS) II prime general circulation / chemical transport model (GCM/CTM), the MM5 regional meteorological model, and PMCAMx-2008, a regional chemical transport model. The Model of Emissions of Gases and Aerosols from Nature (MEGAN, v2.04) was added to provide meteorology-dependent biogenic emissions. Meteorology from ten representative years in the 1990s (present-day) and ten from the 2050s (future) is used. Future meteorology is based on the Intergovernmental Panel on Climate Change (IPCC) A2 scenario, detailing a heterogeneous world without a focus on sustainability. The future model predictions of ozone levels and fine PM constituents for the Eastern US are compared to present-day distributions, averages and extremes. Previous work by Dawson et al. (2009) covered similar ground, but lacked dynamic biogenic emissions, treated the primary organic aerosol as non-volatile and non-reactive, and simulated only the first generation of secondary organic aerosol production. In PMCAMx-2008, organic aerosol (OA) is simulated using the volatility basis set approach, in which primary emissions are semi-volatile and gas phase organic compounds are oxidized and result in products with lower volatility. For this reason, special focus is given to OA changes, particularly because there is less certainty about the OA response to climate than that of other fine PM components.

References

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8CC.19

The Effect of Ozone Stress on the Output of Volatile Organic Compounds and the Resulting Aerosol Properties Produced by Eastern White Pine. Yin Wang, Dabrina Dutcher, TIMOTHY RAYMOND, *Bucknell University*

Small Eastern White Pine trees were placed inside a Teflon smog chamber and exposed to varying concentrations of ozone. One small branch of each tree was further enclosed in another Teflon bag with a solid-phase microextraction (SPME) needle used to collect the emitted volatile organic compounds (VOCs). A scanning mobility particle sizer (SMPS) was used in the main chamber to analyze the particle distribution produced from the oxidized VOCs. A cloud condensation nuclei counter (CCNC) was also used in the main chamber to study the activation diameter of the resulting aerosol using scanning mobility CCN analysis (SMCA). A gas chromatography mass spectrometer (GCMS) was used to analyze the SPME in order to identify the VOCs produced and to roughly quantify the species. Results indicate that when exposed to ozone stress, the pine trees emitted higher concentrations of most monoterpenes but lower concentrations of sesquiterpenes. The resulting particle distributions and their CCN behavior were also affected. While these results were for only one tree species and more research on additional species is necessary, implications for future climate and particulate pollution scenarios are obvious.

8EN.1

Novel 3D Numerical Simulations to Calculate the Capacitance of Nanoparticle Aggregates with Necking Effect and Loose Agglomerates. LEO N.Y. CAO, Jing Wang, Heinz Fissan, Max L. Eggersdorfer, David Y. H. Pui, *University of Minnesota*

The electrical capacitance of aerosol particles is an important property for particle research as electric charging is frequently used to characterize the particles, e.g.measurement of agglomerates by their charging properties (Wang et al. 2010, Shin et al. 2010). Few 3D numerical simulations for the capacitance of loose agglomerates with large amounts of primary particles have been done; studies calculating the capacitance of compact aggregates with necking effect are even more scarce. In this work, we model the capacitance of loose agglomerates and obtain the charge distribution on the agglomerates by using a minimum energy method (Brown & Hemingway, 1995) in three dimensions. Diffusion limited cluster-cluster agglomerates are generated with a fractal dimension around 1.8. The change in the capacitance of such compact aggregates with necking effect in a sintering process is also modeled in this study. The complete arbitrary shaped aggregate is divided into finite elements using a mesh and every element is treated as a primary particle. The approximation provides satisfactory results when the mesh number is sufficiently high. There is only a 2 percentage overestimation for a big sintered sphere compared to the theoretical results.

KEYWORDS: Necking Effect; Capacitance; Charge Distribution; Sintering; Agglomerate

8EN.2

Cerium Oxide Nanoparticle Nose-Only Inhalation Exposures Using a Low-Sample-Consumption String Generator. Allen Ledbetter, Kevin Dreher, MARK HIGUCHI, *EPHD, NHEERL, U.S. EPA*

The health effects associated with exposure to commercial nanoparticle (NP) production, which are more morphologically and size heterogeneous, is required for risk assessment. Generation of stable and low concentrations of nanoscale aerosols in nose-only chambers can be difficult, and when agglomerates form during generation, the problems are substantial. One problem is that many nanoscale aerosol generators have higher aerosol output than can be accommodated by a nose-only inhalation chamber, requiring much of the generated aerosol to be diverted to exhaust. Another problem is that mixing vessels used to modulate the fluctuating output from aerosol generators can cause substantial wall losses, consuming much of the generated aerosol.

To overcome these problems, a low-consumption nanoscale aerosol generator was developed to deliver stable concentrations in the range of 10–5000 micrograms/m^3 to a nose-only exposure chamber using all of the generator output. The generator airflow of 10–15 L/min supplies all the needed air for the exposure chamber, and a 6-hour exposure at 10–1500 micrograms/m^3 consumes as little as 200–300 mg of material. The cerium oxide (CeO_2) aerosol delivered to the nose-only inhalation exposure chamber had a median number size distribution of 53.2 nm and with geometric standard deviation of 1.88. This aerosol reflects the aggregate sizes of CeO_2 NPs with primary diameter (5-7 nm) commonly found in diesel exhaust generated with CeO_2 NP additive. The generator uses the principle of a continuous feed-string to pick up particles from a small reservoir, carry them through an orifice and into a small chamber where an air jet blows the particles off the string. In short, this novel string generator is not only low consumption, but more importantly, allows for the generation and modification to nanoscale aerosols of commercially produced NPs.

This abstract does not necessarily reflect U.S. EPA policy.

8EN.4

The Application of the Universal Nanoparticle Analyzer for the Real-time Measurement of Engineered Nanoparticles in the Workplace. DREW THOMPSON, Jing Wang, David Y. H. Pui, *University of Minnesota*

Engineered nanoparticle-enabled nanotechnology is experiencing unprecedented growth. With this comes greater opportunity for workers to be exposed to nanomaterials which some toxicological studies have shown to be hazardous. There is a clear need for the monitoring of this potential worker exposure. The purpose of the presented research is to extend the capabilities of the recently developed Universal Nanoparticle Analyzer (UNPA) for use in occupational nanoparticle exposure measurements. The UNPA consists of a differential mobility analyzer (DMA), a condensation particle counter (CPC), and a Nanoparticle Surface Area Monitor (NSAM). In the UNPA, monodisperse nanoparticles are simultaneously measured by a CPC and NSAM, which measure particle number concentration and lung-deposited surface area concentration, respectively. The ratio of these two measures, coined the UNPA sensitivity, can be used to characterize the morphology of nanoparticles. The instrument has already been demonstrated to be well-suited for process control in nanomaterial manufacturing. In this poster the potential use of the UNPA in nanoparticle exposure measurements will be investigated. There are three goals of this research. One, operate the UNPA in a scanning mode, by varying the voltage in the DMA, to allow for the simultaneous measurement of size distributions, lung-deposited surface area distributions, and UNPA sensitivity distributions. Two, evaluate the UNPA response to nanoparticles which are heterogeneous in shape. Three, relate UNPA sensitivity to parameters frequently used in toxicology studies: mass concentration and BET surface area.

8EN.5

Formation of Nanoparticles as an Undesired Byproduct of an Industrial Accident. SHERYL EHRMAN, Yoon Shin, *University of Maryland*

Although industrial scale processes often form nanoparticles as the desired product, nanoparticles may also form as a result of an industrial accident. In this work, an accident at a polysilicon processing plant, specifically the rupture of a pipeline containing silicon tetrachloride, was simulated. Silicon tetrachloride reacts with water vapor to form silicic acid and hydrochloric acid fume, which react further to an aerosol consisting of a mixture of silica and hydrochloric acid. Plume parameters were estimated using a standard Briggs plume rise formulation. The National Oceanic and Atmospheric Administration’s HYSPLIT model was used to simulate the dispersion of the plume downwind of the accident site. The HYSPLIT model used actual atmospheric data from its meteorological archive. Simulations were conducted on a hypothetical accident occurring in Curtis Bay, MD, an arbitrary location that does not contain a polysilicon plant, over four dates in November and December of 2012. Results indicate that within 12 hours of the release, the accident could result in aerosol concentrations greater than 10 micrograms per cubic meter, as far away as 100 km downwind of the plant site.

8IM.1
Performance Testing of MSP Model 1120 Water-based Condensation Particle Counter. LIN LI, Francisco Romay, William Dick, *MSP Corporation*

A condensation particle counter (MSP Model 1120) that uses water as the working fluid has been recently introduced. One critical aspect of its performance is the effect of the particle composition on the induced growth before counting. For a water-based particle counter, there is a difference between hydrophobic and hydrophilic particles. The temperature of the saturator, which provides a water-vapor-saturated stream, also affects the minimum particle size that can be activated.

In this study, the performance of the Model 1120 water-based condensation particle counter (WCPC) was characterized for several aerosol compositions, including silver, sodium chloride, sucrose and silica particles generated by evaporation-condensation or by electrospray techniques. All particles were size-classified using a short differential mobility analyzer (DMA) to select monodisperse test aerosols. The challenge aerosol was mixed uniformly with clean makeup air and split between the WCPC and an aerosol electrometer, which was used as the reference instrument to determine the counting efficiency. The D50 (i.e., the particle diameter with 50% counting efficiency) of the WCPC was somewhat dependent on aerosol composition (mainly hygroscopicity). The saturator temperature of the WCPC was also varied in the tests. As expected, D50 values decreased with increasing saturator temperatures.

8IM.2
New Measurement System for PM and Ultrafine Particles. JUERGEN SPIELVOGEL, Maximilian Weiss, *Palas GmbH*

According to a recently published report by the European Environment Agency about one third of Europe’s population in cities is exposed to excessive concentrations of particulate matter (PM). These people are also exposed to high concentrations of ultrafine particles caused for example by traffic and heating.

We will present a new measurement system that can measure the number concentration and size distribution of airborne particles from 8 nanometer to 18 micrometer. In addition, it also reports simultaneously different PM-fractions such as PM-1, PM-2.5 and PM-10. With a time resolution of 5 minutes it can further capture dynamic changes in the aerosol distribution caused for example by rush hour traffic in the morning and afternoon.

The measurement system combines a scanning mobility particle sizer in which the working fluid to condense the particles can be chosen to be water or butanol with a continuous ambient air quality monitoring system. In the latter a polychromatic light source is used to illuminate aerosol particles as they pass through the optical sensing volume. The scattered light of each individual particle is then detected with a photomultiplier.

The system is operated through a touchscreen with intuitive graphical user interface and integrated data logger. Data can be easily viewed on the screen or later extensively evaluated through the included software.

We will show and discuss selected measurements in which the additional information of particle size distribution helps to interpret the PM-data and also facilitates source apportionment.

8IM.3

The Iron Lung: A Device for the Continuous Delivery of Fine Particulate Matter. IAN ARNOLD, Cory Berger, Hans Moosmuller, Noopur Sharma, Claudio Mazzoleni, *Desert Research Institute*

Bag sampling techniques have been employed in aerosol research for many years for temporary aerosol storage. They have been used to age samples and to sample from changing sources, integrating over fluctuations in aerosol properties and concentrations. Here, we describe an “Iron Lung” aerosol sampler for the continuous delivery of fine particulate matter that has been built by our groups. Its performance for the storage and sampling of fine particulate matter has been evaluated using soot from a kerosene lamp.

8IM.4

Beam Characteristics of Fiber-Based Supercontinuum Light Sources with Mirror- and Lens-Based Beam Collimators. IAN ARNOLD, Hans Moosmuller, Noopur Sharma, Claudio Mazzoleni, *Desert Research Institute*

Multispectral aerosol absorption and scattering measurements with photoacoustic spectrometers and nephelometers are typically performed by multiple instruments or by combining the output from multiple light sources. Currently, our groups are developing a photoacoustic aerosol light absorption and albedo spectrometer (PALAAS) using a supercontinuum light source with continuous wavelength-coverage from 400nm to 2500nm. This system critically depends on the beam characteristics of its supercontinuum light source. Here, we discuss the characterization and evaluation of beam properties of supercontinuum light sources utilizing mirror- and lens-based collimators.

8IM.5

Application of an Eight-Channel Optical Particle Counter to Continuous, Long-term PM2.5 Monitoring. ODELLE HADLEY, Mark Moore, *Olympic Region Clean Air Agency*

When air-operating permits were issued for two biomass cogeneration plants, one in Port Angeles and the other in Port Townsend, citizens in the region expressed concern and attempted to halt progress on these permits through appeals and community protests. Chief among their concerns was that current ambient air quality monitors were inappropriately sited to properly assess regional air quality and the potential emissions increase from these facilities. In response, the Olympic Region Clean Air Agency (ORCAA) implemented a study measuring the neighborhood scale variability of ambient PM2.5 concentration throughout the Olympic Peninsula. The data will be used to determine the most representative location for long-term ambient air quality monitors in each county. ORCAA currently uses Radiance Research M903 nephelometers to obtain real-time air quality data throughout the region. The study incorporates four, MetOne 212-2 optical particle counters (OPC) into ORCAA's existing air monitoring network. The OPCs produce size resolved, atmospheric particle number concentrations ranging from 0.3 to 10 microns. The OPC data are evaluated against the Radiance Research M903 and the EcoTech Aurora 1000 nephelometer, as well as a tapered-element oscillating microbalance (TEOM), configured to meet the PM2.5 federal equivalence method (FEM) criteria. Results from these side-by-side comparisons, as well as preliminary field measurements, are presented. The OPC, hourly-averaged particle number concentrations correlate well (R2 > 0.9) with both nephelometers and the TEOM, however the strength of the correlation and the linear relationship depend on the aerosol sizes selected and the location and season in which the measurements are made.

8IM.6

Airborne Measurement of Vertical and Horizontal Aerosol Distribution within Air Boundary Layer. JAN HOVORKA, Veronika Docekalova, Jan Bendl, Filip Kobrzek, Petr Marecek, *Charles University in Prague*

Aerosol vertical/horizontal distribution within the air boundary layer, though it is an important parameter for receptor or dispersal aerosol source models, is rather than directly determined calculated from earthbound measurements. To conduct airborne aerosol measurements, we constructed gondola attached to the airship. The airship, about 9m long and 2.5m height, was able to carry experimental cargo about 7 kg. There were three instruments for aerosol parameter determination accommodated in the gondola and connected to the inlets preheated to 50 Celsius degrees. Parameters determined were PM10, PM2.5 and PM1 and aerosol particle number concentrations of fine and ultrafine particles. Both the airship position and the aerosol data were acquired with frequency of 1Hz. Since the airship velocity ranges from 3 to 8 metres per second, highly spatial-temporal data for the aerosol mass/number were retrieved. Measurements were conducted above a large coal strip mine and in an urban air in winter 2012/2013. This work was partially supported by the project CENATOX under grant GAČR P503/12/G147.

8IM.7

Performance Evaluation of Miniature Cyclones with Multiple Inlets.

DI LIU, Da-Ren Chen, *Virginia Commonwealth University*

The adverse heath effect of ultrafine particles reported in recent epidemiological studies leads to the high demand of compact particle detectors for spatial or personal monitoring of ultrafine particles. However, large particles in the sampling stream have to be removed in order to keep the proper performance of these detectors. Size-selective inlets are thus needed for compact detectors. Cyclones and impactors are examples of such size selective inlets. To reduce the particle cutoff sizes of cyclones, ones often operate them either at a high flow rate or use the feature of multiple inlets. Operating at a high flow rate often results in the increase of the pressure drop across a cyclone, which is undesirable for compact detectors with limited air pumping power. Meanwhile, multi-inlet cyclones may have the potential to minimize the sampling issues often encountered in a single inlet cyclone, because of variation of ambient wind orientation.

In this study, we design a set of miniature tangential cyclones with different numbers of inlet (i.e., single-, dual- and quarto-inlets). The performance of these cyclones was evaluated at different operational flow rates. The pressure drop and cutoff sizes of these cyclones were measured. The result of this study will be presented in the conference.

8IM.8

Modeling and Experimental Characterization of a Large Particle Inlet (LPI).

GUAN ZHAO, Thomas Holsen, Suresh Dhaniyala, *Clarkson University*

A design of high flowrate large particle inlet (LPI) was introduced by Lee et al., (2008) for sampling of particles as large as 100 μm under a range of ambient wind conditions. Initial field measurements with the inlet suggested that the inlet was indeed able to sample large particles effectively in the ambient. The sampling performance of the first version of the LPI obtained from computational fluid dynamics (CFD) simulations, however, did not entirely match wind-tunnel experimental results. Reanalysis of the CFD simulation results suggested that the distribution of particles at the exit of the LPI was non-uniform and this was not initially considered in the analysis. To improve the spatial uniformity of the particles exiting the LPI, several design modifications were considered and the modified geometries were simulated for a range of flow conditions. Improved computational resources made it possible to run higher order turbulent models (Reynolds Stress Model) with high mesh density near wall (y+~1) so that particle depositions could be predicted more accurately. The sampling efficiencies calculated with the new models match reasonably well with experimental data. Details of the redesigned LPI, the numerical modeling approach, and the wind-tunnel experiments will be presented.

8IM.9

Aerosol Dry Powder Dissemination Device Characterization for Small-Scale Use. ANDRES SANCHEZ, Crystal Glen, *Sandia National Laboratories*

With an increased need to understand the current technological capabilities to disseminate dry powder aerosols, five commercially available dissemination devices were evaluated for usability, reliability, and stability. The five devices evaluated were the Palas Rotation Brush Generator (RBG), the TSI Inc. Fluidized Bed Aerosol Generator (FBAG), the BGI Incorporated Wright Dust Feeder II (WDF), the CH Technologies Vilnius Aerosol Generator (Vilnius), and, finally, the Topas ultralow flow Solid Aerosol Generator (SAG). Dry powder aerosols, from each device, were disseminated into a constant flow, turbulent aerosol chamber under various instrument parameters, including pressure, feed rate, and rotational speed, for example. Size distributions from the aerosol chamber were measured using a TSI, Inc. Aerodynamic Particle Sizer (APS) for each device and instrumental parameter used. Results from each test were then evaluated according to user operation (operator safety, ease of setup, operation, and cleanup), reliability in size distribution, and concentration stability. Both the Wright Dust Feeder II and Vilnius performed above average in all four categories of user operation, primarily due to their ease of use and cleanup. Three of the five dissemination devices (RBG, FBAG, and Vilnius) performed slightly above average under size distribution reliability, with a better than average performance by the Wright Dust Feeder II. Concentration stability was clearly seen for the Vilnius, RBG, and FBAG. After evaluating each device, only the Vilnius Aerosol Generator performed above average in all categories.

8IM.10

Preventing the Spray Break-up in Electrohydrodynamic Atomization. CHRISTIAN LUEBBERT, Jan Marijnissen, Wolfgang Peukert, *FAU Erlangen-Nuremberg, Germany*

Electrohydrodynamic atomization is a process, where a liquid is disintegrated into small droplets under the influence of electrical stress. The mostly used cone-jet-mode is well understood and known to produce almost mono-dispersed particles as an outstanding property [1]. With this type of electrospray, the droplets emitted from liquid jets are strongly affected by the space charge. Therefore, the initially well aligned particle beam, emitted from the liquid jet under axial break-up conditions, spreads up into the typical spray-cone. This seemingly inevitable behavior prevents in practice the patterned deposition of the electrosprayed particles. Recent strategies in direct pattern formation from electrosprays have shown to be limited in mono-dispersity, precision of the deposition and might as well suffer from the plugging risk due to the small capillaries used (e.g.[2]).

We propose a robust and easy to clean setup, in which the spraying process is carried out under modified conditions. The resulting spraying mode produces highly mono-disperse microdroplets at a constant emission frequency under conditions of a constant volumetric flow rate and dc voltage. The break-up of the spray-cone can be prevented resulting in perfectly aligned particle chains for comparably long distances in the cm-range. Hence, an operation mode for well-defined pattern deposition was found.

The influence of the applied voltage and the volumetric flow-rate on the emission frequency will be discussed in detail. Requirements on the liquid and limitations on the obtainable particle size will be shown for various liquids. Experimental results are discussed in comparison to theoretical predictions based on analytical estimations for the interactions between the spray and the external electric field.

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8IM.11

Performance Study of the "Impaclone", a Miniature, Switchable Size-selective Inlet for a Compact Particle Sizer. SIQIN HE, Da-Ren Chen, Paul Greenberg, *Washington University in St. Louis*

As response to the increasing concern of the health effect due to the exposure of submicrometer particles, lots of low-cost particle sizers enabling to measure the spatial distribution of particles are recently developed, with various designs based on the particle electrical mobility technique. However, the presence of large particles in the sampling stream often interferes the performance of these sizers. One of size-selective inlets to remove large particles is the mini-cyclones developed by Hsiao et al. (2009). Most of the conventional cyclone/impactor designs have fixed cutoff particle sizes, limiting the flexibility of sizers in use. To make the cutoff particle size switchable or variable, a new compact size-selective inlet, by integrating a cyclone and an impactor, was designed and tested in this study.

The efforts have been mainly devoted to the combination of a cyclone chamber and an impaction chamber. The prototype has a switchable cutoff size from 0.5 to 1 μm by splitting the flow operation for the cyclone and impactor. With the new design, the prototype improves the sharpness of the particle cutoff curves and the dust holding capacity. The experimental result of this study will be presented in the conference.

8IM.12

Data Merging of Size Distributions from Electrical Mobility and Optical Measurements. AXEL ZERRATH, Sherrie Elzey, Hee-Siew Han, *TSI Incorporated*

The measurement of size and concentration of aerosol to quantify potential exposure to nanomaterials has received increasing attention during the last years. The size range of interest covers usually a few nanometers to 10 µm (PM10).

A reference technology to determine size and concentration of particles in the nanometer range is electrical mobility. Recently TSI introduced the NanoScan SMPS, a small, portable and easy to handle version of the TSI Scanning Mobility Particle Sizer (SMPS) (Elzey 2012), enabling easier access to occupational environments.

The size range of SMPS systems can be extended to coarse particles with light-scattering based instruments such as the Optical Particle Sizer (OPS).

Particle diameters determined from instrumentations are equivalent diameters, such as the electrical mobility diameter measured by the SMPS or optical diameter measured by the OPS.

We present here a novel data merging tool for optical diameter and electrical mobility diameter: Multi Instrument Manager (MIM). This software module compiles a single data set describing the particle size distribution from 10 nm to 10 µm. The MIM is easy to use and it allows reviewing and averaging data from SMPS, NanoScan SMPS and/or OPS. More importantly, when merging the OPS and SMPS/NanoScan distributions, the MIM can take the aerosol optical properties into account by automatically determining the aerosol effective refractive index.

The software allows several pre-settings, data averaging and adjustments. The curve fitting algorithm uses up to 3 modes of lognormal distribution function to curve fit the data. The presentation will show different merged data sets and merged options to demonstrate their impact on the composite fit accuracy.

Elzey, S., Caldow, R., Johnson, J.P., Grose, M., Morell, S. and Jensen, D. (2012), EAC 2012 proceedings, WG08S2O06

8IM.13

Filter Leak Detection by Various Gases Using the Schlieren Imaging Technique. SHIGERU KIMOTO, Lin Li, David Y. H. Pui,*University of Minnesota*

There are several detection methods for filter leaks (e.g., scanning, fluorescence, particle image velocimetry, thermal imaging, etc). For aerosol related methods, particles passing through the filter leak can be detected by a scanning probe connected to a particle counter to locate the leakage, or by Particle Image Velocimetry (PIV), obtaining the flow speed and direction using the scattered light from particles. In the fluorescence detection, a UV light source is used to examine the filter bags for leaks. Wherever there is a leak, the tracer powder will glow brightly under the detector lamp. However, the aerosol methods are usually time consuming and particles are loaded on the filter, which is avoided in some applications and test environment. The imaging methods, (e.g. thermal imaging using infrared radiation to form an image, and Schlieren imaging technique), have the advantage of visibility, quick response, simplicity and prevention of particle loading.

In this study, we use a Schlieren imaging technique for filter leak detection. Schlieren technique uses light from a single collimated source shining on or from behind a target object (the space downstream of the filter). Variations in refractive index caused by density gradients in the fluid distort the collimated light beam, creating a spatial variation of light intensity, which can be visualized directly. Gas composition affects the Schlieren image because density gradient is changed. The effect of purge gas composition is evaluated and the detail results will be presented.

8IM.14

A Scanning Mobility Particle Sizer for Nanoparticle Size Distribution Measurements in the Upper Troposphere/Lower Stratosphere. JOHN ORTEGA, James N. Smith, David C. Rogers, Suresh Dhaniyala, Steve Gabbard, *National Center for Atmospheric Research*

A Scanning Mobility Particle Sizer (SMPS) was recently developed for use in airborne measurements on board the two aircraft operated by the National Center for Atmospheric Research: the C-130 and the Gulfstream V (GV). The latter aircraft can fly at altitudes above 45,000 ft. (~13,700 m), in the upper troposphere/lower stratosphere, requiring precise control of gas flows at pressures ranging from ~15 kPa to atmospheric pressure. One of the limitations of using a commercial Differential Mobility Analyzer (DMA) at low pressures is electrical discharge that occurs at the highest applied voltages. To address this, we have modified a TSI 3085 nano-DMA to eliminate electrical discharges at up to 10 kV at reduced pressures. The SMPS is configured to obtain a complete size distribution, from ~ 7nm to 390 nm, over a scan time of one minute. The instrument was successfully deployed on the GV during the Deep Convection Clouds and Chemistry (DC3) Experiment in the summer of 2012, and will participate in NOMADSS (Nitrogen, Oxidants, Mercury and Aerosol Distrubutions, Sources and Sinks) on board the C130 in 2013. This presentation will focus on instrument development, performance, and several scientific results (including size distributions, new particle formation, in-cloud sampling artifacts, and particle growth) from these campaigns.

8IM.15

Extending the Size Range for Calibrating the Counting Efficiency of the Light Scattering Airborne Particle Counters toward Larger Particle Sizes. Kenji Beppu, Shinjiro Takeyama, Toshio Kubota, KENJIRO IIDA, Hiromu Sakurai, Kensei Ehara,*JQA*

JQA has been providing the service for calibrating the particle-counting efficiency and size classification threshold of the light-scattering airborne particle counters (LPCs). The calibrated counting efficiencies are traceable to Japan's national primary measurement standard for the aerosol particle number concentration. The current upper size limit of the service is 0.2 µm which corresponds to the upper size limit of the national primary standard. However, there are a number of LPCs whose detectable size range is beyond 0.3 µm; therefore, there is a need for extending the calibration size range toward larger sizes. In this study, the counting efficiency of LPCs and their uncertainties were evaluated. The polystyrene latex spheres (PSL) at 0.2, 0.3, 0.5, and 0.8 um were used as the challenge aerosol. The mobility-classified PSL particles were dispersed in a 2 L cylindrical metal chamber which has twelve sampling ports at its bottom end. Two types of LPCs (RION KC-22A and KC-22B) were calibrated simultaneously using a condensation particle counter as a reference instrument. The sampling flowrates of KC-22A and 22B are 2.83 L/min and 0.3 L/min, respectively. The matrix of the measured counting efficiencies has five dimensions: two LPCs, four particle diameters, six combinations of sampling ports, five repeated measurements within a day, and four days of identical experiments. The matrix was used as the input of the analysis of variance (ANOVA). The size dependence of the counting efficiency between two LPCs were not statistically significant indicating that the size-dependent particle motions in our calibration system do not cause any bias in the calibration results over the size and sampling flowrate range investigated. On the other hand, the variation among different days was statistically significant suggesting such effect needs to be accounted in the uncertainty budget of the calibrated counting efficiency.

8IM.18

Development of a Non-Specific Monodisperse Aerosol Generation System. JONATHAN ESHBAUGH, Shanna Ratnesar-Shumate, Paul Dabisch, Francisco Romay, *The Johns Hopkins University Applied Physics Laboratory*

Size specific monodisperse aerosols have been used to investigate respiratory and non-respiratory deposition and thus absorption of inhaled biological aerosols. Generally, the aerosol of interest is produced with a monodisperse aerosol generator, which uses either a spinning disk or an oscillating orifice to atomize a liquid. Biological aerosols, or aerosols which contain spores, viruses, or proteins are typically aerosolized from a liquid suspension within the confines of a biological safety cabinet. Monodisperse generators that utilize an orifice typically aren't compatible with liquid suspensions while other monodisperse generators aren't compatible with the vibration and reduced access of a biological safety cabinet. Additionally, the interaction of viability, infectivity, or activity of the biological particle, atomization stress, and particle size is difficult to study since the atomization required to generate the monodisperse aerosol is fixed. Thus an inertial sorting monodisperse generation method compatible with varying biological suspensions, the confines of a biological safety cabinet, and any atomization technique that can generate particles within the size range of interest was designed. The current design couples an ultrasonic atomizer to a series of clean air core virtual impactors designed by MSP. Airflow for the entire system is controlled and monitored with valves, laminar flow elements, and differential pressure gauges. The system was designed to generate a monodisperse or near-monodisperse aerosol at four discrete particle sizes (2, 4, 7 and 12 micro-meter) from a biological suspension. The system design as well as initial experimental results will be presented.

8IM.19

Calibrating Black Carbon Mass Measurement Instruments Using the CPMA-electrometer System. MATTHEW DICKAU, Tyler Johnson, Kevin Thomson, Gregory Smallwood, Jason S. Olfert, *University of Alberta*

Previously, it has been shown that a centrifugal particle mass analyzer (CPMA, Cambustion) can be used in conjunction with an aerosol electrometer to measure the mass concentration of a charged aerosol in real time (Symonds et al 2013). The CPMA selects the aerosol by mass-to-charge ratio and the electrometer measures the charge concentration. This system can be used to rapidly calibrate less traceable mass measurement instruments.

Soot from an inverted burner, with a median mobility diameter of 270 nm, was passed through a denuder to eliminate organic carbon (verified by EC/OC analysis), and then through a unipolar diffusion aerosol charger (UDAC, Cambustion) before passing through the CPMA. Downstream of the CPMA, the flow was split between the electrometer and the challenge instrument. The mass concentration was varied from around 5 $\mu g/m^3$ to 150 $\mu g/m^3$ by manipulating the CPMA setpoint. This experiment compared the results of the CPMA-electrometer system with those of two laser-induced incandescence instruments (LII 300, Artium Technologies) and two Micro-Soot Sensor photoacoustic instruments (MSS, AVL). The challenge instruments had been previously calibrated to the NIOSH 5040 standard, which has a stated uncertainty of 16% at concentrations of 23 $\mu g/m^3$.

The correlations between the CPMA-electrometer system and the challenge instrument were highly linear for both the LII and the MSS, and agreed well with the previous calibration. The LII models both had a slope of 0.956, and had R^2 values of 0.999 and 0.996. The MSS models had slopes of 1.05 and 1.09, both with R^2 values of 0.999. The uncertainty in the CPMA-electrometer system averaged 7% and was as low as 3% for some measurements. The lower uncertainty and speed of measurement support the use of the CPMA-electrometer system as a mass measurement calibration method for nanoparticulate black carbon.

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Symonds, J., Reavell, K., & Olfert, J. (2013). The CPMA-Electrometer System - A Suspended Particle Mass Concentration Standard. Aerosol Science and Technology, Vol. 47, Iss. 8.

8IM.20

Development of Optical Particle Sensor for Estimating Mass Concentration in Real Time. JINHONG AHN, Kitai Kang, Yongtaek Kwon, *HCT Co., Ltd.*

The recently public and scientific study is going on health effects related to particulate matter (PM). Thus ambient air quality standards are being discussed worldwide A new optical particle sensor(PM-101P, HCT Co., Ltd.) has been developed that measures aerosol mass concentration(TSP, PM10, PM2.5, PM1.0) in real time. It is instrument that measures the particle size and mass concentration range of 0.3 micro-meter to 25 micro-meter and 0.01 to 20 mg per cubic meter. This instrument measures simultaneous optical sizing of single particles count and PM data. The optical particle sizing is dividing with 15 channels. The electrical pulse heights generated by light scattering from particles larger than 0.3 micron are calibrated to the diameter of PSL particles. And the PM data is based on optical particle sizing and counts. To test the performance of the PM-101P, we carried out a series of experiments to compare PM-101P with a TEOM (Series 1400a, Thermo Scientific), beta-ray (EBAM, MetOne) and APS (TSI Model 3321) for ambient aerosols. The PM mass concentration correlations between the TEOM, APS and PM-101P shows are good agreements approximately within 10%. Also we measured the particle mass concentration using the PM-101P and APS. The agreement between these two instruments is also good for these two mass fractions.

8IM.21

Determination of Complex Refractive Index For Submicron Absorbing Spheres. JEONGHOON LEE, *Korea University of Technology and Education*

Real part and imaginary part of refractive index for absorbing spheres were determined using a multiangle absorption photometer together with Mie theory. For the absorbing spheres generated using a constant output atomizer, absorption coefficient was measured with a multiangle absorption photometer and number concentration was measured with a condensation particle counter. The absorption cross sections estimated from the absorption coefficients and particle number concentrations were fitted to the absorption cross sections calculated from the Mie theory. For the nigrosin, the refractive index obtained by the best fit corresponded to the 1.70 + 0.24i, which was obtained by minimizing the chi-square of the data. The refractive index measured by our method holds valid as long as the absorption phenomenon takes place in the near field surrounding particles surface. This method was applied to the measurement of the optical properties for non-homogeneously dyed absorbing particles. It was observed that the larger particle was less black than the smaller one. In this case, the absorption cross section was independent on the particle size. Furthermore, the refractive index for the non-homogeneous absorbing particles was investigated from the refractive index point of view.

8IM.22

Visualization of Restructuring of Oil Droplets Collected in Filter Media. HIROAKI MATSUHASHI, Shoji Hirota, Hidenori Higashi, Mikio Kumita, Takafumi Seto, Yoshio Otani, *Kanazawa University*

Air filters are commonly used for the removal of oil droplets generated by various machining processes. However the restructuring of droplets accumulated in a filter as a result of their coalescence and re-entrainment is so complicated that the prediction of time dependency of filter performance remains as a difficult task because many factors such as droplet size, surface tension and viscosity of liquid composing the droplets, as well as filtration velocity and filter structure influence the phenomenon. In the present work, the time evolution of restructuring of droplets collected in a filter was observed under an optical microscope by applying newly devised observation cell while monitoring the changes in collection efficiency and pressure drop of filter. The final goal of this work is to find the effect of filter’s factors, such as fiber diameter and packing density, and aerosol’s factors, such as filtration velocity, oil viscosity and surface tension, on the filter collection efficiency and pressure drop.

8IM.23

A Laboratory Inter-comparison of CPC and SMPS Measurements of Submicron Aerosols. Shouwen Zhang, ARI SETYAN, Véronique Riffault, *Ecole des Mines de Douai*

Three scanning mobility particle sizers (SMPS) and three condensation particle counters (CPC) (all commercial instruments) have been compared within the framework of this study. For the comparison in terms of particle number concentrations, one of the CPCs was used as a reference and connected to the sampling line in parallel with each of the other instruments. Measurements were carried out on monodisperse ammonium nitrate particles, which were generated by atomization of a 10^{-2} M solution, dried using silicagel, and passed through a differential mobility analyzer (DMA) to select one size (from 50 to 300 nm in mobility diameter, Dm). The particle number concentration varied in the range 50-60000 #/cm3. For the comparison in terms of particle size distributions, measurements were performed with polystyrene latex (PSL) spheres of different sizes (from 350 to 900 nm in Dm), and one of the SMPS was connected to the sampling line in parallel with each of the two other SMPS. Diffusion loss correction was applied for all SMPS data.

All the instruments were very well correlated in terms of particle number concentrations, with a correlation coefficient r2 > 0.99. However, the scatterplots vs. the reference CPC had slopes far from 1 in some cases, and varied between 0.5 and 3.0, which means that there was a factor of 6 between the smallest and highest measured concentrations. Moreover, for one of the SMPS, the slope vs. the reference CPC increased from 1.9 to 3.0 for particles varying from 50 to 300 nm. In terms of size distributions, the agreement between the different SMPS was satisfactory.

These discrepancies in particle counting between different instruments may be a serious problem in field campaigns or lab experiments, since people often bring just one SMPS or one CPC to calibrate instruments, and to measure particle concentrations and size distributions.

8IM.24

Application of Surface-Discharge Microplasma Device to Ion Mobility Spectrometer. YOSHIKAZU MIZUTORI, Tetsuya Maekawa, Hidenori Higashi, Mikio Kumita, Takafumi Seto, Yoshio Otani, *Kanazawa University*

In the present work, Surface-discharge Microplasma Device (SMD) was applied to ion mobility measurement under atmospheric conditions. We designed a simple ion-mobility spectrometer (IMS) with the SMD. The SMD ion mobility spectrometer ionizes gaseous species in carrier gas with pulsed surface discharge and ionized gaseous species migrate toward to the collecting electrode where the ion current is recorded as a function of flight time. Since the SMD employs surface discharge and is capable of generating uniform and high-concentration unipolar ions over a wide area in the vicinity of discharge electrode, the detection limit of ion current can be lowered by increasing the length of discharge electrode. By analyzing the time dependency of ion current we may identify ion species and ion concentration.

8IM.25

System for the Absolute Calibration of Black Carbon Mass Concentration Measurement Instruments. KEVIN THOMSON, Fengshan Liu, Gregory Smallwood, *National Research Council Canada*

Previously, it has been shown that real time mass concentration measurement instruments such as those based on photo-acoustic methods or laser-induced incandescence show very good linearity with black carbon (BC) concentration. However, these instruments either intrinsically require absolute calibration or benefit in terms of improved measurement accuracy when calibrated against an absolute reference for Black Carbon.

A system for the absolute calibration of black carbon mass concentration measurement instruments has been developed which uses the elemental carbon component of a thermal/optical filter analysis as the basis of calibration. The source of black carbon is an inverted flame burner which produces steady and repeatable exhaust concentration of about 70 mg/m³ with a low organic carbon concentration. A sample is extracted from the exhaust and diluted using a series of dilutors to achieve concentrations in the range of 50 µg/m³ to 1000 µg/m³. A multi-port splitter splits the flow over multiple mass concentration instruments to be calibrated as well as to a filter for the acquisition of sample for thermal/optical analysis.

The calibration system has been applied for the calibration of 7 mass concentration measurement instruments which were used in an SAE-E31 civil aviation aircraft engine non-volatile particulate matter (nvPM) measurement campaign conducted in Switzerland in summer 2013. The SAE E-31 Aircraft Exhaust Emissions Measurement Committee has been tasked with designing and documenting a sampling system and instrumentation for measuring aircraft engine nvPM mass and number emissions, in anticipation of new certification requirements aimed at limiting the emissions of BC. This will be used in the development of a new international standard and a recommended practice which will address black carbon emissions from the aviation sector.

8NM.1

Synthesis of Pt-nanoparticles-Laden Graphene Crumples and Evaluation of Their Electrocatalytic Activity. HEE DONG JANG, Sun Kyung Kim, Hankwon Chang, Jeong Woo Choi, Jiayan Luo, Jiaxing Huang, *Korea Institute of Geoscience and Mineral Resources*

Pt-nanoparticles-laden graphene (GR) crumples was directly synthesized from a colloidal mixture of aqueous chloroplatinic acid (H2PtCl6) and graphene oxide (GO) nanosheets via aerosol spray pyrolysis (ASP). Effects of Pt content in the Pt/GR composite and temperature of heating zone on the particle morphology, diffraction pattern and specific surface area were investigated. The morphology of Pt/GR was the shape of a crumpled sheet of paper and the average size of the composite was around 1.3 µm in diameter. As Pt content increased from 2 to 20 wt %, higher numbers of Pt nanoparticles are observed on the GR at higher Pt content and the specific surface area of the composite also increased from 122 to 146 m2/g. Also, the intensity of the GR peak decreased but that of the Pt peak increased. As temperature increased from 500 to 900 oC, an increase of the particle size of Pt due to sintering was observed. Electrocatalytic application of the Pt/GR composites was examined through methanol oxidation reaction. The 20 wt% Pt/GR synthesized at 900 oC showed higher performance on methanol oxidation than a commercial 20 wt% Pt/carbon black catalyst.

8NM.2

Accounting for the Variable Df during Coagulation and Sintering of Fractal-like Particles.

Eirini Goudeli, MAX L. EGGERSDORFER, Sotiris E. Pratsinis, *ETH Zurich*

Nanoparticle formation by coagulation in atmospheric and industrial systems typically results in fractal-like structures. Though the asymptotic form of such structures is described well with the so-called fractal dimension, D_f, little is known for the D_f evolution, from that of initially tiny spheres (D_f=3) to that of large fractal-like aerosol particles (D_f=1.9-2.1). In simulating such aerosol dynamics, usually the evolution of D_f is neglected or simplified with a constant D_f. Here, the effect of evolving structure on primary particle, d_p, and collision diameters, d_c, of fractal-like TiO_2 particles is explored non-isothermally accounting for simultaneous coagulation and sintering over the entire process parameter space, from laboratory to industrial scale conditions by intefacing molecular dynamics, mesocale and continuum models. The evolution of agglomerate morphology is presented for varying D_f based on mesoscale simulations (Schmid et al. 2006; Eggersdorfer et al. 2011) as well as constant and arbitrarily-varying D_f (Artelt et al. 2003) using the characteristic sintering time of rutile from molecular dynamics (Buesser et al., 2011). The effect of process conditions, such as maximum temperature, cooling rate and initial precursor volume fraction on d_p, hard- and soft-dc are investigated. Accounting for the D_f evolution does not affect the asymptotic d_p and d_c compared to those obtained assuming constant D_f. Neglecting, however, the D_f evolution overpredicts the d_c up to 30% during the hard- to soft-agglomerate transformation even though d_p is not affected. A similar analysis is performed for amorphous SiO_2 and compared to that of titania.

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8NM.3

Gas Detection by Engineered Multi-scale Structures Composed of Nanoparticles.

YONGJUN BAE, Woongsik Nam, Hyesung Cho, Mansoo Choi, *Seoul National University*

The three-dimensional (3D) structures in a nanoscale dimension have been demonstrated for various sensor devices such as molecular or gas sensing platforms via conventional or non-conventional patterning approaches. Here, we present multiscale 3D gas sensors by utilizing an ion assisted aerosol lithography method, which induces a spontaneous self-assembly of charged ions to generate complex structures from thin films to flower-like architectures. In this method, we collected and focused an amount of nanoparticles to form an array of the porous bridges by simply generating charged nanoparticles (~ 5 nm in diameter) in a spark discharge chamber. A variety of metals can be employed to make the aforementioned nanoparticles such as copper, tin, carbon in a reproducible and controllable manner. The obtained structures are sufficiently robust to measure the changing of the gas concentration in a sensing chamber, resulting in a significant sensing ability for the introduced gases. By performing various sensing experiments with 3D lines and bridges, the presented sensor shows a relatively high sensitivity, based on a change of the resistance [S=(R_gas - R_air)/R_air] against to the external CO gas by comparison to a film-like 2D sensor. This is mainly due to the fact that our 3D metallic structures from self-assembly have nanoscale pores in its surface to make an easy diffusion of the target gases so that a rapid and reliable absorption of the gas molecules was occurred around the surface of the structure. In the experiment, 3D sensor from the self-assembly of copper oxide shows much enhanced sensing result (S=1.65) at 100 ppm of the CO, which is more sensitive than other type of 2D structures (film, lines). Also we can modulate the porosity of the structured sensors by utilizing an IAAL technique with much larger nanoparticles, finally resulting in a successful 3D gas sensor application.

8NM.4

Supramolecular Self-assembly of Photosynthetic Dyes in Aerosolized Droplets.

VIVEK SHAH, Pratim Biswas, *Washington University in St. Louis*

Self-assembled materials often have properties very different than that of individual molecules. For example, excitonic transfers can take place only in self-assembled chlorin molecules. Hence they are of interest in photonics, opto-electronics and solar cells (Modesto-Lopez et al., 2010). Materials with high order, which is characteristic of self-assembled materials, are hard to synthesize by covalent chemistry. Various solution-based techniques have been developed for supramolecular self-assembly (Mass et al., 2011; Miyatake & Tamiaki, 2010). Due to mixing the structural growth is hard to control. A one step aerosol-based self-assembly technique has been developed, to overcome limitations of solution-based techniques. Although aerosol routes have been used to self-assemble mesoporous structure, not much work has been done on supramolecular assembly.

In this study, the photosynthetic dye molecules are dissolved in a solvent which is atomized by electrospray. The monomers assemble in the droplets as the solvent evaporates. After the solvent evaporates, the agglomerates are deposited onto a transparent substrate. These agglomerates, when self-assembled, show a characteristic red-shift in absorption compared to their monomers. Experiments show that electrospray-based technique is a promising method to synthesize self-assembled structures and the results are explained with help of the classical nucleation theory. Results show that in case of single solvent, the evaporation time should be longer than nucleation time for the assembly to take place. Further control over the size of nucleated self-assembled structures can be obtained by judiciously selecting the spray solvents and the initial concentration of dye.

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8NM.5

DMA Characterization of Sub-50nm Silica Nanoparticle Size Standards and Comparison with PSL Size Standards.

ZEESHAN SYEDAIN, Benjamin Hunt, William Dick, *MSP Corporation*

Advanced manufacturing of semiconductor devices at technology nodes below 30nm requires new defect review and inspection tooling to maintain device yield. Historically, wafer inspection tools, photomask inspection tools, and other defect review tools have been calibrated with polystyrene latex (PSL) spheres, which are relatively uniform in size and shape. New inspection tools utilize deep ultraviolet (DUV) or extreme ultraviolet (EUV) radiation of high intensity to detect and measure defects smaller than 20nm. Repeated exposure to intense UV sources can cause degradation of the PSL. In addition size distribution of commercially available PSL spheres becomes broader with decreasing particle size, which limits their applicability as size standards. Silica nanoparticles provide a suitable alternative to PSL, as they can be synthesized with amorphous and uniform quasi-spherical structure and high thermal stability. In this study, thermal stability and monodispersity of 18-50nm silica nanoparticle size standards were compared to commercial PSL size standards. For measuring size distribution, the nanoparticles were suspended in buffer solution and generated as airborne particles using electrospray (TSI model 3480) and classified with a DMA. At 30nm, the silica size standard had a peak diameter of 29.5±0.7nm and relative full-width half maximum (RFWHM) value of 11%, while the PSL size standard had a peak diameter of 30±1 nm with RFWHM of 60%. The distribution differences between silica and PSL particles were comparable at 20nm and 50nm sizes. Silica particles deposited on silicon wafers tolerated high thermal treatment without any change in size, further demonstrating their suitability for sub-50nm calibration of defect inspection tools.

8NM.6

Controlling Composition and Morphology of Mixed Oxide Thin Films Synthesized by Aerosol Chemical Vapor Deposition (ACVD) Process. TANDEEP CHADHA, Jiaxi Fang, Pratim Biswas, *Washington University in St. Louis*

Mixed oxides of the form $Li_{1+x}Mn_{2-x}O_4$ and $LiMn_{2-x}Ni_xO_4$ find application as cathodes in lithium ion batteries. Current synthesis methods involve multiple steps, first producing a nanoparticle powder, followed by coating onto a conductive substrate and then annealing. These processes offer less control over the morphology and crystallinity of the cathode active material. A single step process for the synthesis of nanostructured thin films would facilitate the synthesis of nanostructured cathodes directly on a conductive substrate without the use of any binding agent.

The ACVD process is a single step, low cost process for the synthesis of nanostructured thin films. This process has been successfully demonstrated for the synthesis of metal oxides such as TiO_2 and NiO with dense, single crystal columnar, granular and branched morphologies (An et al. 2010). The existing ACVD process involves decomposition of a metal organic precursor in the reactor to yield metal oxide molecules which by homogenous nucleation yield particles. These particles deposit onto a heated substrate where they sinter to form thin films of different morphologies. The synthesis of mixed oxide thin films would involve heterogeneous nucleation of multi component metal oxides to yield mixed oxide particles. This work focuses on controlling the composition and morphology of mixed oxide thin films synthesized by the ACVD process. Control over the characteristic times and the reaction rates was used to control the morphology and the stoichiometry of the synthesized thin films. The surface morphology of the films was characterized by scanning electron microscopy and the crystal structure was examined by x-ray diffraction analysis. X-ray photoelectron spectroscopy was used to probe the chemical composition of the films. The role of the reaction kinetics and thermodynamics in controlling the stoichiometry of the particle and the composition of the film will be presented.

8NM.7

Fabricating WO3-based Nanostructured Materials for Solid-State NOx Gas Sensors. JULIEN GAURY, George Biskos, *Delft University of Technology*

Energy production from fossil fuels results into emissions of gaseous species (e.g., CO, SO2, NOx, etc.) that can threaten human health and affect regional and global climate. Sensors for monitoring gaseous emissions from energy conversion processes are therefore very important for controlling their environmental effects. Despite the great efforts in fabricating such sensors, most of them have the disadvantage of being technologically complex and expensive. Methods for producing simple and cost-effective sensors are therefore highly needed.

In this paper we fabricate WO3-based nanostructured materials, using Electrostatic Spray Deposition (ESD), for chemiresistive solid-state NOx gas sensors. In ESD, nanoparticle building blocks are synthesized by atomizing a liquid precursor solution using electrical forces, and are deposited onto heated chip substrates by electrostatic field. By tuning the temperature during deposition, we produce nanostructured thin films having granular and dendritic morphologies. By further annealing of the samples we produce hexagonal WO3 nanowires out of the as-deposited amorphous aggregates. This nanowire structures exhibit a higher surface-to-volume ratio compared to the non-annealed sample, thereby increasing the sensitivity of the sensor. To further enhance the electrical properties and thus the sensitivity of the materials towards NOx species, we also dope our sample with Niobium and Tantalum. The addition of doping species results in the formation of oxygen vacancies within the stoichiometric WO3 layer, thereby creating active sites for NOx adsorption.

8NM.8

Gas-phase Synthesis of Single-phase Spherical a''-Fe16N2/Al2O3 Core-shell Nanoparticles. TAKASHI OGI, Rizka Zulhijjah, Asep Bayu Dani Nandiyanto, Toru Iwaki, Kikuo Okuyama, *Hiroshima University*

Research on a''-Fe16N2 has attracted tremendous attention both for fundamental research and for the application to giant magnets—the high density of magnetic recording devices and the life science study of alternatives for rare earth magnetic materials. In the present study, we intended to prepare a''-Fe16N2 nanoparticles with a core-shell structure (coating an Al2O3 layer onto the surface of a''-Fe16N2 nanoparticles) to avoid the lateral interaction between magnetic nanoparticles along with a retardation of the oxidation of the a''-Fe16N2 nanoparticles. By using a fluid-bed method, the a''-Fe16N2 nanoparticles were synthesized directly via ammonia gas nitriding of alumina-coated spherical a-Fe nanoparticles that were uniquely prepared in one step using a Radio Frequency induction thermal plasma. We also used X-ray absorption fine structure analysis, which to the best of our knowledge has not been used in the characterization of iron nitride. Magnetic properties analysis is also reported in this paper. The implantation of nitrogen into the iron nanoparticles to constitute the a''-Fe16N2 structure showed a great effect on the production of rare-earth-free giant magnetization materials.

8NM.9

Synthesis of Spherical Macroporous WO3 Particles and Their High Photocatalytic Performance. Asep Bayu Dani Nandiyanto, Osi Arutanti, TAKASHI OGI, Kikuo Okuyama, *Hiroshima University*

Tungsten trioxide (WO3) materials have excellent performance in transferring visible-light energy and are widely used in photocatalysis, solar cells, and hydrogen generation. However, WO3 is expensive and in short supply. It is therefore important to develop efficient materials that use smaller amounts of WO3. One strategy is to produce porous materi-als so that the entire area of the WO3 material can be used and activated effectively. In this study, we synthesized macroporous WO3 particles using a spray-pyrolysis method with colloidal templating. Ammonium tungsten pentahy-drate (ATP) was used to produce WO3 without impurities, and polystyrene (PS) spheres were used to promote spheri-cal macropore formation. The synthesized particles were characterized using a thermogravimetric analysis, an X-ray diffraction, a nitrogen adsorption, a scanning electron microscopy, and a transmission electron microscopy. Several process parameters (i.e. initial precursor concentration and mass ratio between ATP and PS) were investigated to get highly ordered porous particles with controllable porous structure and particle outer diameter. Photocatalytic analysis results showed that the amount of PS that provided the optimum photocatalytic enhancement. Our results showed that a PS/ATP mass ratio of 0.60 provided WO3 particles with a photocatalytic rate 2.5 times that of dense WO3. TEM analysis showed that highly ordered macropores were produced, enabling better penetration and interaction of mole-cules and light in the deepest part of the active catalyst, resulting in enhancement of the photocatalytic rate. This method will be useful for large-scale synthesis of small amounts of WO3 with high photocatalytic performance.

8NM.10

Preparation of Crumpled Graphene Particles with Enhanced Properties by Microwave Plasma-Assisted Capillary Compression Process. HANKWON CHANG, Eun-Hee Jo, Hee Dong Jang, *Korea Institute of Geoscience and Mineral Resources*

Graphene has attracted much attention due to its possible applications in various fields. However, graphene tends to aggregate and restack easily due to strong van der Waals attraction. Thus novel method for the rapid and continuous synthesis of aggregation-resistant graphene was suggested and achieved by morphing graphene sheet into crumpled paper ball-like graphene via an aerosol-assisted capillary compression process. Here we report new method for the preparation of the crumpled graphene particles with enhanced properties via microwave plasma-assisted capillary compression process. Aerosol droplets containing graphene oxide (GO) sheets were evaporated and reduced by passing through a tube reactor equipped with a microwave plasma system, resulting in crumpled and chemically reduced graphene (a.k.a., reduced GO, r-GO) particles. The crumpled morphology was observed by FE-SEM and the chemical reduction of GO was verified by XPS result. Superior specific surface area (409 m^2/g) was measured by nitrogen absorption. The higher energy by microwave plasma enhanced the properties of crumpled graphene particles.

8NM.11

Investigation of Transient Structural Behavior of Aerosol Particles during Their Aggregation Process Using Off-Lattice Kinetic Monte Carlo Simulations. Riyan Zahaf, Kwang-Sung Lee, Song-Kil Kim, Dudi Adi Firmansyah, Michael Zachariah, DONGGEUN LEE, *Pusan National University, Busan, South Korea*

The transient behavior of aerosol particles during their coagulation were studied through off-lattice kinetic Monte-Carlo (MC) simulations under either dilute or non-dilute concentration of particles. Algorithms of space doubling and time matching were employed to allow for a real-time tracking of the coagulating particles from monomers to fractal-like aggregates. The structural evolution of aggregates/particles was characterized with time in terms of fractal dimension, coordination number, and shape anisotropy. At the lowest volume fraction considered, the particles were coagulated with the slowest kinetics to form most open structures, and their fractal dimension steadily increased and then reached an asymptotic value of 1.7 corresponding to a diffusion-limited cluster-cluster aggregation (DLCA). When increasing the initial volume fraction, the aggregation kinetics became increased together with the gradual increase of the fractal dimension (denser structure) over 2.0, suggesting a possible transition from the DLCA to percolating regime. It was also found that the fractal dimension was well correlated with the shape anisotropy and the coordination number as well during the coagulation processes.

8RA.1

Sources of Carbonaceous Aerosol in the Free Troposphere.

HILKKA TIMONEN, Dan Jaffe, Jon Hee, Honglian Gao, Bob Cary, *University of Washington, Bothell, WA, USA*

In this study concentrations of organic (OC) and elemental carbon (EC) in free tropospheric fine particulate matter were measured from March to September, 2012 with a semicontinuous OC/EC carbon aerosol analyzer (Sunset Laboratory Inc., Oregon, US) at top of Mt. Bachelor in Central Oregon, USA (2.8 km a.s.l). The average concentrations of OC and EC in the free troposphere (FT) were low (OC: 1.87 ± 6.10 micrograms m^{-3}, EC: 0.07 ± 0.26 micrograms m^{-3}; average ± stdev) but much higher during specific pollution episodes. The OC/PM and EC/PM ratios were on average 0.40 (R^2= 0.925) and 0.020 (R^2= 0.735). The main source of carbonaceous matter in the FT was Asian long-range transport in spring and regional biomass burning during summer. Highest OC and EC concentrations were measured during biomass burning episodes (OC up to 146 micrograms m^{-3}, EC up to 18.7 micrograms m^{-3}). Good correlation between OC and EC (R=0.90) was measured during biomass burning episodes. During the measurement period, a wide variety OC/EC –ratios were measured. For long-range transported Asian pollution mixed with dust the OC/EC –ratios were between 8 and 15, for long-range transported anthropogenic pollution the average OC/EC –ratios were between 20 and 30. The highest OC/EC –ratios (25-40) were measured for biomass burning emissions. Lower OC/EC –ratios (25-30) were measured for local biomass burning plumes, whereas higher ratios were measured for biomass burning plumes originating from longer distance (CA, Siberia, Asia), possibly due to SOA formation. Our OC/EC ratios observed in the free troposphere are higher than measurements at lower elevation sites, suggesting significant SOA formation. As part of my presentation, I will compare the OC/EC ratios observed in the free troposphere at Mt. Bachelor with source measurements (e.g. Asian and biomass burning) to give information on changes to the OC/EC ratio during transport.

8RA.2

Secondary Organic Aerosol Precursor Concentrations and Fluxes from a Temperate Deciduous Forest in East Tennessee.

RICK SAYLOR, Ariel Stein, *NOAA Air Resources Laboratory*

Forests are a dominant source of biogenic volatile organic compound (BVOC) emissions into the earth’s atmosphere and thus play an important role in the formation of secondary organic aerosol (SOA). To arrive at a better scientific understanding of the complex chemical and physical processes of forest-atmosphere exchange and provide a platform for robust analysis of field measurements of these processes, a process-level, multiphase model of the atmospheric chemistry and physics of forest canopies is being developed. The initial gas-phase version of the model, the Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS) currently includes processes accounting for the emission of BVOCs from the canopy, turbulent vertical transport within and above the canopy and throughout the height of the planetary boundary layer, detailed chemical reactions, mixing with the background atmosphere and bi-directional exchange between the atmosphere and the canopy and the forest floor.

The Walker Branch Watershed (WBW) is a dedicated ecosystem research area on the U. S. Department of Energy’s Oak Ridge Reservation in east Tennessee. A flux tower located within the watershed (35°57′30″N, 84°17′15″W; 365 m above mean sea level) and 10 km southwest of Oak Ridge, Tennessee, served as a focal point for BVOC chemical flux measurements from the forest canopy in 1999. At the time of the measurements, the forest stand was approximately 50 years old, the overstory canopy height was 26 m, and the whole canopy leaf area index was 6.0 m^2 leaf/m^2 ground area. In this presentation, the ACCESS model will be briefly described and results from its application to the WBW forest canopy will be presented and compared to measurements made at the site. Levels of background NO_x concentrations are found to significantly influence both the magnitude and chemical composition of fluxes of SOA precursors from the canopy.

8RA.4

Assessing PM Concentrations at Urban Spatiotemporal Scale by Image Analysis Based on the Image Effective Bandwidth Measure. YAEL ETZION, David M. Broday, Barak Fishbain, *Technion - Israel Institute of Technology*

Size and concentration of airborne particulate matter (PM) are important indicators of air pollution events and public health risks. However, the important efforts of monitoring size resolved PM concentrations in ambient air are hindered by the highly dynamic spatiotemporal variations of the PM concentrations. Satellite remote sensing is a common approach for gathering spatiotemporal data regarding aerosol events but its current spatial resolution is limited to a large grid that does not fit high varying urban areas. Moreover, satellite-borne remote sensing has limited revisit periods and it measures along vertical atmospheric columns. Thus, linking satellite-borne aerosol products to ground PM measurements is extremely challenging. In the last two decades visibility analysis is used by the US Environmental Protection Agency (US-EPA) to obtain quantitative representation of air quality in rural areas by horizontal imaging. However, significantly fewer efforts have been given to utilize the acquired scene characteristics (color, contrast, etc.) for quantitative parametric modeling of PM concentrations. We suggest utilizing quantitative measures of image characteristics, mainly related to contrast, for predicting PM concentrations. In particular, we examined an innovative measure, called image effective bandwidth (IEB) that tallies the image blurriness. The method was validated by assembling and analyzing a large data set of time-series images, capturing a selected urban scene by horizontal imaging, versus PM concentrations and meteorological data (wind direction and velocity, relative humidity, etc.) that were simultaneously measured from air quality monitoring stations located in the imaged scene and its neighborhood. Quantitative and qualitative statistical evaluation of the suggested method shows that dynamic changes of PM concentrations can be inferred from the acquired images.

8RA.5

Changes in Organic Aerosol in the United States over the Last Quarter-Century. KELSEY BOULANGER, Jesse Kroll, *MIT*

Recently-developed analytical techniques have provided new insight into atmospheric organic aerosol (OA) chemistry and their impacts on climate forcing and human health, but our understanding of these impacts is hindered by the uncertainties in how OA has changed over the past few decades. This analysis uses existing aerosol data from the U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE) Network to examine recent trends in aerosol species concentrations. Using data from as early as 1988 in many locations, monthly and yearly trends of aerosol concentrations are considered to provide insight into the long-term OA evolution across dozens of rural sites in the U.S. Changes in OA are characterized both on an absolute scale and relative to other key atmospheric constituents, including sulfate, nitrate, and ammonium. These are interpreted in terms of historic changes to a number of factors that may affect relative and absolute loadings: emissions of primary organic aerosol (POA), changes in emissions of precursors to both secondary organic aerosol (SOA) and secondary inorganic aerosol, and other factors that may affect aerosol formation (e.g., NOx levels and aerosol acidity).

8RA.7

Investigating Missing Sulfur Sources at Fairbanks, Alaska. KABINDRA M. SHAKYA, Richard E. Peltier, *University of Massachusetts, Amherst*

Series of intensive field measurement studies of fine particle chemical components at Fairbanks, Alaska has revealed unusual aerosol climatology where, at times, significantly more elemental sulfur was observed from X-ray Fluorescence (XRF) compared to sulfate as measured by chromatographic (IC) separation. Sulfur and organic carbon are the largest fraction of aerosol mass in Fairbanks, a subarctic small city characterized by exceptionally polluted wintertime conditions, and relatively clean conditions during the summer. We observed large inconsistencies when comparing these two sulfur measurements at the single EPA monitoring site at Fairbanks after analysis all of all available chemical measurements by XRF and IC from 2005 until 2012. We analyzed data where the ratio of sulfur by XRF to sulfur by IC was significantly different from unity after propagating reported instrument uncertainties. We observed a significant deviation in 28% of total measurements since 2005 where elemental sulfur (by XRF) exceeding the inorganic sulfur (by IC) indicating the presence of apparently unmeasured sulfur compounds. The largest discrepancies between elemental sulfur and sulfate were most frequently observed in the summer, though discrepancies were observed year round. An analysis of all available AQS data suggest that this recurring phenomena is linked to seasons, and total carbon, nitrate, and zinc sources (for colder temperatures) and ozone (for warmer temperatures). This suggests that it is more than a simple systematic bias indicating the missing sulfur sources and unmeasured sulfur species at Fairbanks, a finding that has important implications for interpretation of data from the larger speciation trends network.

8RA.8

Infrared Extinction and Visible Light Scattering Properties of Diatomaceous Earth Aerosol. JENNIFER ALEXANDER, Olga Laskina, Vicki Grassian, Mark Young, Paul Kleiber, *University of Iowa*

Northern Africa is known to be one of the largest sources of atmospheric mineral dust aerosol, especially the Bodélé Depression, located in northern Chad. This atmospheric dust affects the earth’s radiation balance and climate by scattering and absorbing the incoming visible solar radiation and outgoing IR terrestrial radiation. In order to accurately model these radiative transfer effects, dust optical properties must first be known. However, mineral dust optical properties are dependent on particle shape, which is typically nonspherical and can be highly complex. In this work, IR extinction and visible phase function and linear polarization profiles for diatomaceous earth aerosol, a major mineral component of the dust from the Bodélé Depression, are measured and modeled using T-matrix theory based simulations. The particle shape distribution is determined by spectral fitting of experimental infrared (IR) extinction spectral line profile with T-matrix simulations for diatomaceous earth dust. It is found that a particle shape model that peaks toward both extreme rod-like and disk-like shapes results in the best fits to the IR spectral data. SEM images support the extreme particle shape found from spectral fitting. This particle shape model is then used as a basis for modeling the visible light scattering properties, showing a significant improvement over Mie theory based simulations.

8RA.9

Ammonia Emissions from Beef, Swine, and Poultry Production Estimated with Process-Based Models.

ALYSSA MOORE, Peter Adams, *Carnegie Mellon University*

Ammonia plays a key role in the formation of fine particulate matter in the atmosphere. [Ansari, 1998] In the United States, the animal livestock sector contributes up to seventy five percent of national ammonia emissions, with the largest emitters being dairy cattle, beef cattle, swine, and poultry. [USEPA-NEI, 2004] The goal of this work is to better estimate emissions from beef cattle, swine, and poultry using a process-based modeling approach previously developed by Robert Pinder. [Pinder, 2004] Ammonia emissions from livestock production depend strongly on meteorological conditions (e.g. temperature, wind speed, and precipitation), management practices (e.g. stocking density of housing, type of storage, etc.) and manure characteristics (e.g. dry matter and nitrogen content of wastes). Variability in these factors results in literature animal emission factors varying by a factor of 10 for beef cattle and a factor of 15 for swine. Regional and seasonal variations in emissions must therefore be accounted for in emission inventories and chemical transport models. Emissions cannot be measured for all practices and conditions so a model that describes how emissions occur during manure management will be used to estimate ammonia emissions from livestock. Using existing model framework, we can tune our model to predict ammonia emissions from a single farm and animal type. This procedure is repeated for all management practices and animal types, comparing model performance to literature reported emission factors. Our initial results show that a process-based model is able to explain 36% of emission factor variability for beef and 65% for swine housing based on manure characteristics, management practices, and temperature. Additional model evaluation was done using National Air Emissions Monitoring Study (NAEMS) data for swine and poultry. NAEMS was a multi-year measurement campaign conducted at a number of farms throughout the country and monitored many kinds of emissions from the farms.

8RA.10

A Self-Consistent Global Emissions Inventory Spanning 1850-2050 – Why We Need One.

KRISTINA WAGSTROM, Sherri Hunt, *University of Connecticut*

While emissions inventory development has advanced significantly in recent years, the scientific community still lacks a global inventory utilizing consistent estimation approaches spanning multiple centuries. In this analysis, we investigate the strengths and weaknesses of current approaches to effectively address inventory development over not just a global spatial scale but also a timescale spanning two centuries – from early industrialization into the near future. We discuss the need within the scientific community for a dataset such as this and the landscape of questions it would allow the scientific community to address. In particular, we focus on questions that the scientific community cannot adequately address using the currently available techniques and information.

We primarily focus on the difficulties and potential obstacles associated with developing an inventory of this scope and magnitude. We discuss many of the hurdles that the field has already overcome and also highlight the challenges that researchers in the field still face. We detail the complexities related to the extent of spatial and temporal scales required for an undertaking of this magnitude. In addition, we point to areas where the community currently lacks the necessary data to move forward. Our analysis focuses on one direction in which the development of global emissions inventories is heading rather than an in-depth analysis of the path of emissions inventory development thus far. We intend for this analysis to provide an overview to aide researchers currently working on inventory development as the science continues to advance.

8RA.11

Sources and Processes of Submicron Particles at an Urban Downwind Location - Long Island New York. SHAN ZHOU, Jianzhong Xu, Fan Mei, Jian Wang, Arthur J. Sedlacek, Stephen Springston, Yin-Nan Lee, Qi Zhang, *University of California, Davis*

The Department of Energy (DOE) sponsored Aerosol Life Cycle Intensive Operational Period (ALC-IOP) field campaign took place at Brookhaven National Laboratory (BNL) on Long Island, New York, from July 1 to August 15, 2011. An Aerodyne High-Resolution Time-of-flight Aerosol Mass Spectrometer (AMS) was deployed after a temperature-stepping thermodenuder during this study to acquire highly time resolved data on the mass-based size distribution, chemical composition, and volatility profile of the non-refractory species in submicron particles (NR-PM_{n1}). The average mass concentration of NR-PM_{n1} was 15.3 (±8.9) microgram per cubic meter, with organics (64.8%) and sulfate (24.2%) dominating the composition. Back trajectory analysis showed that particles observed at Long Island were influenced by heavily polluted urban plumes from New York City, regional eastern US pollutions enriched of ammonium sulfate and LV-OOA, forest fire plumes transported from Canada, and relatively clean air mass form ocean emissions. Positive Matrix Factorization analysis of the high-resolution mass spectra of organics identified three distinct secondary OA factors: a highly oxidized oxygenated LV-OOA (O/C = 0.79), a semi-volatile SV-OOA (O/C = 0.41) and a nitrogen-enriched NOA (O/C = 0.15 and N/C = 0.185). According to the average volatility profile of individual aerosol component, LV-OOA was less volatile than nitrate but more volatile than sulfate. NOA, which appeared to be mainly composed of amine salts according to its high resolution mass spectrum, was less volatile than ammonium nitrate but had a similar volatility profile as organic nitrate. The volatility of SV-OOA was comparable to that of ammonium nitrate and both showed a strong diurnal variation pattern that was higher during the night and early morning and lower during the day. Based on these results, we will discuss the sources and processes of OA in this urban downwind location.

8RA.12

Examining Spatial-Temporal Variation Air-Quality in Marcellus Shale Industrial Regions Using Stratified Mobile Monitoring. ERIC LIPSKY, Yi Tan, Rawad Saleh, Albert A. Presto, *Pennsylvania State Greater Allegheny, McKeesport, PA*

Southwestern Pennsylvania has seen a rapid increase in natural gas drilling using the method of Hydraulic Fracturing into the Marcellus Shale formation. The large number of well sites gives concern for industrial impact on regional air quality. Due to the variety of stages and emissions from the Hydraulic Fracturing Gas Industry, the Carnegie Mellon University Mobile Air-Quality lab was developed to take continuous measurements while traveling in and out of regions of new and old gas development. A suite of air pollutants were measured (black carbon (BC), particle-bound polycyclic aromatic hydrocarbons (PAH), Methane, NOx, and a small range of volatile organic compounds including benzene, and toluene). Measurements are synched with GPS and wind data to map the air quality in high density regions of Marcellus industrial sites. Measurements were made between May 2012 and August 2012. A wide variety of levels were observed indicating substantial range of emissions from different well sites.

8RA.13

Dimethyl Sulfide Control of the Clean Summertime Arctic Aerosol and Cloud. RICHARD LEAITCH, Sangeeta Sharma, Lin Huang, Desiree Toom-Sauntry, Alina Chivulescu, Annie-Marie Macdonald, Knut von Salzen, Jeffrey Pierce, Allan Bertram, Jason Schroder, Nicole Shantz, Rachel Chang, Ann-Lise Norman, *Environment Canada*

One year of observations from Alert, Nunavut shows that new particle formation is common during clean periods of the summertime Arctic, associated with low condensation sinks and the presence of methane sulfonic acid. The clean aerosol time periods, defined using the distribution of refractory black carbon number concentrations, increase in frequency from June through August as the anthropogenic influence dwindles. During the clean periods, the number concentrations of particles that can act as cloud condensation nuclei increase from June through August suggesting that dimethyl sulfide, and possibly other oceanic organic precursors, exert significant control on the Arctic summertime submicron aerosol, a proposition supported by simulations from the GEOS-Chem-TOMAS global chemical transport model with particle microphysics. The cloud condensation nucleus concentrations increase for the clean periods across the summer is estimated to be able to increase cloud droplet number concentrations by 23-44 cm-3, comparable to the mean increase in droplet number concentrations needed to yield the current global cloud albedo forcing from industrial aerosols. These results suggest that dimethyl sulfide contributes significantly to modification of the Arctic summer shortwave cloud albedo.

8RA.14

Elemental Composition of PM10 and PM2.5 in Windblown Dust in Shiprock and Churchrock, New Mexico. Cristina Gonzalez-Maddux, AURELIE MARCOTTE, Nabin Upadhyay, Pierre Herckes, Yolanda Williams, Gordon Haxel, Marin Robinson,*Arizona State University*

The composition of fine particulate matter (PM2.5) in urban or industrial areas has been shown to be enriched in anthropogenic emissions of toxic metals and other pollutants. In this work, PM2.5 and PM10 samples were collected at two sites on the Navajo Reservation: Diné College in Shiprock, NM and a residential property in Churchrock, NM. Shiprock was selected because of its proximity (<25 km) to more than 500 abandoned uranium mine tailings sites and various industrial facilities including a coal-burning power plant. The Churchrock site was selected because of its close proximity (<1 km) to a partially restored abandoned uranium mining site. A specific goal of the project was to determine if uranium from Shiprock or Churchrock abandoned tailings sites could be detected in the windblown dust. Dust samples from each site were analyzed for concentrations of various elements including those typically associated with uranium mining and coal-burning activities by inductively coupled plasma mass spectrometry (ICP-MS). In addition, samples collected in Churchrock were analyzed for uranium isotope abundances using a multicollector ICP-MS. In Shiprock, six elements were notably enriched (Enrichment Factor (EF) values > 10) including Cu, Zn, Sn, Pb, Sb, and Bi. In Churchrock, four elements were found to be enriched (EF values > 10) including Cu, Pb, Sb, and Bi. Results from principal components analysis (PCA) and HYSPLIT trajectories suggest that sources of PM in Shiprock and Churchrock are both natural (soil) and anthropogenic (combustion) in origin. Uranium isotope ratios suggest that the delta 238/235U values are all within error of one another (2sd) and are typical of crustal rocks, including basalts and granite. The aerosol samples collected were typically less enriched in the 234U as compared to the soil samples, suggesting that the aerosol uranium pool is not entirely derived from local soil dust.

8RA.15

A Long Term Variation of Chemical Species in $PM_{2.5}$ and PM_{10} in the Ambient Atmosphere at Background Site in Jeju, Korea during 2008–2012. KWANGYUL LEE, Tsatsral Batmunkh, Young Joon Kim, Kihong Park, *Gwangju Institute of Science and Technology (GIST), Korea*

Concentrations of elemental carbon (EC), organic carbon (OC), ions (sulfate, nitrate, and ammonium), and elements in $PM_{2.5}$ and PM_{10} were measured at Gosan during spring in 2008, fall in 2008, spring in 2009, fall in 2009, spring 2011, fall in 2011, and spring in 2012 to investigate a long term variation of chemical characteristics of atmospheric aerosols. The highest PM_{10} and $PM_{2.5}$ concentration were observed as high as 161.08 and 56.89 micro-gram per cubic meter, respectively due to the Asian dust during the spring in 2011, while the lowest PM concentrations were observed as low as 9.41 and 14.86 micro-gram per cubic meter in $PM_{2.5}$ and PM_{10}, respectively during the fall in 2011. On May 21 and 22 in 2008, OC concentration increased 4.4 times (6.59 micro-gram carbon per cubic meter) higher than other days due to the biomass burning emissions from China. From October 17 to 20 in 2009, Na+ and Cl- increased 2.3 times and 1.7 times in $PM_{2.5}$ and 3.7 times and 2.5 times in PM_{10}, respectively when the air masses originated from the Sea. After the Asian dust events (May 12 and 13 in 2011), OC and sulfate increased till 6.50 micro-gram carbon per cubic meter and 10.13 micro-gram per cubic meter, respectively, while PM concentration decreased on May 14 and 15 in 2011. Sulfate increased to 13.24 micro-gram per cubic meter (31.5% of PM2.5) and 15.31 micro-gram per cubic meter (28.8% of PM10) in $PM_{2.5}$ and PM_{10}, respectively on April 22 and 23 during the spring intensive measurement in 2012. The frequency of the long-range transport (LTP) event or Asian dust (AD) event typically occurred in spring and fall were not significantly different from years to years. More detailed analysis is in progress, and will be presented.

8RA.16

Chemical Characterization of Particles Sampled in Revin, France, during the EMEP 2012 Summer Campaign. ARI SETYAN, Vincent Crenn, Véronique Riffault, Jean Luc Jaffrezo, Antoine Waked, Stéphane Sauvage, Jean-Luc Besombes, Thierry Leonardis, Nadine Locoge, *Ecole des Mines de Douai*

Understanding the different processes governing PM concentration remains an important issue for air quality in Europe. In the frame of the EMEP Program (http://www.emep.int) and in cooperation with ACTRIS (http://www.actris.net/), ChArMEx (http://charmex.lsce.ipsl.fr) and PEGASOS (http://pegasos.iceht.forth.gr/) projects, two intensive measurement periods were held in summer 2012 and winter 2013. The main objective is to obtain high resolution and extended measurements of aerosols and its precursors in order to improve the knowledge regarding the temporal and spatial variability of PM speciation and to assess chemical transport models. Five monitoring sites in France were equipped with additional on-line and off-line instruments to measure particle chemical and physical properties, as well as precursor gases.

Preliminary results obtained at a remote site in Revin, France, during the summer campaign (June 8-July 12, 2012) will be shown. The average concentration of non-refractory submicron particles (NR-PM1) was low, and the chemical composition was dominated by organics (56% of total NR-PM1) and sulfate (25%). Three organic factors were identified by positive matrix factorization (PMF), including two oxygenated organic aerosols (OOA) with different O/C ratios (more oxidized OOA: 0.94; less oxidized OOA: 0.41), and one hydrocarbon-like organic aerosol (HOA). Taken together, the two OOA factors accounted for 82% of the total organic mass and correspond to secondary organic aerosols (SOA), while HOA accounted for 18% of organics and corresponds to anthropogenic emissions. The organic-to-elemental carbon ratio (OC/EC) was 8.4 (±2.8) on average ($\pm 1\sigma$). Three events (June 28, night of June 28-29, and July 3-5) analyzed with back trajectories showed that the site was mainly under the influence of long-range transport from the Paris megacity (~230 km from the site). New particle formation and growth events have never been observed during this study. These results suggest that particles sampled at Revin were mainly SOA formed during long range transport.

8RA.17

Investigation of Aerosol in the Southeastern U.S. during the SOAS Field Campaign: Cloud Condensation Nuclei Activity, Hygroscopicity, Droplet Activation Kinetics, and Volatility of Ambient and Water-Soluble Aerosol. KATE CERULLY, Aikaterini Bougiatioti, Lu Xu, Hongyu Guo, Rodney Weber, Nga Lee Ng, Athanasios Nenes, *Georgia Institute of Technology*

It is well known that complexities of aerosol partitioning can impact a multitude of aerosol properties including cloud condensation nuclei (CCN) activity, hygroscopicity, volatility, and droplet activation kinetics as a result of changes in organic mass and composition, among other things. For many ambient measurements, combined biogenic and anthropogenic emissions make it difficult to deconvolute the properties of POA and SOA from different sources. In this study, aerosol were collected during the 2013 SOAS field campaign in rural Alabama, a strongly biogenic site with little anthropogenic influence, making it possible to investigate the major impacts of biogenic emissions on aerosol properties.

During the 2013 SOAS field campaign, a suite of instruments, including a cloud condensation nuclei counter (CCNC), thermodenuder (TD), and high resolution time-of-flight aerosol mass spectrometer (AMS), were used to measure CCN activity, aerosol volatility, and aerosol composition and oxidation, respectively. Particles were either sampled directly from ambient or with a Particle Into Liquid Sampler (PILS), allowing for the investigation of water-soluble aerosol properties. The difference in key aerosol properties (e.g., activation kinetics, hygroscopicity, and volatility) between ambient aerosol and water soluble aerosol components, primarily the oxidation state of the organic fraction, is investigated.

8RA.18

Ferrous Iron and Hydrogen Peroxide Produced by Marine Aerosols Deposited in Ocean Water of the Equatorial Pacific Ocean. HSIANG TENG, Hoi Ting, Dan Hinz, Anne Johansen, *Central Washington Universtiy*

The Equatorial Pacific Ocean is limited in primary productivity by the micronutrient iron, which is delivered to the ocean through the deposition of continental aerosols. Despite the fact that the amount and speciation of this iron controls phytoplankton productivity and thus has implications on the carbon cycle and global climate, accurate estimates of the atmospheric contribution of bioavailable iron to the surface ocean are difficult to attain. To further our understanding of reactions that transform iron after it is deposited into the ocean we performed photochemical experiments of real collected aerosol particles in real ocean water. Subnanomolar levels of ferrous iron (Fe(II)) and hydrogen peroxide ($H2O2$) were determined with chemiluminescence detection in the presence of luminol and acridinium ester, respectively. In general, Fe(II) and H2O2 increased in the presence of light during the course of the dissolution experiments. When extracts were spiked with small amounts of dimethyl sulfide or isoprene, which are compounds emitted by phytoplankton, Fe(II) production was enhanced. These results show that Fe(II), which is the more bioavailable form or iron compared to its oxidized and insoluble counterpart, is produced by compounds that are co-deposited with aerosol particles as well as compounds directly emitted by phytoplankton. These mechanisms of iron redox cycling in surface ocean waters allow us to better predict the impact of changing aerosol loadings on the carbon and sulfur cycles and global climate.

8RA.19

Measurement of Gas and Aerosol Agricultural Emissions. PHILIP SILVA, *USDA - Agricultural Research Service*

Studies of air quality indicate that agricultural emissions may impact particulate mass concentrations through both primary and secondary processes. Agriculture impacts can include primary dust emission, on-facility combustion from vehicles or seasonal field burning, and gaseous emissions such as ammonia that produce secondary aerosol. During this study we field tested an ambient ion monitor (AIM) adapted for detection and quantification of gaseous agricultural emission components that potentially convert to the aerosol phase. Ions of interest include ammonia, small amines, and carboxylic acids. Sampling took place at Mammoth Cave National Park where the AIM instrument was co-located with regulatory measurements for the state of Kentucky and an IMPROVE network monitor. Sampling took place during two time periods; one during spring when seasonal burns take place and a second during summer in peak ozone season. Results in both cases show that ammonia dominates the cation component of the particles. While sulfate is the dominant anion detected by the AIM at the site, carboxylic acids were also detected as significant components by anion chromatography. Correlations of the AIM data with other measurements and implications for its suitability for detecting primary and secondary aerosol from agricultural emissions will be discussed.

8ST.1

Calibration and Assessment of Low-cost, Portable Particle Counters for Accurate In-field Monitoring of Cookstove Emissions. DOMINIQUE INGATO, Alba Aguilar, Sunny Karnani, Rufus Edwards, Ali Mohraz, Derek Dunn-Rankin, *UC Irvine*

Cookstove emissions in the developing world have a major influence on local health outcomes and are a significant source of short-lived climate forcing agents both regionally and on a global scale. The basis for these calculations, however, is relatively poor and improved in-field emissions characteristics from these sources are required. Low-cost portable emissions counters have the potential to significantly improve the spatial representation of emissions from cookstoves when variability between individual stoves is large. However, the accuracy of such counters has not been well characterized for anisometric particles in the 0.5-3.0 micro-meter effective diameter range known to have negative health effects. A method of effectively calibrating a portable electronic particle counter, Dylos DC1100 Pro Air Quality Monitor, is presented using spherical, monodisperse silica particles synthesized via the Stober method, polystyrene spheres and soot. Separate calibration curves have been generated in order to achieve reliable particle counts for spherical particles, as well as soot and other anisometric particles within the 0.5-3.0 micro-meter range. This method may be applied to similar particle counters prior to in-field use.

8ST.2

A Low-Cost Real-Time Detector for Airborne Asbestos Fibers. CHRIS STOPFORD, Paul Kaye, Edwin Hirst, Richard Greenaway, Zbignieu Ulanowski, *University of Hertfordshire*

Inadvertent inhalation of asbestos fibers and the subsequent development of incurable cancers is a leading cause of work-related deaths throughout the industrialized world. Indeed, in 2010, the World Health Organization estimated that more than 100,000 people die each year from asbestos-related lung cancer, mesothelioma and asbestosis resulting from occupational exposure.

Currently, there is no real-time in situ method for detecting airborne asbestos. We describe a relatively low-cost sensor technology that seeks to address this deficiency. It is based on two complementary measurements: firstly, the analysis of 2-dimensional light scattering patterns from individual particles carried in a sample airflow to allow discrimination of fiber particles from all other particle types; and secondly, the subsequent measurement of the behaviour of each of these fibers during their transit through a magnetic field (produced by two small rare-earth magnets). While most commonly occurring airborne fibers (gypsum, glass, rock-wool, cotton, etc) are unaffected by the magnetic field, asbestos fibers, as a result of their magnetic anisotropy, exhibit strong rotation to align with (or normal to) the field. This rotation is therefore used to discriminate asbestos fibers from other fiber particles that may be present in the aerosol.

Current prototype instruments are capable of analysing up to 600 particles per second and have demonstrated high detection sensitivities for both crocidolite (blue) and chrysotile (white) asbestos. Details of sensitivity estimates together with results from field trials carried out at various building renovation and demolition locations will be presented . The method has been developed with the aim of providing a compact low-cost real-time warning device that can be worn or carried by trades-people such as plumbers, electricians, builders, etc., and others at similar risk from inadvertent exposure to airborne asbestos.

8ST.3

Simple Low–Cost Aerosol Field Sampler for Deployment by Volunteers. ANDREY KHLYSTOV, A. Clint Clayton, David S. Ensor,*Research Triangle Institute*

Due to the complexity of the chemical and physical properties of atmospheric aerosol, its ambient concentrations and the effects remain extremely difficult to predict. In our analysis of the situation, the use of a very few sophisticated, yet very expensive instruments may provide high fidelity information at a few locations for a short period of time, but at a high cost of hardware and highly trained scientific personal in the field. Instead, our objective is to develop a very simple, inexpensive (price target below $100) sampling device based on advanced technology that could be simply deployed by personnel without scientific training and then retrieved for return to a central laboratory where the captured aerosol particles would be analyzed for mass, ion, carbon, metals, and biological materials. In addition to off-line analysis, the simple sampling device might have very simple real-time monitoring capability using light emitting diodes to obtain time series data. The sampler is enabled by consumer electronics and by nanofiber filters which have sufficiently low pressure drop with acceptable collection efficiency to allow the use of a computer cooling fan to provide an air flow of 3 lpm for 24 hours. In this presentation we will discuss the results of a pilot study aimed to characterize a prototype of the sampler.

8ST.5

Next-Generation Air Monitoring - A Review of Portable Air Pollution Sensors. PAUL A. SOLOMON, Margaret MacDonell, Ron Williams, Eben Thoma, Dena Vallano, Michelle Raymond, Olson David, *US EPA*

New technologies and architectures for sensing gases and particles in air are emerging, for criteria pollutants, air toxics, and greenhouse gases. These technologies are generally designed to be mass-fabricated through innovative processes (e.g., microfabrication) and are: 1)small; 2) able to autonomously and directly read pollutant levels; 3) have low power consumption; and 4) support flexible deployment options [White et al. Environmental Manager, pp. 36-40, May 2012]. These traits translate to reduced total cost of ownership, enabling a higher density of air pollution measurements and personal exposure applications to be considered.

Measurements from, the existing national air monitoring network can be used to infer community-wide concentrations of ozone and fine particle (< 2.5 micro-meter) mass. However, other pollutants directly emitted into the air, such as elemental carbon, coarse particles (between 2.5 and 10 micro-meter), carbon monoxide (CO), nitrogen oxides (NOx), and various air toxics have been shown to have much higher variability between regional air pollution monitors compared to pollutants like ozone that are secondarily formed in the atmosphere. Portable air pollution sensors can potentially provide more location-specific information desired by individuals, and communities. There is also a desire to use portable sensors to monitor indicator pollutants or classes of pollutants, like methane and total volatile organic compounds (VOCs), as well as nuisance pollutants, like hydrogen sulfide (H2S) and ammonia, which indicate the presence of pollution sources.

Current technologies for portable sensors for air pollutant gases reviewed include: electrochemical, metal oxide, spectroscopic, ionization, and pellistor sensors. Current technologies for portable particle sensors include: light scattering, light absorption, and those based on a change in frequency of an oscillating impaction surface. Attributes that indicate the appropriateness of these technologies for sensing the pollutants mentioned above will be discussed, including: estimated range of measurement, selectivity (when applicable), appropriate deployment platforms, response and recovery time, battery lifetime, and expected range of acceptable operating conditions. Information will also be provided about the potential of emerging sensor technologies to address the deficiencies in the abilities of existing sensor technologies to measure these pollutants.

8ST.6

Measuring In-field Emissions of Biomass Combustion. RYAN THOMPSON, Cheryl Weyant, Tami Bond, *University of Illinois at Urbana-Champaign*

Approximately half the people in the world rely on solid biomass fuels (wood, dung, agricultural waste, etc.) for residential cooking and heating needs. The emissions are a serious health risk to those exposed (mostly women and children), causing lung disease and many other serious health problems. These emissions also have a significant effect on the earth's climate. Field measurements are needed to understand the magnitude and composition of these emissions for climate models and health studies.

Field measurements of rural residential emissions are lacking, and one reason is because appropriate emissions equipment does not exist. In order to conduct large-scale, on-the-ground field campaigns, there is a need for equipment which is small, light-weight, has low power consumption, has appropriate measurement range, and is durable enough to withstand physical shock, dust, and temperature swings seen in the field. Good laboratory equipment exists, but is generally designed for the lab environment, and does not meet the above design criteria. Portable, hand-held equipment is available, but one unit generally measures only one or two species. Running several units at once to perform a thorough emission characterization is cumbersome to package the equipment and later download and combine the data.

This poster describes the portable equipment we are developing to characterize real-time in-field emissions of biofuel combustion. The equipment is an integrated sensor box that measures CO, CO2, PM scattering, and PM absorption in real-time and collects PM filter samples to determine mass concentration and composition. Measurements have been performed on cookstoves, heating stoves, kilns, and other rural industrial and residential emission sources. Example data is presented. The equipment is a useful tool to improve emission inventories for climate models, to develop more-representative lab tests for small combustion appliances, and to improve existing biofuel combustion technologies through R&D.

8ST.7

An Efficient Algorithm for Very Low Cost Personal Particulate Monitors. MICHAEL TAYLOR, Nourbakhsh Illah, *Carnegie Mellon University*

In this paper we demonstrate that a weighted estimation algorithm can be effectively used to process noisy or unreliable data from inexpensive mass-produced sensors. Given the rising interest in low-cost portable environmental monitoring, we can expect the availability of higher-quality and lower-cost sensors in the next decade. In the meantime, we propose a method for processing and filtering currently available low-cost sensors to acquire data with higher accuracy and precision than are typically achieved using static formulae or simple time averages and low-pass filters. Specifically, we present an algorithm for estimating 2-micron particle concentrations from an inexpensive dust sensor in addition to a simple calibration method. The concentration estimate is adjusted at every time step by increasing or decreasing depending on whether the sensor is or is not triggered, respectively. The rate of change is weighted according to the probabilistic behavior of the sensor. This takes into account the significantly higher probability of false negatives than false positives. In other words, because we know that we see only a fraction of the particles passing through the inexpensive sensor, we give a much greater weight to detection than absence. We compare our estimate versus the formula given in the datasheet and a scaled time average of the raw signal against reference 2-micron particle counts from the Hach HHPC-6. We show how this dust sensor is incorporated into Speck, a $100 desktop PM monitor for commercial deployment, and AirGo, a wearable PM and carbon monoxide monitor for the EPA's My Air My Health Challenge. We discuss design decisions regarding the cost of including various additional features and the theoretical price points of adding additional functionality. We also outline future plans for developing mobile and wearable monitors based around this inexpensive dust sensor and data processing algorithm.

8ST.8

Inexpensive Microfluidic Devices for Multiplexed Metal Measurement in Particulate Matter. David Cate, Poomrat Rattanarat, Killean OConaill, John Volckens, CHARLES HENRY, *Colorado State University*

Metal exposure remains an important topic in human health. While there are many sources of metals, metals in particulate matter (PM) are particularly concerning because PM is ubiquitous and individual exposure can vary substantially across a regional population. Furthermore, PM exposure can be high in some jobs such as welding. At present, most methods collect PM on filters using long sampling times (24 hours) and high flow rates. Quantification is subsequently done using Atomic Absorption Spectroscopy or Inductively Coupled Plasma coupled with either Mass Spectrometry (ICP-MS) or Optical Emission Spectroscopy (ICP-OES). While these techniques are exquisitely sensitive and selective, they are also expensive and required highly trained laboratory staff for operation. As a result, analyzing a single filter can cost hundreds of dollars. Our group has developed an alternative approach using microfluidic devices made from filter paper (microfluidic paper-based analytical devices or mPADs) that can quantify low levels of metals in minutes. The results can be read using either the naked eye or simple, low-cost instrumentation. As a result, the assays cost pennies and can be used by virtually anyone. To demonstrate multiplexed metals analysis, we developed chemistry to measure Fe, Ni, Cu, Cr, Pb, and Cd in welding fume samples. Fe, Ni, Cu, and Cr are detected using colorimetric reactions while Pb and Cd are detected simultaneously on the same mPAD using electrochemistry. PM samples were digested on filter using 5 µL of acid and then transferred to the mPAD by elution with buffer. Detection limits of 0.1µg were achieved for colorimetric assays while electrochemical assays provided detection limits of 100 pg (1 ppb solution levels). We subsequently applied the mPADs to measure metal concentrations in welding fume PM plumes where samples were collected with personal samplers. Results from the mPAD were validated against ICP-OES.

8ST.9

Quantification Methods for Metal-Oxide Semiconductor Gas Sensors. NICHOLAS MASSON, Ricardo Piedrahita, Xiang Yun, Michael Hannigan, Qin Lv, Robert Dick, Li Shang, *University of Colorado at Boulder*

Metal-oxide semiconductor (MOx) sensors offer promising advantages in the growing field of remote air quality monitoring. Specifically, MOx technology enables the widespread dissemination of small, inexpensive monitors, allowing researchers and citizens to ask new and compelling questions. Despite their advantages, commercially available MOx sensors present many practical difficulties. Sensor responses are highly non-linear with respect to the pollutant of interest, and exhibit complex coupling with interference species, temperature, and, to a lesser degree, humidity. Here we present a generalized, empirical model to quantify MOx sensor responses with compensation for temperature and inter-sensor variability. Lab experiments and knowledge of general semiconductor characteristics were used in deriving the model, which was then verified using ambient data from a colocation with reference instruments. Methods are also proposed for calibrating MOx sensors in a cost and time effective manner.

8ST.10

Low Cost Air Quality Monitors for Citizen Science. JOANNA GORDON, Ashley Collier, Ricardo Piedrahita, Nicholas Masson, Michael Russel, Michael Hannigan, *University of Colorado at Boulder*

Recent strides in MEMS design and fabrication techniques have brought about a new generation of low cost gas phase sensors that can be incorporated easily into portable monitors. The two most common types of sensors employed are metal oxide and electrochemical. An integrated circuit can be populated with multiple sensors, yielding an inexpensive, versatile tool that is capable of measuring a number of gas phase chemical species, and that can be tailored to a variety of applications.

Ambient air instrumentation is often bulky and expensive, but yields good data quality. Because of their cost and complicated operability, most air instruments are out of reach for curious or concerned citizens. Low cost air quality monitors are well suited for use in citizen science efforts, in which community members or students can be engaged at various levels in data collection and processing, to better understand both their local air quality and scientific methods. To ensure success with the low cost monitors, the quality of the resultant data must undergo continuous evaluation. Citizens could simply operate the instruments, or could become more engaged in data analysis, where challenges such as sensor cross sensitivity can be addressed.

We have developed low cost air quality monitors (U-PODS) and are working with environmental science interns from Dine College and Haskell University to better characterize air quality in their local environment. A critical component of these collaborations is data quality assessment, which we are working to improve upon through these initial efforts. The citizen scientists (the interns) are engaged in the research at a participatory science level, in which they work to develop the research question, plan the field campaign, deploy the instruments, and collect the data. By collecting and annotating data, the interns are empowered to make observations and form new questions.

8UA.1

United States National PM2.5 Chemical Speciation Monitoring Networks – CSN and IMPROVE: Description of Networks. PAUL A. SOLOMON, Jeff J. Lantz, Dennis Crumpler, James B. Flanagan, R.K.M. Jayanty, Edward E. Rickman, Charles McDade, Lowell Ashbaugh, *U.S. EPA, Office of Reserach and Development, Las Vegas, NV*

EPA initiated the national PM2.5 Chemical Speciation Monitoring Network (CSN) in 2000 to support evaluation of long-term trends and to better quantify source impacts of particulate matter (PM) in the size range below 2.5 micro-meter aerodynamic diameter (PM2.5). The network peaked at about 200 sites in 2005. In response to the 1999 Regional Haze Rule and the need to better understand the regional transport of PM, EPA also augmented the long existing Interagency Monitoring of Protected Visual Environments (IMPROVE) visibility monitoring network in 2000, adding nearly 100 additional IMPROVE sites in rural Class 1 Areas across the country. The IMPROVE network peaked to about 170 sites in 2004. Both networks measure the major chemical components of PM2.5 using historically accepted filter-based methods. Components measured by both networks include major anions, carbonaceous material, and a series of trace elements. CSN also measures ammonium and other cations directly whereas IMPROVE estimates ammonium assuming complete neutralization of the measured sulfate and nitrate. IMPROVE also measures chloride and nitrite. In general, the field and laboratory approaches used in the two networks are similar; however, there are numerous, often subtle differences in sampling and chemical analysis methods, shipping, field quality control practices, and data handling and flagging. These could potentially impact merging the two datasets when used to better understand source impacts and the regional nature and long-range transport of PM2.5. This presentation describes these networks as they existed in 2001 to 2006, outlines differences in field and laboratory approaches, provides a summary of the analytical parameters that address data uncertainty, and summarizes major network changes since 2006.

8UA.2

Consistency of Long-term Black Carbon Trends from Thermal and Optical Measurements in the U.S. IMPROVE Network. L.-W. ANTONY CHEN, Judith Chow, John Watson, Bret Schichtel, *Desert Research Institute*

Decreasing trends of black carbon (BC), also termed elemental carbon (EC) as determined by thermal/optical analysis, have been reported at the U.S. IMPROVE (Interagency Monitoring of PROtected Visual Environ-ments) network from 1990 to 2004, consistent with the phase-in of cleaner engines, residential wood combustion technologies, and prescribed burning smoke mitigation practices. BC trends for the past decade (2000–2009) are examined in this study to address an upgrade of IMPROVE carbon instruments at 2005. The 2005 upgrade led to a transition from the IMPROVE to IMPROVE_A protocol. The new protocol does not change the temperatures plateaus but rather reflect the “actual” analysis temperatures that have been implemented since the inception of the IMPROVE network. It also enables simultaneous monitoring of filter reflectance and transmittance for charring correction. Filter attenuation determined from reflected light (T_R) provides an independent measure of light absorption coefficient as well as BC on the filter. Digital thermograms of > 83 000 samples from 65 IMPROVE sites from 2000 through 2009 were reprocessed to obtain the T_R values. The changes in regression coefficients between BC and T_R before and after 2005 were examined, and relationships between BC measured from the two periods (2000–2004 versus 2005–2009) were established. The variability is shown to be within ±10% in general with larger deviations occurring for high or low extreme BC levels. BC and T_R trends assessed using a nonparametric test show universal decreasing trends across the U.S. The trends are well correlated, with national average downward rates (relative to the 2000–2004 baseline medians) of 4.5 %/yr for BC and 4.1 %/yr for T_R. The consistency between BC and T_R measurements adds to the weight of evidence that BC reductions are real rather than an artifact of changes to the measurement process.

8UA.3

Evaluation of Fine Particulate Matter (PM2.5) and Ultrafine Particulate Matter (PM0.1) in the Airshed of Tijuana, BC - San Ysidro, CA Border. JAVIER EMMANUEL CASTILLO QUIÑONES, Guillermo Rodriguez, Penelope Quintana, Nina Bogdanchikova, *Universidad Autónoma de Baja California, Tijuana, México*

The location of the Tijuana-Rosarito-San Diego within the same air basin has generated implications deteriorating air quality. Recent studies indicate that the levels of PM2.5 and PM0.1 in urban air show a high correlation with carbon monoxide (CO) and black carbon (BC) which are associated with vehicle emissions. This study presents the results of the evaluations performed in 3 simultaneous monitoring sites in Tijuana, México, and 3 monitoring sites in San Ysidro, USA, during the Cal-Mex campaign in 2010, to understand the spatial and temporal variability in fine and ultrafine particulate matter, to identify the potential source areas, and to assess the cross-border transport of these air pollutants.

Overall, during the campaign, PM2.5 and PM0.1 concentrations at sites located in Tijuana was 1.6 and 1.7 times greater than that presented in the sites of San Ysidro, respectively. PM2.5 and PM0.1 15 minutes average concentrations (± SD) for sites in San Ysidro was 16.2 (± 10.1) µg/m3 and 5186 (± 2635) pt/cm3, whereas for sites in Tijuana was 26.6 (± 19.8) µg/m3 and 8919 (± 4577) pt/cm3.

Average PM2.5 values show the trend of presenting high concentrations during daytime and low concentrations during nighttime. BC levels are up 10-20% compared to the levels of PM2.5 and this relationship is consistent with other studies that evaluated air quality by mobile sources. Correlation between concentrations of BC and PM2.5 indicate that probably generating emission sources are the same, suggesting that the main source is the fleet. Averages of PM0.1 presented at both sites were higher in daytime, which indicates that probably the biggest contribution is from mobile sources. In UABC, one of the measurements site in Tijuana, presents high levels of PM0.1 were observed at 13:00-14:00 and 02:30-03:30 hrs. due to plentiful arriving and departed aircrafts those times in the city's airport.

8UA.4

Evaluation of PM10 Trace Metals in the Airshed of Tijuana, México. YANETH GUTIERREZ, Guillermo Rodriguez, Penelope Quintana, Nina Bogdanchikova, Miguel Zavala, Luisa Molina, *Universidad Autonoma de Baja California, Tijuana, Mexico*

Trace metal associated to PM10 in the urban air basin of Tijuana, B C, Mexico, where local industries, transportation, and urbanization are adversely affecting air quality. Air sampling was done in four sampling sites: commercial (SS1), traffic (SS2), residencial (SS3) and industrial area (SS4), using a high-volume sampler and metals were estimated in PM10 by ICP-OES analysis. To distinguish soil suspension from anthropogenic input, enrichment factor was calculated for site and seasonally variations. An daily and annual mean PM10 was calculated for SS1 to SS4, three dayly violations was found related to (SS2) and (SS3) (120 µg/m3) and three annual violations corresponding to (SS!, SS2 and SS4) only residential (SS3) was inside anual PM10 mean (50 µg/m3), related to mexican regulation NOM-025-SSA1-1993 during 2012 and 2013.

The PM10 metals concentration and enrichment factor related to urban background were calculated for Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Se, Sr, Zn, and compared with those reported in literature for other regions. Metals concentration with enrichment factor greater than 10, means that is generated by an antropogenic emission thus SS: metal relation is as follow: for SS1 (As, Cu, Zn), SS2 (Cu, As), SS3 (As, Cu, Zn) and SS4 (Cu, Zn, Ni, Pb). Highest levels was found for Lead at industrial area, Cooper for comercial, Arsenic for residential, and Zinc in all SS.

Metals concentration average difference between the sampling sites and corresponding urban background aerosol was influenced by metereology and site activities.

8UA.5

Correlation between Atmospheric Visibility and the Physical Properties and Chemical Compositions of Aerosol. CHISUNG LIANG, Sheng-Kai Jan, Jin-Yuan Syu, Wen-Yinn Lin, *Institute of Environmental Engineering and Management*

This study investigates the correlation between atmospheric visibility and the chemical composition and physical properties (number concentration, surface area concentration, and volume concentration) of aerosols. In order to understand how urban and suburban aerosol influence visibility, we collected the data from Taipei City and Yunlin County during four seasons. Ambient aerosol were sampled and analyzed for 12 constituents: water-soluble ionic species (Na+, NH4+, K+, Mg2+, Ca2+, F-, Cl-, NO3- , S042-) and carbonaceous contents (OC, EC, and TC). The result showed that the number concentration of particles increased significantly in the evening and morning when compared with other times, probably due to the effect of mobile sources in rush hours. Comparing the number concentration, surface area concentration, volume concentration with regards to their influence on visibility, the study finds that surface area concentration is most strongly correlated with visibility. The composition of ion and carbon affected the size of particles and so did the relative humidity. When relative humidity reached 70%, the atmospheric water affected the suspended size of particles. During the winter, the particle size and concentration of the water-soluble ionic species were smaller than in the fall. The results will be discussed in detail in this paper.

8UA.6

Characterization and Near-Field Evolution of Fine Particles Emitted by a Metallurgy Plant: Results of the NANO-INDUS Project. ARI SETYAN, Pascal Flament, Karine Deboudt, Nadine Locoge, Véronique Riffault, Laurent Alleman, Coralie Schoemaecker, Jovanna Arndt, Patrick Augustin, François Blond, Fabrice Cazier, Hervé Delbarre, Dorothée Dewaele, Pascale Dewalle, Marc Fourmentin, Paul Genevray, Robert Healy, Philippe Le Louer, Thierry Leonardis, Hélène Marris, Saliou Mbengue, Mickaël Starosta, John Wenger, *Université du Littoral Côte d'Opale*

Industrial areas can be a significant source of particulate pollution and companies are therefore required to measure the particle concentration emitted from stacks. However, the physico-chemical properties of the particles leaving an industrial area are often poorly characterized and there is little information on the evolution of the plume between the source and the surrounding areas. The aim of the NANO-INDUS project is to study the evolution of the physico-chemical properties of industrial fine particles over a short-range distance, before they reach surrounding urban areas. First, measurements were performed directly at the stacks of a plant manufacturing iron-manganese alloy near Dunkirk, France. Separately, an intensive field campaign was undertaken at a site located close (<1 km) to the stacks.

The comparison between different air masses shows significant differences in terms of particle concentration, chemical composition and size distribution. Under air masses coming from the studied plant, the particle and gas (CO, CO2, NOx, SO2) concentrations were much higher than during periods dominated by urban or marine backgrounds. The concentration of non-refractory submicron particles (NR-PM1) was 10.2 µg/m3 on average, but displayed a huge variability likely due to plumes reaching the receptor site. These particles were dominated by inorganic species (67% of the total mass), with organics accounting for 33%. The concentrations of several metallic species (Fe, Mn, V, Cu) were higher than those typically observed at urban environments, and their presence is likely related to monitored industrial activities. The industrial plumes were also characterized by a high contribution of nitrate, a low contribution of sulfate, and a high Mn/Fe ratio, compared to other air masses.

In parallel, the physico-chemical properties of particles sampled at the stacks were compared to those determined at the near-field site, in order to assess their evolution over a short-range distance.

8UA.7

Wintertime PM2.5 in Edmonton, Alberta, Canada. MATTHEW PARSONS, Wally Qiu, Yayne Aklilu, Andrew Clayton, Amy MacTaggart, Rachel Mintz, *Environment Canada*

The Edmonton, Alberta area is located at the transition between boreal forest and northern Canadian prairies with a cold climate that can drop below -20 C in the winter but still receives among the most hours of sunlight in Canada. As the northern-most urban centre in North America with a population over 1 million and a hub for Alberta's energy-based industries, the Edmonton area is home to many sources (i.e., transportation, industrial, residential, agricultural) of primary particulate matter and precursor gases for secondary particulate matter. Stagnant meteorological conditions—especially in the wintertime—can lead to significantly elevated concentrations of PM2.5 (and other pollutants) in the area. In an effort to identify the most effective PM2.5 reduction strategies, this study attempts to better understand the meteorological and air quality scenarios during episodes of high PM2.5 concentrations through the use of trends, source apportionment, and other analyses of continuous monitoring data and 24-hour integrated PM speciation data.

8UA.8

Characterization of Size-segregated Particulate Matter in Houston TX. INKYU HAN, Yuncan Guo, *University of Texas School of Public Health*

Exposure to ambient particulate matter (PM) is a known risk factor for human health outcomes. While a number of studies have characterized ambient PM between 2.5 and 10 micro meter, limited information is available for the characterization of size-segregated PM including ultrafine particles (UFPs) except particle number concentrations. To characterize UFP in a highly populated urban area, size-segregated PM has been being measured in Houston TX since November 2012. One active sampling site (ASS) is located at a distance of 1 km on the east side of the I-610 freeway where passenger cars and diesel trucks pass by. The other sampling site is located on the roof of University of Texas School of Public Health (UTSPH) representing urban background without known significant combustion sources. At each site a cascade impactor sampler was simultaneously deployed and continuously collected PM for weekly. Size-segregated PM was collected on PTFE filters in 5 size fractions (coarse PM [larger than PM2.5], PM2.5-1, PM1-0.5, PM0.5-0.25, quasi-UFP [PM0.25]) during the weekly sampling periods. We planned to analyze mass concentrations and polycyclic aromatic hydrocarbons (PAHs) by different particle sizes for source apportionment in Houston TX. Between November 2012 and February 2013, preliminary results showed that weekly average concentrations of fine PM in ASS (11.64 micrograms/m3) were significantly higher than UTSPH (7.48 micrograms/m3). The weekly average concentrations of quasi-UFP in ASS (4.84 micrograms/m3) were also significantly higher than UTSPH (3.71 micrograms/m3). The preliminary results suggest that elevated levels of fine PM and quasi-UFP may be attributed to mobile sources during the sampling periods. The future study includes chemical analysis of individual PAHs for the source apportionment of both fine PM and quasi-UFP.

8UA.9

Metal Concentrations in Fine Particulate Matter from the Ground-Level Light Rail System in Denver Metro.

BENTON CARTLEDGE, Brian Majestic, *University of Denver*

Many studies have linked increased concentrations of airborne heavy metals, such as chromium, manganese, and iron, to subway systems. These higher concentrations have been investigated to determine potential health risks to personnel who operate or almost exclusively ride the subway. Health studies have shown that the inhalation of submicron particles with increased metal concentrations can lead to increased redox activity at the cellular level and heightened occurrences of cancers and respiratory illnesses. Very few studies have been performed examining the effects of ground-level, outdoor light rail transit systems. The current study focused on the light rail system in Denver, Colorado. Size-segregated air samples were collected using Sioutas personal cascade impactor samplers (PCIS) at three locations around downtown Denver. The first location was the background site located away from the light rail lines. The second site was one meter from the tracks as all five light rail lines entered and exited the downtown area. The third site was onboard the light rail trains. Samples were collected onboard all five lines each day. Outside samples were collected for 42 hours a week while onboard samples were collected 36 hours a week. Four sets of samples were collected from January 24 to February 16, 2012. Metal concentrations were determined via a strong acid digest in a microwave digestion system and analysis via inductively coupled plasma mass spectrometry (ICP-MS). Soluble iron and iron speciation was also determined by extracting the samples in a buffer and measuring UV absorbance on a long pathlength capillary cell spectrometer. Results suggest that higher metal concentrations (especially steel components) are found near and onboard the train. Soluble iron was determined to be present mostly as Fe(II). While these levels may not be as high as in subways, metal concentrations could still pose serious health risks.

8UA.10

Characterization of Coarse Aerosol in St. Louis and Phoenix: Results from EPA's 2010-2011 Pilot Study.

STEVEN BROWN, Jay Turner, Hilary Minor, Joann Rice, Paul Roberts, James B. Flanagan, Jeffrey Nichol, *Sonoma Technology, Inc.*

The coarse PM (PMc) pilot speciation study included one year of 1-in-3 day sampling at sites in Phoenix (AZ) and East St. Louis (IL), from June 2010 through May 2011. Among the instruments at each site were two Thermo 2025D sequential dichotomous (dichot) samplers, one Thermo 2025 sequential PM10 Federal Reference Method (FRM) sampler, and one Thermo 2025 sequential PM2.5 FRM sampler. Samples were collected on Teflon filters with Nylon filter backups for analysis of elements by XRF and of ions by ion chromatography, respectively, or quartz/quartz (Q/Q) filter sandwiches for analysis of carbon via thermal-optical analysis. PMc was directly measured via the dichot, and by the difference between PM10 and PM2.5 FRM concentrations.

On average, PMc at both sites was predominantly composed of crustal oxides, with 15% of the mass attributed to organic carbon (OC) and less than 5% of the mass attributed to other species such as sulfate and nitrate. Average PMc mass was 9.4 and 18.8 µg/m3, compared to fine PM mass of 10.7 and 7.6 µg/m3, at St Louis and Phoenix, respectively. Sum of species, assuming an OM/OC ratio of 1.6 and using standard equations for calculating crustal mass, exceeded measured mass at Phoenix by 13% and was 1% higher at St Louis. This finding that the PMc reconstructed mass is biased high, especially in Phoenix, suggests systematic errors in the estimation methodology, such as improper multipliers for estimating crustal PMc from elemental concentrations or x-ray fluorescence (XRF) attenuation corrections for light elements (e.g., Al, Si, Ca) that are too large. Further analysis of a subset of filters by ICP-MS suggested that the XRF attenuation corrections for crustal elements are too large, and will likely need to be revised prior to full-scale deployment of a national, routine monitoring network.

8UA.11

Source Characterization of Aerosol Metal and Trace Element Measurements in High-Time Resolution. CHEOL-HEON JEONG, Jon M Wang, Greg J. Evans, *SOCAAR, University of Toronto*

Traffic-related atmospheric pollutants often exhibit high temporal and spatial variability near roadways. Chemical compositional measurements in high-time resolution of particulate matter (PM) become crucial in order to evaluate exposure to these pollutants. Further, the variation in concentrations with time of day or meteorological conditions can help to elucidate and resolve the contributions of local traffic-related sources as compared to city-wide and regional scale sources. While versatile near real-time analytical methods of major inorganic and organic PM chemical species have been developed, the measurement of metals and trace elements in PM is often limited by labour-intensive conventional analysis, i.e., filter sampling methodology. Fast quantitative analysis of PM metals in conjunction with major organic/inorganic PM chemistry measurements can lead to more effective source identification.

Hourly concentrations of 23 metals including Ag, As, Ba, Br, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb, Rb, Se, Si, Sn, Sr, Ti, V, and Zn were measured by the Xact 625 Particulate Metal Monitor (Pall) in downtown Toronto, Canada. The Aerosol Chemical Speciation Monitor (ACSM, Aerodyne) was used for measuring the atmospheric sulphate, ammonium, nitrate, and organic matter in PM at a time resolution of 30 minute. The quantitative and optical properties of carbonaceous compounds were obtained by a field thermal-optical OCEC analyzer (Sunset Lab), a photoacoustic soot spectrometer (PASS, DMT), and a 7-wavelength aethalometer (AE33, Magee Sci).

This presentation will describe the contributions of different local sources and processes identified by applying positive matrix factorization (PMF) analysis to the high-time resolution PM speciation data. Temporal variability in PM sources at the metropolitan site will be further explored and presented.

8UA.12

Bacterial Bioaerosol Enrichment Downwind from a Conventional Wastewater Aeration Basin Manifests from Selective Actinomycete Partitioning. Mark T. Hernandez, JANE TURNER, Charles Robertson, Odessa Gomez, Alison L. Ling, Bharath Prithiviraj, J. Kirk Harris, Daniel N. Frank, Alina M. Handorean, Norman R. Pace, *University of Colorado at Boulder*

Over a period of eleven days, size segregated aerosols were collected in consecutive 24 hour sampling campaigns, which were simultaneously executed upwind and downwind of a conventional activated sludge wastewater treatment plant. Airborne particulate matter was separated by mean aerodynamic diameter and continually impacted on polycarbonate filters, which were subsequently extracted with ethanol and chloroform to isolate and purify DNA. As judged by analyses of 16s rDNA sequences from an Illumina Miseq platform, airborne bacteria immediately downwind from the aeration basin was enriched with Actinomycetes when compared to the airborne microbes recovered upwind of this site. Concurrent DNA analyses of the activated sludge suggest that the aerated wastewater was the source of the airborne Actinomycetes, and that selected genera were selectively partitioning into a local bioaerosol which included, but was not limited to, Mycobacteria spp., Saccaropolyspora spp., and Streptomyces spp.. Laboratory studies using log-growth pure cultures of Mycobacterium parafortuitum and Psuedomonas aurigenosa as models, showed that M. parafortuitum cells have a markedly higher partitioning potential from warm, aerated waters than do P. aeruginosa cells. These results suggest than engineering works purposely designed to entrain air bubbles in temperate waters can induce a selective partitioning of bacteria into aerosols, and that bioaerosol partitioning potential is related to microbial physiology.

8UA.13

An Assessment of Particulate Air Pollution in Jeddah, Saudi Arabia. HAIDER A KHWAJA, Omar S. Abu-Rizaiza, Azhar Siddique, Abdullah Aburizaiza, Shedrack R. Nayebare, Mirza M Hussain, Jahan Zeb Qurashi, Jamal Qethmi, David Carpenter, Zafar Fatmi,*King Abdulaziz University, Jeddah, Saudi Arabia*

Urban air pollution is rapidly becoming a major environmental problem of public concern in several developing countries of the world. It can influence public health and local/regional weather and climate. Ambient air pollution in major cities of Saudi Arabia is a substantial environmental and health concern. The present study was undertaken to assess the particulate air pollution of a major city of Saudi Arabia. The 24 h concentrations of respirable particulate matter (PM2.5) were collected at a fixed site. BC measurements were obtained from PM2.5 filters using an optical transmissometer. PM2.5 and BC concentrations in the city ranged 23 - 186 µg/m3, 0.70 – 3.09 µg/m3, respectively. The mean concentration was 74.2 µg/m3 and 1.53 µg/m3 for PM2.5 and BC, respectively, with significant temporal variability. Maximum BC contribution to PM2.5 was 5.6%. Atmospheric PM2.5 concentrations were well above the 24 h WHO guideline of 20 µg/m3. An Air Quality Index (AQI) was calculated for PM2.5 at Jeddah, with highest pollutant-specific value reported as a “level of health concern” (moderate: 16 - 35 µg/m3, unhealthy for sensitive groups: 36 - 65 µg/m3, unhealthy: 66 - 150 µg/m3, very unhealthy: 151 - 250 µg/m3, and hazardous: 251 - 300 µg/m3). Based on the AQI, it is evident that there were 8% days of moderate air quality, 28% days of unhealthy air quality for sensitive groups, 55% days of unhealthy air quality, and 9% days of very unhealthy air quality during the study period. Results suggest that major sources of emissions affecting Jeddah include industrial sources along with contributions from mobile sources and wind-blown dust. This study highlights the importance of focusing control strategies not only on reducing PM concentration, but also on the reduction components of the PM as well; to most effectively protect human health and the environment.

8UA.14

Effects of Diesel Particle Filters on the Size Distribution of Emitted Particles. CHELSEA PREBLE, Nicholas Tang, Timothy Dallmann, Nathan Kreisberg, Susanne Hering, Robert Harley, Thomas Kirchstetter, *University of California, Berkeley*

Diesel particle filters (DPFs) reduce the mass of particles emitted from diesel trucks. However, there may be some unintended consequences of using these filters, such as a concomitant increase in emission of ultrafine particles (UFPs). UFPs are not specifically regulated by current air quality standards but they may pose a health risk that larger particles do not because of their small size (< 100 nm in diameter).

The present study measured pollutants emitted from trucks at the Port of Oakland, California in November 2011. At this location, the California Air Resources Board’s Drayage Truck Regulation required replacement of trucks with pre-1994 engines and retrofit with diesel particulate filters (DPFs) of trucks with newer engines. The size distribution of particles in the exhaust plumes of individual heavy-duty trucks en route to the Port were measured at a frequency of 1 Hz using a Fast Mobility Particle Sizer (FMPS, TSI model 3091). Emissions were linked on a truck-by-truck basis to installed emission control equipment via the matching of transcribed license plates to a Port truck database.

This analysis examines particle size distributions in the exhaust of trucks (1) retrofitted with DPFs, (2) equipped with DPFs as original equipment, and (3) not equipped with DPFs. Preliminary findings indicate that (a) most trucks emitted particles characterized by a single mode of approximately 100 nm in diameter and (b) new trucks originally equipped with DPFs were 5 to 6 times more likely than DPF-retrofitted trucks and trucks without DPFs to emit particles characterized by a single mode in the range of 10 to 30 nm in diameter. This analysis also indicated a sampling artifact of the FMPS, which overstates the presence of ultrafine particles on the trailing side of a peak when concentrations are rapidly decreasing.

9AC.1

Modeling SOA Formation in Mixed Anthropogenic Biogenic Plumes. MANISHKUMAR SHRIVASTAVA, Jerome Fast, Alla Zelenyuk, John Shilling, Chen Song, Richard Easter, Qi Zhang, Rahul Zaveri, Ari Setyan, *Pacific Northwest National Laboratory*

During the Carbonaceous Aerosols and Radiative Effects Study (CARES) conducted in June 2010 near Sacramento, a suite of ground based and aircraft instruments measured organic aerosol (OA) in mixed anthropogenic-biogenic plumes and also in relatively non-mixed conditions depending on ambient winds. In this study, we investigate the ability of the Weather Research and Forecasting model coupled with chemistry (WRF-Chem) to simulate secondary organic aerosol (SOA) formation. We investigate challenges in representing either anthropogenic or biogenic SOA formation using the volatility basis set (VBS) approach. These include poorly constrained SOA precursor emissions, gas-phase aging parameterizations which have excluded fragmentation reactions, non-representative SOA yields measured in smog chambers, and our previous findings which suggest it rapidly transforms into a non-volatile and non-absorbing semi-solid due to particle phase processes as oligomerization. We show that before investigating the nature and magnitude of recently proposed anthropogenically enhanced biogenic SOA formation, models need to better constrain the individual contributions of anthropogenic and biogenic SOA in non-mixed plumes. After constraining our SOA model in regions dominated by either anthropogenic or biogenic SOA, we investigate the expected synergistic effects between anthropogenic and biogenic SOA formation in mixed plumes. In addition, we explore some additional mechanisms for enhanced biogenic SOA formation depending on VOC and NOx levels and peroxy radical chemistry, mainly related to anthropogenic emissions. We conduct model sensitivity to different OA mechanisms and evaluate the spatial and temporal variation of simulated OA against ground-based and aircraft measurements. We also investigate the role of delta OA to delta CO ratios which have been used to compare SOA formation in previous studies.

9AC.2

In-Situ Chemical Characterization of Sub-micron Organic Aerosols Using Direct Analysis in Real Time Mass Spectrometry (DART-MS): The Effect of Aerosol Size and Volatility. MAN NIN CHAN, Theodora Nah, Kevin Wilson, *Lawrence Berkeley National Laboratory*

Direct Analysis in Real Time (DART) mass spectrometry is an atmospheric pressure ionization technique suitable for in situ chemical analysis of organic aerosols. The mass spectra are obtained by introducing a stream of nanometer-sized aerosols into the ionization region, which is an open space between the DART ionization source and the atmospheric inlet of mass spectrometer. Model single component aerosols are used to show how the aerosol size and volatility influence the measured ion signals at different DART gas temperatures.

We found that for equivalent aerosol mass concentrations, the ion signal scales with particle surface area, with smaller diameter oleic acid aerosols yielding higher ion signals relative to larger diameter aerosols. For the aerosols of the same size, but different vapor pressures, the ion signal is larger for more volatile succinic acid aerosols than less volatile adipic and suberic acid aerosols. While the aerosols are not completely vaporized in the ionization region, the radial probing depth for these model aerosols range from 1 to 10 nm. The magnitude depends upon the physiochemical properties of the aerosols and DART gas temperature. An aerosol evaporation model is proposed to explain the correlation between the measured ion signal and aerosol size and volatility. We also demonstrate the potential application of DART for in situ chemically analyzing wet aerosol particles.

9AC.3

Chemical Analysis of Organic Aerosols Using Reactive Nanospray Desorption Electrospray Ionization Mass Spectrometry.

ALEXANDER LASKIN, Julia Laskin, Sergey Nizkorodov, *Pacific Northwest National Laboratory*

Nanospray Desorption Electrospray Ionization (nano-DESI) technique integrated with high resolution mass spectrometry (HR-MS) enables molecular-level analysis of organic aerosol (OA) samples. In nano-DESI, analyte is desorbed into a small volume solvent bridge formed between two capillaries positioned in contact with analyte and enables fast and efficient characterization of OA collected on substrates without sample preparation. We report applications of the nano-DESI/HR-MS approach in a number of our recent studies focused on molecular identification of organic compounds in laboratory and in field collected OA samples. Reactive nano-DESI approach where selected reagent is added to the solvent is used for examining the presence of individual species containing specific functional groups and for their quantification within complex mixtures of OA. Specifically, we use the Girard's reagent T (GT) to probe and quantify carbonyl compounds in the SOA mixtures. We estimate for the first time the amounts of dimers and trimers in the SOA mixtures. We found that the most abundant dimer in limonene/O3 SOA was detected at 0.5 pg level and the total amount of dimers and trimers in the analyzed sample was 11 pg. Understanding of the OA composition at the molecular level allowed us to identify key aging reactions, including the transformation of carbonyls to imines and carbonyl-imine oligomerization, that may contribute to the formation of brown carbon in the atmosphere.

9AC.4

Investigating Chemical Variation in Particulate Matter during the Polarimetric Cloud Analysis and Seeding Test (POLCAST) 2012 Campaign in Grand Forks, North Dakota.

RICHARD COCHRAN, Haewoo Jeong, David Delene, Alena Kubatova, *University of North Dakota*

Organic material accounts for a large fraction of particulate matter (PM) in the atmosphere and can have an influence on our climate. Additionally many organic constituents within the organic fraction have been attested to various negative effects on human health. The sources of the thousands of compounds typically present within PM include primary emissions through various anthropogenic and natural sources as well as through oxidation pathways leading to secondary organic products or SOA. Chemical variation among PM in different environments is a product of different primary emission sources as well as the extent to which secondary oxidation reactions occur. While many natural and anthropogenic primary emission sources have been evaluated in terms of their contribution to the chemical fingerprint of PM studies, the data assessing the contribution of harvesting activities on chemical variance is limited. In this work we investigate organic (OC) and elemental (EC) carbon content as well as the chemical speciation of PM filter samples collected in weekly cycles through a sixteen week campaign in Grand Forks, ND. Filter collection began in early summer and extended through the local harvesting season during late summer/early fall. Filter samples were collected in parallel with PM measurements from a scanning mobility particle sizer, tapered-element oscillating microbalance, and a cloud condensation nuclei counter. OC and EC content of all filters samples were determined using a thermal optical analyzer. For chemical speciation of the collected filter samples a thermal desorption/pyrolysis-gas chromatography/mass spectrometry method was deployed. Variations in classes of compounds (i.e., alkanes, alkenes, polycyclic aromatic hydrocarbons and their oxidation products, etc.) and individual species throughout the campaign were evaluated.

9AC.5

A New Inlet for Simultaneous Gas and Particle Phase Measurements Coupled to a Chemical Ionization High-resolution Time-of-Flight Mass Spectrometer. CLAUDIA MOHR, Felipe Lopez-Hilfiker, Ben H. Lee, David S. Covert, Douglas Worsnop, Joel A. Thornton, *University of Washington*

We present data from a newly developed inlet coupled to a chemical ionization high-resolution time-of-flight mass spectrometer (CI-HRToF-MS). The inlet allows simultaneous measurements of the chemical composition of organic compounds in both the gas and the particle phase, crucial for partitioning studies. This new inlet has the following features:

- The gas and particle phase inlets are separate up to the entrance to the mass spectrometer, allowing separate flow, pressure, and temperature conditions for both channels. Thus artifacts in the particle phase due to gas adsorption to surfaces are minimized.
- Particles are collected on a PTFE filter and subsequently desorbed using heated UHP N_2 or zero air programmed to temperatures up to 200 °C allowing for volatility studies. Measured thermograms are of equal quality as any metal surface we've tested.
- The PTFE filter collects particles with diameters between 10 and 1000 nm with > 99.9% efficiency, and has minimal gas adsorption effects.
- In addition, the PTFE filter does not suffer from size-dependent collection as do inertial impactors.

This new inlet coupled to a CI-HRToF-MS provides intriguing new possibilities to explore organic and inorganic compounds in the atmosphere in both the particle and the gas phase. It has successfully been tested at the plant aerosol atmosphere chamber facility (JPAC) at Forschungszentrum Jülich, Germany, and using a 1 m^3 teflon bag at the University of Seattle to study products of alpha-pinene ozonolysis and reaction with OH.

We discuss results from deployment of the new collector coupled to an HR-ToF-CIMS as part of chamber experiments and spring and summer field campaigns in systems dominated by biogenic emissions (alpha-pinene and isoprene). We also discuss the first results from the implementation of a MOUDI (Micro-Orifice Uniform Deposition Impactor) upstream of the PTFE filter of the inlet to study the chemical composition of sub-100 nm particles, specifically.

9BA.1

Continuous Measurements of Biological Particles with the Wideband Integrated Bioaerosol Sensor (WIBS-4A). GAVIN MCMEEKING, Greg Kok, Gary Granger, Darrel Baumgardner, *Droplet Measurement Technologies, Boulder, Colorado, USA*

The WIBS-4A measures five properties of sampled individual particles: a) optical size via light scattering, b) fluorescent emissions in the wavelength range 310-400 following excitation by 280 nm light, c) fluorescent emissions in the wavelength range 420-650 following excitation by 280 nm light, d) fluorescent emissions in the wavelength range 420-650 following excitation by 360 nm light, and e) particle asymmetry factor based on intensities of forward scattered light onto a 4-element detector. Together, these properties aid the classification of sampled particles that contain biofluorophores such as tryptophan or NADPH, which are found in biological particles. Here we present results from a series of field and laboratory measurements of biological particles using the WIBS-4A, which took place mostly in Colorado, USA. The experiments focused on both the characterization of the instrument response as well as demonstration of its suitability for performing ambient measurements. We also describe several modifications to the original WIBS design and explore different data collection and analysis methods that may be useful in future deployments. Finally, we discuss several on-going and planned measurement campaigns using the instrument.

9BA.2

Using Real-time Multiband Fluorescence Signatures to Discriminate between Bioaerosol Classes. Darrel Baumgardner, Kevin McCabe, Greg Kok, Gary Granger, MARK T. HERNANDEZ, *University of Colorado Boulder*

Ultraviolet laser induced fluorescence (UV-LIF) is gaining increased attention for its ability to rapidly identify large numbers of airborne particles, which contain materials of primary biological origin. While a new generation of commercial UV-LIF instruments has demonstrated the utility of particle fluorescence in a multitude of field trials, the resolution of these instruments in discriminating between different classes of aerobiological particles remains to be catalogued.

We report here the characteristic responses of a Waveband Integrated Bioaerosol Sensor (WIBS-4) to recognize bioaerosols which serve as model aerobiological classes germane to public health. A research grade WIBS instrument was challenged in environmentally controlled chamber with pure cultures of airborne vegetative bacteria, bacterial spores, fungal spores and pollen grains. Following calibrations, the instrument was used to continuously monitor airborne particle loads under both dry and humid conditions containing the following (pure culture) bioaerosols: vegetative Gram positive bacteria of Bacillus subtilis, aerosolized at various stages of their growth cycle, (azide) inactivated cells, and nascent bacterial spores. The more common fungal spores, including but not limited to Aspergillus, Alternaria, Penicillium, Chaetomium, and Cladosporium spp., as well as more than 15 species of temperate pollen grains were included in these aerosol challenges: Acer, Alnus, Ambrosia, Artemesia, Betula, Carya, Eucalyptus, Fragus, Juglands, Juniperous, Morus and Phelum spp.

Distinct fluorescent signatures emerged which corresponded to phenotypic groupings as challenged in the following channels: emission between 310–400 nm, and 420–650 nm wavebands following 280 nm excitation; and, subsequent emission in a 420–650 nm waveband following 370 nm excitation. As judged by relative intensity, the ratio of 280/370 excitation response in the 420-650 nm bandwidth is a sensitive metric which can be used to resolve fungal spores from pollen. These results suggest that with an expanded library, multi-channel LIF offers a reliable platform for phenotypic bioaerosol discrimination.

9BA.3

Measurements of Changes in the Fluorescence and Viability of Biological Particles Exposed to Outdoor Conditions in the Washington D.C. Metro Area. JOSHUA SANTARPIA, Don Collins, Yong-Le Pan, Shanna Ratnesar-Shumate, Crystal Glen, Andres Sanchez, Steven Hill, Carlos Antonietti, Jill Matus, Nathan Taylor, Christopher Bare, Sean Kinahan, Elizabeth Corson, Danielle Rivera, Mark Coleman, Chatt Williamson, *Sandia National Laboratories*

Biological aerosols are studied for many reasons, including their effects on cloud properties as both cloud condensation and ice nuclei. Predominantly, however, biological aerosols are studied for their effects on human, plant and animal health. This can range from allergy to disease and is often concerned with detection and measurement of bioaerosols used as biological weapons. A variety of methods have been used to study atmospheric bioaerosols. One of the most often used of these techniques is the natural fluorescence of biological particles when excited by ultraviolet light. In October, 2012 we examined the changes in the fluorescence spectra and viability/infectivity of biological aerosol particles seeded into a chamber that exposed them to ambient conditions in Adelphi, MD for periods of several hours. The Captive Aerosol Growth and Evolution (CAGE) chambers used in this study employ a rotating drum constructed with an exterior FEP Teflon film, to allow sunlight to penetrate, and an inner ePTFE membrane to allow ambient trace gasses to permeate the drum, while still containing the biological particles being studied. Biological aerosol particles were sampled with a TSI UV-APS (ex. 355 nm), a Single Particle Fluorescence Spectrometer (ex. 351 and 263 nm) and AGI-30 impinger. The data indicate that significant changes in both fluorescence and viability/infectivity of both Bacillus thuringiensis var. kurstaki spores and MS2 bacteriophage particles occurred during replicate experiments. Solar intensity, relative humidity and ozone concentration were measured locally, and other meteorological data and air quality measurements were retrieved from a local Maryland Department of Environmental Quality monitoring site. The observed changes in these particles appear to be due to a combination of factors, rather than any single factor. These observations indicate that biological aerosol properties may be significantly changed by aerosol processes, and that these changes may affect measurement by UV-LIF.

9BA.4

Design and Performance of Low-cost Aerosol Micro-Channel Collector. IGOR NOVOSSELOV, Riley Gorder, John Scott Meschke, *Enertechnix, Inc*

Bio-aerosol detection and identification is vital for assessment and control of airborne pathogens, allergens and toxins. A low-cost bio-aerosol collector was developed and tested at flow rates of 1- 3 slpm. Unsteady, 3-D computational fluid dynamics (CFD) modeling was used to develop and optimize the designs of the micro-Channel Collector (micro-CC). The collector can be readily integrated with microfluidic detection devices where a variety of assays may be performed. The performance of the low-cost collector has been validated in laboratory studies using polystyrene spheres, single organism bacterial spores (Bacillus subtilis). Collection efficiency tests of the sampler were performed in a well-mixed aerosol chamber using aerosolized fluorescent microspheres in the 0.8 to 5 micro-meter diameter range. The samples were collected in the micro-CC and eluted into a 100 microliter liquid volume. Culture and PCR methods were used to determine the performance of the biological aerosols. Typical efficiencies of the sampler are 50 % for 0.5 micro-meter particles and 90% for particles larger than 1 micro-meter. The experimental results agree with the CFD modeling, showing that concentration and capture efficiency of polystyrene spheres and microorganisms are a function of their aerodynamic diameters.

9BA.5

A Relaxed-Eddy Accumulation System for Measuring Microbial Emission Fluxes from the Vegetation. YVES BRUNET, Jean-Marc Bonnefond, Didier Garrigou, Frédéric Delmas, Christel Leyronas, Cindy E. Morris, *INRA Bordeaux, France*

Evidence has been gathered that a substantial proportion of atmospheric micro-organisms originates from plant canopies. However, only very few field measurements of surface fluxes have been performed so far, so that the emission and deposition rates of biological aerosol particles are still largely unknown. One major reason for the lack of experimental data is that such measurements are difficult: (i) fast-response sensors, as required by the reference eddy-covariance method, do not exist for biological particles, and (ii) the gradient method, where the flux is estimated from the concentration difference between two levels above the surface, is only applicable at “ideal” field sites. One potential alternative is the “relaxed-eddy accumulation” method (REA) that has been developed for scalar species for which no fast concentration measurements can be collected. Here we investigate the possibility of adapting the REA method to the measurement of microbial emission from vegetated surfaces. After a presentation of the underlying principles of REA and its conditions of use in the field, we describe a prototype that has been recently built. The system has been tested over four field campaigns, during which the performances of several particle-sampling sensors have been evaluated (impactors, virtual impactors, filters). The first results are given along with a list of recommendations and issues to be solved.

9IM.1

Advances in Water Condensation Particle Collectors and Concentrators. GREGORY LEWIS, Steven Spielman, Arantzazu Eiguren-Fernandez, Susanne Hering, *Aerosol Dynamics Inc.*

We describe advances in our three-stage laminar flow water condensation system for particle collection. The three-stage system has a lower output temperature and dew point, which provide sub-saturated flow at room temperature. Particles as small as 8 nm can be activated and grown without exceeding 25 degrees C in the majority of the flow. This makes the approach amenable to the sampling of volatile and biological materials. We have coupled the growth tube with an aerodynamic focusing nozzle, increasing the flow rate to 5 lpm without increasing the liquid sample volume. The new continuous wick design conserves water, lengthens the life of the wick, and eliminates a water reservoir. This design avoids potential flooding problems if the inlet is inadvertently blocked and allows the collector to be operated in any orientation.

9IM.2

Towards a Miniature, Tippable, Water Condensation Particle Counter. SUSANNE HERING, Gregory Lewis, Steven Spielman,*Aerosol Dynamics Inc.*

Using the three stage growth concept coupled with a continuous wick, we have developed a laminar-flow, water-based condensation particle counting method that is potentially small and portable. Our prototype instrument can be operated in any orientation, as there are no water reservoirs. It runs for several days without addition of water. The continuous wick spans three temperature regions, the middle one of which is warmer than the other two. Water evaporation from the warmed, middle section provides the water vapor that creates the supersaturation for particle activation and growth. This water vapor is recovered by the cooler, downstream section of the wick and transported back to the warmed mid-section via capillary action. This approach has been demonstrated successfully for sampling both dry and humid air. We have attained four days of continuous operation, without addition of water, for typical room conditions, ie 30-70% RH at 20-25°C. Measured particle number concentrations are within 10% of those from a bench-top WCPC. This approach should be miniaturizable, with potential as a wearable instrument for ultrafine particle number concentration monitoring.

9IM.3

Laboratory Characterization of a Size-Resolved CPC Battery to Infer the Composition of Freshly Formed Atmospheric Nuclei. CHONGAI KUANG, Juha Kangasluoma, Daniela Wimmer, Katrianne Lehtipalo, Jian Wang, Markku Kulmala, Tuukka Petäjä, *Brookhaven National Laboratory*

Atmospheric particle nucleation is an important environmental nano-scale process, with climate models indicating that nearly half of the global cloud condensation nuclei (CCN) may be formed from freshly nucleated particles. However, our understanding of atmospheric nucleation and its influence on climate is limited since few direct measurements have been made of either the nucleation rate or the chemical composition of the freshly formed clusters. In this study, we have developed an instrument to infer the size-resolved composition of freshly formed atmospheric particles, addressing a key knowledge gap in the composition of nucleated aerosol below 3 nanometers. This size-resolved condensation particle counter battery (SR-CPCb) is composed of a nanoparticle mobility spectrometer that has been optimized for the sampling and mobility classification of sub 3 nanometer particles. By sampling mobility-classified particles, the SR-CPCb accounts for the strong dependence of CPC detection on particle size and charge below 2 nanometers. Any measured differences in CPC response can then be attributed to composition-specific interactions between the particle and the various working fluids. The CPCb utilizes the following CPCs with their accompanying working fluids: a Particle Size Magnifier (diethylene glycol), a DEG-UCPC (diethylene glycol), a TSI 3786 UCPC (water), and a TSI 3025A UCPC (butanol). The following methods were used to generate challenge aerosols for the CPCb characterization: (1) electrospray generation of molecular ion mobility standards, (2) evaporation of solid sodium chloride via tube furnace, (3) evaporation of solid ammonium sulfate via tube furnace, (4) tungsten oxide formation via a wire generator, (5) candle aerosol generation, (6) limonene ozonolysis in a flow tube reactor, and (7) electrospray generation of sucrose. Presented results will include the particle composition dependent response of the SR-CPCb.

9IM.4

Method for Calibration of the Detection Efficiency of Condensation Particle Counters at Concentrations as Low as 1 cm^{-3} Using a Faraday-cup Aerosol Electrometer. HIROMU SAKURAI, Kensei Ehara, *AIST*

We developed a method to calibrate the detection efficiency of condensation particle counters (CPCs) that utilizes a Faraday-cup aerosol electrometer (FCAE) as reference at concentrations down to 1 cm^{-3}. In a conventional CPC calibration using an FCAE as reference, the CPC under calibration and the reference FCAE sample aerosols of the same concentration after the flow splitter, and the ratio of the concentration indicated by the CPC under calibration to that by the reference FCAE essentially gives the detection efficiency of the CPC under calibration if the reference FCAE is calibrated. In our method, a diluter is inserted between the inlet of the CPC under calibration and the flow splitter so the aerosol for the CPC under calibration can be diluted. The ratio of the concentrations read by the two instruments is no longer the detection efficiency, but is the product of the detection efficiency of the CPC under calibration and the dilution ratio. Our method, the detail of which will be explained in the presentation, allows evaluation of the change of the detection efficiency for different concentration levels, by using the known concentration linearity response of the reference FCAE, without requiring the knowledge of the dilution ratio of the diluter. By combining this technique with the conventional one, we can determine the absolute detection efficiency at different concentration levels. We are able to calibrate the detection efficiency of a CPC down to 1 cm^{-3} with the relative expanded uncertainty of about 3 % with the coverage factor $k = 2$. Our method is similar in the calibration capability to the method by Owen et al. (Aerosol Sci. Technol. 46:444-450, 2012) and the differences between the two methods will be discussed in the presentation.

9IM.5

A Fast-Response Condensation Particle Counter (CPC) for Detection of 1 nm Particles. Avin Andrade, JILL CRAVEN, Richard Flagan, *California Institute of Technology*

Current condensation particle counter (CPC) technologies employ butanol as the working fluid to grow particles large enough to be detected by a laser; however, this method does not efficiently activate and grow ultrafine (< 10 nm) particles. Iida et al. (2009) demonstrated that particles as small as 1 nm diameter can be detected efficiently by operating two CPCs in series, the first CPC operating with a low vapor pressure, high surface tension working fluid (diethylene glycol, DEG) to activate the small particles and grow them to a few tens of nanometers in size, while the second CPC grows the activated particles to optically detectable size using a higher vapor pressure, lower surface tension fluid (butanol, BuOH). Variants of this design have been built using a Particle Size Magnifier as the DEG first stage, and a conventional BuOH CPC as the second, “booster” stage. These instruments have provided important insights into the early growth rate of freshly nucleated clusters, but problems remain. The use of two CPCs in series results in slow instrument response. Efforts to use the two-stage CPC as a detector for a nano-radial differential mobility analyzer (nRDMA) have been severely constrained by the slow response, forcing operation of the DMA in stepping rather than scanning mode. This paper will present a novel, integrated CPC that retains the nanoparticle detection capability of the two-stage CPC, but enables the rapid response required for scanning electrical mobility spectrometer measurements to be made using the nRDMA. Model predictions of the performance of the new instrument will be presented.

9NM.1

Graphene Synthesis via Controlled Detonation of Hydrocarbons. CHRIS SORENSEN, Arjun Nepal, Gajendra Singh, Bret Flanders, *Kansas State University*

Graphene is a two dimensional monolayer of sp2 bonded carbon atoms in a hexagonal crystal structure which has been drawing considerable interest because of its unique physical properties. We report a simple, one-step, gas-phase, catalyst-free, high yield method to produce gram quantities of pristine graphene nanosheets (GNs) via controlled detonation of hydrocarbons (e.g. acetylene). The obtained GNs were analyzed by TEM, XRD, XPS, Raman spectroscopy and etc. The method allows for the control of the number of layers, shape and size of the graphene nanosheets by variation of the oxygen/hydrocarbon ratio. The high temperature of the detonation, ca. 4000K, is proposed as the cause of graphene production rather than normal soot. The process can be scaled up for industrial production.

9NM.2

Development of Crumpled Graphene-based Nanocomposites via Aerosol Route for Environmental Applications. WEI-NING WANG, Yi Jiang, John Fortner, Pratim Biswas, *Washington University in St. Louis*

A possible solution to solve the restacking issue of graphene oxide (GO) nanosheets during large-scale production is to turn the 2D nanosheets into 3D crumpled balls that have excellent compressive properties but still maintain high free volumes. An aerosol-based process has been proven to be a rational method for this purpose, in which, the crumpling phenomenon, however, has hitherto remained unclear. In this work we present a detailed understanding of the crumpling of GO nanosheets by a systematic investigation conducted in aerosolized droplets by means of in-line (e.g., scanning mobility particle sizer) and off-line (e.g., electron microscopy) measurements. Correlations between the confinement force and various parameters, such as evaporation rate and precursor concentration were established to derive a universally applicable equation.

In addition, the synthesis of ternary crumpled graphene-TiO_2-magnetite nanocomposites via aerosol route was also demonstrated in this work. The as-synthesized core-shell nanostructured photocatalyst, with controllable size and functionality, exhibited enhanced photocatalytic activity compared to bare TiO_2; and is readily to be magnetically collected and redispersed in water. Compared with bare TiO_2, crumpled graphene-TiO_2 could increase lifetime of photo-induced holes and electrons by significantly reducing their recombination. By employing various hole and radical scavengers, we proposed the main reaction pathways for photo-induced holes and electrons, and based on which we demonstrated the shifting of oxidation pathway toward reduction one. This study provides new insights into synthesizing ternary crumpled graphene-based multifunctional nanocomposites for various environmental applications.

9NM.3

TiO_2 Nanoparticle Formation and Growth in ACVD Systems: Discrete Sectional Simulation. TANDEEP CHADHA, MengMeng Yang, Shuiqing Li, Pratim Biswas, *Tsinghua University*

Flame synthesis is one of the most widely used commercial scale techniques for the manufacture of nanoparticles. Many types of flames, such as diffusion, premixed and flat flames, are adopted in the synthesis apparatus, providing a suitable framework for nanoparticle formation and growth. In this study a comparison of these flames is made by a simulation study using a discrete sectional aerosol model. The temperature and velocity field in the different flame systems are obtained by simulation with COMSOL, and compared to each other. A discrete sectional model is used to predict particle formation and growth process in these flames. The differences of particle growth history of these flame systems are analyzed. The influences of flow rate and initial precursor concentration on the finial particle size distribution are discussed. An additional investigation of flame dilution and substrate effect is also provided. We end the study with the conclusion of features of different flames and how to choose proper operating factors to generate nanoparticles with desired properties.

9NM.4

The Crystallinity and Coalescence or Sintering Mechanism of Aerosol Nanoparticles by Molecular Dynamics. Beat Buesser, SOTIRIS E. PRATSINIS, *ETH Zurich*

Recent computational advances have led to accelerated molecular dynamics unraveling the evolution of morphology by coalescence of nanoparticles with initial diameter 2 - 4 nm. This bridges the gap of knowledge from molecular sizes to the bulk properties of materials. That way it was shown that coalescence of titania aerosol nanoparticles proceeds by surface diffusion rather than grain boundary diffusion as it was believed from sintering of much larger particles (30-100 nm). This shift in understanding is attributed to the free surface of aerosol nanoparticles in contrast to the constrained surfaces of powder compacts that are routinely employed in materials science (1). Here sintering of Ag nanoparticles is investigated by molecular dynamics at various temperatures and arrangements. The melting temperature of these nanoparticles was reduced with decreasing particle size but converged to the bulk value of Ag for bigger particles. Sintering below these temperatures is dominated again by surface diffusion whereas a transition towards plastic flow is observed near the size-dependent melting temperature. The characteristic sintering time of straight chains of three particles is longer than that of two of the same diameter while the most compact, triangular, structure of three particles sinters even faster than two nanoparticles! Star configurations of four nanoparticles sinter nearly as fast as chains of three. Sintering by surface diffusion either increased the number of crystals by forming new grains right at the sintering neck or decreased it by consuming up smaller grains.

Buesser, B, Grohn, A, Pratsinis, SE (2011) Sintering Rate and Mechanism of TiO_2 Nanoparticles by Molecular Dynamics. J. Phys. Chem. C 115, 11030-11035.

9NM.5

Diffuse Vs. Specular Algorithms to Explain Electrical Mobility in Diatomic Gases. Carlos Larriba-Andaluz, CHRISTOPHER HOGAN JR., *University of Minnesota*

Electrical Mobility measurements of polyatomic ions are ubiquitously used as capable ways of separating molecular entities by cross section and charge. Collision Cross Sections(CCS) are a measure of drag and include not only the Physical Cross Sections(PCS), but the enhancement effects of gas-molecule scatterings and/or electrostatic potentials. Often, CCS are mistaken by their more available counterpart PCS and in general this leads to poor agreement between calculations and experiments, mostly because simulated molecular structures used for calculations focus in matching potential energy surfaces while disregarding bulk physical properties. In this work, we will carefully define MD structures to describe the scattering process as accurately as possible. Room Temperature Ionic Liquids (RTIL), e.g. EMIBF4/ EMI-N(CN)2, are used as candidate structures. The reason behind this choice is that RTIL are non-volatile liquids that form spheres with nearly no exception. These test subjects are guaranteed to achieve their correct size by comparing the density of a single large uncharged MD structure to the bulk density of the material. The structure is subsequently reduced to match the bulk density and the reduction ratio is employed equally in the rest of cases, so that all structures achieve their correct volume fraction that might or might not coincide with the void fraction of the bulk material. A novel and efficient set of momentum transfer algorithms for diatomic gases is invoked on such fixed structures to explore the validity of specular vs. diffusive scattering laws. It will be shown that specular models fail to correctly describe the necessary scattering process that would have to take place in order to achieve experimentally observed enhancement factors. Furthermore, specular scattering cannot predict the constant enhancement factor that appears in mobility experiments in diatomic background gases. In all, diffuse scattering laws must be applied to correctly define electrical mobility measurements.

9SA.1

Spatial and Temporal Assessment of a Hybrid Source Apportionment Model Using Nonlinear Optimization. CESUNICA IVEY, Heather Holmes, Yongtao Hu, James Mulholland, Armistead Russell, *Georgia Institute of Technology*

A hybrid source apportionment model has been developed that takes into account both observed concentrations and measurement uncertainties to estimate source impacts that better reflect the observations. The model employs an effective variance approach to represent model and measurement uncertainties. Sequential quadratic programming (SQP) is used to estimate source impact adjustment factors by minimizing the error between measured and modeled concentrations. Adjustment factors are then applied to improve the original source impact estimates.

This method is employed to generate daily adjusted source impacts for continental United States for the month of January 2004. First, Chemical Speciation Network (CSN) observation data that are available at every third or sixth day are temporally interpolated to produce daily values. Daily observations and modeled daily source impacts are then used for optimization, generating spatially-sparse, daily datasets of adjustment factors. Finally, a kriging technique is employed to spatially interpolate the adjustment factors to a uniform grid covering CONUS that has a 36-km resolution in horizontal. Resulting datasets include temporally and spatially dense source impacts for 33 source categories including diesel and gasoline vehicles, wood burning, natural gas, coal combustion, etc. Optimization and interpolation methods are evaluated by data withholding and comparison to daily concentrations from the Southeastern Aerosol Research and Characterization (SEARCH) Network and EPA funded supersites, including sites in Atlanta, GA; Birmingham, AL; and St. Louis, MO. These data are independent of those used for model development.

The impact of this work extends to epidemiological studies, where daily source apportionment estimates are utilized in time-series epidemiologic analyses to investigate pollutant emissions and adverse health outcomes. The increased spatial and temporal resolution of air quality metrics improves exposure estimates used in health studies.

9SA.2

Source Apportionment of Primary Particulate Matter and its Carbonaceous and Trace Elemental Components in the Eastern US. HONGLIANG ZHANG, Gang Chen, Jianlin Hu, Shu-Hua Chen, Michael Kleeman, Qi Ying, *Texas A&M University*

Trace elements in primary particulate matter (PM), along with elemental and organic carbon, have been assumed to be associated with adverse health effects. Evaluating the ability of chemical transport models (CTMs) in reproducing the observed concentrations of primary particulate matter and its components is essential in applying these models for air pollution epidemiology studies. In addition, quantitative determination of source contributions to these primary PM components is needed for effective control strategies.

In this study, the Community Multi-scale Air Quality (CMAQ) is modified to simultaneously track primary PM2.5 mass concentrations in the eastern US from a large number of sources during a 7-year (2000-2006) air quality modeling study. The meteorological inputs are generated with the Weather Research & Forecasting (WRF) model, version 3.2.1. The Sparse Matrix Operator Kernel Emissions (SMOKE V2.7) Modeling System is modified to generate primary PM emission from the EPA's National Emission Inventory platforms. Source profiles of primary particulate matter with detailed speciation information will be used to find out the concentrations and source contributions to elemental carbon (EC), organic carbon (OC), and trace elements (Fe, Al, Si, Ti, Ca, K, Mn and Mg). The model predicted EC, OC and trace elements are compared with all available surface observations. Annual and seasonal variations as well as main sources of primary PM in seven US cities (Chicago, New York City, Detroit, Pittsburgh, St. Paul, Baltimore, and Winston-Salem) are identified.

9SA.3

Implementation of a High-Resolution Source-Oriented WRF-Chem Model Using Large Eddy Simulation at the Port of Oakland. David Joe, Steven DeNero, Hongliang Zhang, Hsiang-He Lee, Shu-Hua Chen, MICHAEL KLEEMAN, *UC Davis*

A version of the Source-Oriented WRF-Chem (SOWC) model with Large Eddy Simulation (SOWC-LES) was developed and implemented to perform high resolution simulations over the community of Oakland, California, during March 2010. A multiscale set of nested domains was used to predict contributions to elemental carbon (EC) concentrations from ships, trains, and on-road diesel trucks at 250 m spatial resolution. Results of the nested LES model were compared model results using a parameterization scheme and no nested LES (1 km resolution). Model predictions were compared to speciated particulate matter (PM) measurements and source contributions calculated using Positive Matrix Factorization (PMF). The PMF analysis found that on-road diesel traffic was a major EC contributor, a result consistent with previous studies for Oakland.

The average EC concentration predicted by the SOWC-LES model was 0.42 µg m-3, with source contributions of 0.22 µg/m3 from on-road diesel, 0.05 µg/m3 from ships, 0.08 µg/m3 from trains, and 0.09 µg/m3 from other sources. The nested LES and non-LES simulations produced similar EC predictions at the monitoring site, but predictions at other locations showed substantial differences. The LES model predicted higher period-averaged and hourly-averaged EC source contributions. The greatest increase was seen in the maximum hourly EC from the on-road diesel source, which increased by nearly a factor of 2 (3.74 µg/m3 to 6.69 µg/m3).

Population-weighted calculations showed that the SOWC-LES model predicted greater community EC exposure from all sources. The increase in period-averaged EC exposure from each source ranged from +1% to +17%, while the increase in maximum hourly EC exposure was even greater, ranging from +9% to +32%. This evaluation shows that resolving neighborhood scales through the representation of local mixing phenomena can significantly impact pollutant concentration predictions, especially when examining extreme exposures in a densely populated area with many sources and complex terrain.

9SA.4

Source Contributions to Primary and Secondary Particulate Matter during a Severe PM2.5 Pollution Event in Xi'an, China.HONGLIANG ZHANG, Qi Ying, Dexiang Wang, *Texas A&M University*

Airborne particulate matter with aerodynamic diameter of less than 2.5µm (PM2.5) reduces visibility and increases the incidence of respiratory diseases. While studies of PM2.5 have been conducted for years over East and South China, little was done for Central and Northwest China. In this study, the Community Multi-scale Air Quality (CMAQ) model is used to study a severe PM2.5 pollution event that affected many parts of China in January 2013. It is the first time such study is conducted over Northwest China.

Nested simulations of the Weather Research and Forecasting (WRF)/CMAQ modeling system was performed with a 12-km resolution inner domain centered on Xi'an, the capital of the northwest province of Shaanxi. Anthropogenic emissions were generated using the 0. 1x0.1 degree resolution EDGAR (Emission Database for Global Atmospheric Research) inventory while the biogenic emissions are generated using MEGAN (Model of Emissions of Gases and Aerosols from Nature) fused with updated vegetation cover data from local sources.

The model predictions of PM10 and PM2.5 are evaluated extensively with the recently-made-available public PM data, and show excellent agreement with with observations. Monthly averaged PM2.5 concentration in Xi'an exceeds 250 µg m-3. Both secondary inorganic matter (sulfate, nitrate and ammonium) and primary organic matter contribute to PM2.5. Windblown dust also contributes significantly to PM2.5 mass. Success of the WRF/CMAQ model in reproducing the observed high concentrations demonstrates the ability of state-of-art chemical transport model to act as a useful tool to investigate severe pollution events and provide crucial information needed to design control strategies. Source-oriented versions of the CMAQ model will be used to determine contributions to primary, secondary and overall PM2.5 from major emission sources, including residential heating, transportation, power generation, industry as well as windblown dust, to PM2.5 in the region.

9SA.5

Development and Application of a Particle Number Source Tagging Algorithm in an Aerosol Microphysics Model. DANIEL WESTERVELT, Jeffrey Pierce, Peter Adams, *Carnegie Mellon University*

Aerosol nucleation is an important source of particle number in the atmosphere, but nucleated particles must overcome efficient coagulation and grow significantly to act as cloud condensation nuclei (CCN). Past work has tested the sensitivity of CCN concentrations to changes in nucleation rates, and results have been mixed. Some models have predicted large enhancements such that 60-70% of the CCN in the global boundary layer come from nucleation, whereas others found as little as 5% enhancement. These sensitivity studies are important but limited due to the nonlinear nature of aerosol microphysics models. In this work, we develop and apply a method within the TwO-Moment Aerosol Sectional microphysics algorithm (TOMAS) that would avoid these limitations by tracking or tagging the aerosol number size distribution as it evolves during condensation, coagulation, and nucleation. Tags can be assigned by their source process (e.g. nucleation or primary), species type (e.g. sea salt, black carbon, POA), or even source locations or sectors (e.g. cities, vehicles, industry). This is done in a “semi-offline” fashion, in which the core microphysical calculations still operate on total (untagged) number distributions to avoid computational burden. Instead, the rates of key microphysical processes are saved and passed to another module that updates the tagged distributions accordingly. The approach is similar to the Particle Source Apportionment Technology (PSAT) algorithm, developed for aerosol mass source apportionment in Wagstrom et al. (2008). With the number source tagging algorithm in place, we test coagulation, condensation and nucleation and quantify the amount of numerical diffusion present for each process. We apply our tagging method to observed nucleation events in a box model and calculate the nucleation contribution to CCN concentrations. Finally, we incorporate the algorithm into the GEOS-Chem-TOMAS global aerosol model, which will allow us to quantify the sources of CCN in a more definitive manner.

9UA.1

New Particle Formation in an Urban Atmosphere: Seasonal Dependence and Influence of Air Mass Origin. ANNA WONASCHUETZ, Julia Burkart, Richard Haindl, Julia Palmetshofer, Georg Reischl, Gerhard Steiner, Robert Wagner, Regina Hitzenberger, *University of Vienna*

Ultrafine particles in urban areas are a major concern regarding air quality and public health. Local direct emissions of small particles and new particle formation events are sources of fine and ultrafine particles, but meteorological conditions and the properties of the background aerosol moderate both production and fate of freshly produced particles. In this study, a comprehensive dataset of aerosol number size distributions spanning several years is combined with modeled air mass origin (HYSPLIT back-trajectories), weather and solar radiation data, and elemental and organic carbon analyses in order to investigate the conditions under which new particle formation events can take place in an urban environment, as well as their seasonal dependence. A second aim is to establish the extent to which air mass origin affects the properties of the urban aerosol. The shape and development of the size distributions indicate the impact of local sources. Human activity patterns are reflected in the concentrations of black and brown carbon, which serve as tracers for fossil fuel combustion and biomass burning. Pollen on filter samples indicate strong biogenic influences. First results suggest that in summer, higher sub-micrometer aerosol volume concentrations were associated with back-trajectories from the east, lower concentrations with westerly back-trajectories. New particle formation events were often, but not always, linked to diurnal peaks in solar irradiation. In winter, new particle formation events were absent, due to both higher background aerosol concentrations and lower solar irradiation. The contribution of fine and ultrafine particles to total number concentrations in winter was dominated by local anthropogenic sources.

9UA.2

Wintertime Air Pollution and the Greek Financial Crisis.

KALLIOPI FLOROU, Christos Kaltsonoudis, Dimitrios Papanastasiou, Georgios Gkatzelis, Evangelos Louvaris, Michael Pikridas, Spyros Pandis, *University of Patras, Patra, Greece*

During the last couple of years, because of the current high prices of diesel, Greeks have turned to more traditional ways of residential heating, such as fireplaces and pellet stoves. Two field campaigns were conducted during the winter of 2012 and 2013 in two of the largest Greek cities (Athens and Patras) in order to quantify the levels of organic aerosols from domestic wood combustion and to characterize the corresponding particulate matter. The instrumentation used included an Aerodyne High-Resolution Time-of-Flight Mass Spectrometer (HR-ToF-AMS) and a selection of on-line aerosol size distribution and concentration instruments (APS, SMPS, TEOM, MAAP). VOC concentrations were measured using a PTR-MS.

During February of 2012, a significant increase of particulate matter less than 1 micro-meter (PM1) was observed every evening after 6 pm in Patras. The concentration of PM1 usually exceeded 80 micro-g m-3 often reaching values above 100 micro-g m-3. Organic particulate matter represented more than 90% of the fine PM during these periods. The concentration of black carbon was as high as 10 micro-g m-3 often exceeding the sulfate levels. High potassium and nitrate levels were also observed during the night. These concentrations were a lot higher (approximately double on average) than the concentrations measured in Patras during previous winters. In January 2013, these measurements were repeated both in Athens and Patras using a number of field stations. Wood burning once more resulted in extremely high nighttime PM levels. The spatial and temporal distribution of fine PM will be discussed and the effects of the change in heating fuels will be quantified.

9UA.3

Sources and Chemical Processing of Organic Aerosol during the Summer in the Eastern Mediterranean.

EVANGELIA KOSTENIDOU, Kalliopi Florou, Christos Kaltsonoudis, Maria Tsiflikiotou, Magdalini Psichoudaki, Spyros Pandis, *Institute of Chemical Engineering Sciences, ICE-HT, Greece*

During summer 2012 the concentration and chemical composition of fine aerosol was measured in two Greek cities, Patras (population 300,000) and Athens (population 4 million) in an effort to better understand the chemical processing of particles in the high photochemical activity environment of the Eastern Mediterranean. An Aerodyne High Resolution Aerosol Mass Spectrometer (HR-AMS) was used to measure the size-resolved chemical composition of the non-refractory PM_1. Additional measurements included those of the aerosol size distribution (SMPS), optical properties (nephelometer and MAAP), gas-phase concentrations (PTR-MS, NO_x, O_3, SO_2, and CO), filter-based composition, etc.

In both sites the levels and composition of PM_1 levels were surprisingly similar to each other demonstrating the importance of regional sources for the corresponding pollution levels. The PM_1 average mass concentration was 9-12 micrograms m^{-3}, which is very close to the PM_1 levels of a remote location in the Mediterranean during summer (e.g. Finokalia). However, the contribution of sulphate in the urban areas was around 37% quite lower than Finokalia’s (55%). Organic aerosol (OA) contributed approximately 45% in both cities.

Positive matrix factorization (PMF) was applied to the high resolution (HR) organic aerosol mass spectra. For Athens 4 sources could be identified: LV-OOA (low volatility oxygenated OA) related to aged OA, SV-OOA (semi-volatile oxygenated OA) a less oxygenated OA, HOA (hydrocarbon-like OA) associated with traffic emissions and COA (cooking OA) related with food preparation. On average the organic matter consisted of 53% LV-OOA, 16% SV-OOA, 15% HOA and 16% COA. In Patras a 3-factor PMF solution was found to describe best the OA AMS: LV-OOA (29%), SV-OOA (53%) and HOA (18%). The organic to carbon (O:C) mass ratio was 0.64 in Patras and 0.58 in Athens. In both cases the aerosol was acid (ratio of cations to anions 0.73±0.07 in Patras and 0.70±0.08 in Athens).

9UA.4

Rainout, Washout and Dry Deposition Contributions to the Total Deposition Flux of Heavy Metal Aerosol onto Surfaces of a Small Urban Catchment (Pin Sec, Nantes). STÉPHANE PERCOT, Véronique Ruban, Philippe Laguionie, Denis Maro, Pierre Roupsard, Dominique Demare, *IRSN*

Pollutants associated to atmospheric particles in urban areas throughout the world have been characterized in many studies. The nature of surfaces as well as weather conditions and atmospheric turbulence influence the aerosol deposition. Previous studies in Nantes (France) on the Pin Sec catchment allowed the estimation of wet and dry atmospheric deposition fluxes. Thanks to these results further studies can now estimate the origin of atmospheric heavy metals by distinguishing rainout (long range transport) and washout (local scavenging) processes. The objective of this communication is to present the rainout, washout and dry deposition contributions to the total deposition flux of heavy metal aerosol on this catchment. The experiment was conducted between the 1st of September 2010 and the 31st of August 2011. The dry deposition of heavy metals was estimated using the dry deposition velocity of the tracer Beryllium 7 measured on urban surfaces. Regarding monthly wet deposition, the flux is calculated as the ratio of the mass of pollutants collected in a covered pluviometer. The rainout/washout ratio was determined by a new method which used monthly integrated data: heavy metal elements concentrations in rainwater and in aerosol particle, scavenging coefficient, reload rate of the local atmosphere, and meteorological parameters. In average, over the 10-month survey period, heavy metals (except for vanadium and lead) are mainly deposited by rainout process, showing evidence of long range sources. The rest of the atmospheric deposition is composed of dry deposition and washout which is the lowest part of deposition. These results are in good agreement with results of source emission showing that there is no evidence of emission of pollutants from local activity. Lead behaves differently: dry deposition and washout contributions suggest the existence of a local source. The consequences of these results and perspectives will be further discussed at the conference.

9UA.5

Contribution of Atmospheric Aerosols to Urban Stormwater Runoff. JEREMY TAMARGO, Cliff Davidson, *Syracuse University*

There is currently a gap in understanding the contribution of atmospheric aerosols to the contamination of urban stormwater runoff. Stormwater runoff can be influenced by emissions from motor vehicles, aerosol deposition on surfaces in the watershed, vegetation growing in the watershed, trash on the streets and other urban surfaces, and erosion of the material comprising the urban surfaces. Such contaminants can reach bodies of water used for drinking water supplies and thus can cause serious public health problems. However, little research on the various sources of contamination in urban stormwater runoff, especially atmospheric contaminants, has been conducted.

Current research efforts in the city of Syracuse focus on stormwater management, including both the quantity and quality of runoff associated with rain and snow storms. Chemical contaminants transported from the atmosphere are believed to be a major source of contamination of certain species in the runoff, including organics, metals and sulfur. This research focuses on a 60,000 square foot green roof on the Oncenter Convention Center in downtown Syracuse, one of the largest green roofs in the northeastern United States. Airborne concentrations of contaminants are measured at the green roof and at other locations in the Syracuse urban environment. Deposition of airborne contaminants on the green roof is measured directly using symmetric airfoils. Urban runoff samples are collected and analyzed for contaminants of interest. Measured airborne concentrations,deposition measurements and runoff concentrations are compared to data from nearby monitoring sites and to data from the literature.

10AC.1

Photolytic Processing of Organic Atmospheric Particulate Matter. SCOTT A. EPSTEIN, Mallory Hinks, Sergey Nizkorodov,*University of California, Irvine*

The organic multifunctional compounds including peroxides, carbonyls, and nitrates typically found in organic particulate matter (PM) are photolabile and decompose when exposed to solar radiation on atmospherically relevant time scales. Many of these organic molecules and their photolysis products are semi-volatile, and depending on conditions, can have significant concentrations in both the gas and condensed phase. Most past experiments designed to characterize the photochemistry of organic PM mixtures involve photolysis of both gas and condensed phase species inside a reaction chamber. While these experiments reveal the overall behavior of the aerosol mixture, the semi-volatile nature of the constituents makes it difficult to distinguish between direct photolysis and photooxidation processes occurring in the gas phase and the condensed phase. We have designed and built a flow cell system to study the photolysis of organic particulate matter in absence of its corresponding vapors. After sending an organic aerosol mixture through several large denuders lined with activated charcoal to remove gas phase species, residual particles enter a photolysis flow cell containing UV lamps designed to simulate solar radiation. The photolysis chamber contains a large surface area of continuously cooled activated charcoal to remove vapors evolved from PM photolysis. The intensity of radiation exposure is quantified using chemical actinometry methods. Particle composition with and without UV radiation is monitored in real-time with an Aerodyne HR-ToF-AMS. In addition, off-line analysis of particle composition using methods of ultra-high-resolution mass spectrometry provides additional molecular level information about the aerosol constituents. These experiments reveal the effects of solar radiation on several different types of organic particulate matter derived from anthropogenic and biogenic precursors.

10AC.2

A Systematic Evaluation of the Extent of Photochemical Processing in Different Types of Secondary Organic Aerosols. Dian Romonosky, Hyun Ji Lee, Scott A. Epstein, SERGEY NIZKORODOV, Julia Laskin, Alexander Laskin, *University of California, Irvine*

A significant fraction of atmospheric organic compounds are predominantly found in condensed phases, such as organic phase in aerosol particles or aqueous phase in cloud droplets. Many of these organic compounds are photolabile, and can degrade through direct photolysis or indirect photooxidation processes on time scales that are comparable to the typical lifetimes of droplets (hours) and particles (days). We previously reported that compounds in secondary organic aerosol (SOA) from ozonolysis of d-limonene efficiently photodegrade in both organic (Walser et al., 2007) and aqueous phases (Bateman et al., 2011). Significant photolysis was also observed in an aqueous extract of SOA from high-NOx photooxidation of isoprene (Nguyen et al., 2012). More recent experiments found surprising resilience to photodegradation in aqueous extracts of SOA prepared by photooxidation of alpha-pinene (Romonosky et al., unpublished). This paper presents a systematic investigation of the extent of photochemical processing in different types of SOA from various biogenic and anthropogenic precursors. Chamber- or flowtube-generated SOA is collected on an inert substrate, the resulting organic material is photolyzed directly on the substrate, and the extent of change in the molecular level composition of the material is assessed with high-resolution mass spectrometry (HR-MS). The same set of SOA samples is extracted in water, and photolyzed in the aqueous solution, with the molecular composition also probed by HR-MS. The outcome of this study will be improved understanding of the role of condensed-phase photochemistry in chemical aging of aerosol particles and cloud droplets.

Bateman et al. Photolytic processing of secondary organic aerosols dissolved in cloud droplets. Phys. Chem. Chem. Phys. 2011, 13, 12199.

Nguyen et al. Direct aqueous photochemistry of isoprene high-NOx secondary organic aerosol. Phys. Chem. Chem. Phys. 2012, 14, 9702.

Walser et al. Photochemical aging of secondary organic aerosol particles generated from the oxidation of d-limonene. J. Phys. Chem. A 2007, 111, 1907.

10AC.3

Reactive Uptake and Aqueous Chemistry of Isoprene Epoxydiols (IEPOX) and Glycolaldehyde in Aerosol Liquid Water.TRAN NGUYEN, Matthew Coggon, Kelvin Bates, Rebecca Schwantes, Xuan Zhang, Katherine Schilling, Christine Loza, Richard Flagan, Paul Wennberg, John Seinfeld, *California Institute of Technology*

The atmospheric oxidation of isoprene (C5H8) forms many water-soluble oxidation products that may partition into the liquid water of inorganic particles. The fates of the dissolved organic compounds include dark aqueous reactions (like hydration and imine formation), aqueous photooxidation, aqueous direct photolysis, and evaporation of water – reactions that may contribute to the formation of secondary organic aerosol (SOA). In this work, we studied the aqueous chemistry of isoprene photooxidation products glycolaldehyde (GLYAL) and isoprene epoxydiol (IEPOX) using a photochemical smog chamber and a photochemical flow reactor. Gas-phase compounds were measured with a chemical ionization mass spectrometer (CIMS) and particle-phase compounds were measured with a time-of-flight aerosol mass spectrometer (ToF-AMS), alongside traditional aerosol instrumentation. Offline composition analyses were performed using electrospray ionization mass spectrometry (ESI-MS). The reactive uptake of GLYAL and IEPOX onto neutral AS seed particles will be described as a function of particle liquid water content. The composition of particle-phase organics and key mechanisms involved in the aqueous dark chemistry and photochemistry will be discussed.

10AC.4

Atmospheric Reactions between Glycolaldehyde, Formaldehyde, and Ammonium Sulfate: A Product Identification Study.MELISSA GALLOWAY, Alyssa Rodriguez, Jeremy Kua, Katherine Millage, David De Haan, *University of San Diego*

Aqueous reactions of aldehydes with amines or ammonium salts have recently been implicated in atmospheric secondary organic aerosol and brown carbon formation processes. However, few of the reaction products, especially those responsible for visible light absorbance, have been characterized. Using a variety of techniques, including NMR spectroscopy and ESI-MS, the reaction products of small, water soluble aldehydes (e.g. formaldehyde and glycolaldehyde) with ammonium sulfate are identified. According to quantum-mechanical calculations, the most energetically stable product in the formaldehyde – ammonium sulfate reaction is hexamethylenetetramine, but many possible reaction pathways leading to local energy minima can produce other, less volatile nitrogen-containing compounds, many with alcohol functionalization. Experiments verify that hexamethylenetetramine is the major reaction product; this work seeks to verify the importance of these other reaction pathways. Similarly, glycolaldehyde and ammonium sulfate react to form colored solutions. Aqueous glycolaldehyde is found in both monomeric and dimeric forms. Evidence indicates that reaction products of glycolaldehyde – ammonium sulfate have the same equilibrium distribution; imines may be formed on glycolaldehyde monomer and dimer backbones before further reactions proceed. Product identification of these and similar reactions will allow for better understanding of the aqueous chemistry occurring in atmospheric cloud and aerosol droplets.

10AC.5

Aqueous Photooxidation of Water-Soluble Compounds in Po Valley, Italy during PEGASOS: Chemical Insights and Modeling. YONG LIM, Jeffrey R. Kirkland, Ron Lauck, Barbara Turpin, *Rutgers University*

Aqueous chemistry is a potentially important atmospheric pathway to produce second organic aerosol (SOA). Moreover, SOA formed via aqueous chemistry in cloud droplets/wet aerosols helps to explain the high O/C of atmospheric organic aerosols. While aqueous SOA precursors have been proposed, it is not yet clear what the most important precursors are in the atmosphere. Recently, water-soluble organic compounds were scrubbed from the atmosphere using mist chambers in Po Valley, Italy during the PEGASOS campaign (June-July, 2013), and aqueous-phase OH radical reactions were conducted with these mixtures. Precursors and photochemical products were identified and quantified by using an electrospray ionization mass spectrometer (ESI-MS), ion chromatography (IC), and IC coupled with ESI-MS. Several ESI-MS positive mode ions decayed during these experiments (reactants). Subsequently, oxalate, pyruvate and mesoxalate formations were observed. These products are also formed in laboratory glyoxal/methylglyoxal photooxidation experiments. While we saw no evidence for the presence of glyoxal or methylglyoxal in the samples (experiment t = 0), there is some evidence that they may be intermediate products, forming and decaying during the reactions. Expected emission and gas-phase photochemistry were used to develop insights into potential precursors and kinetic modeling was used to link these precursors through glyoxal and methylglyoxal to pyruvate and oxalate. The underlying assumptions and implications will be discussed.

10AC.6

Modelling the Water Uptake and Solubilities of Aminium Sulphate Salts. SIMON CLEGG, Chong Qiu, Renyi Zhang, *University of California, Davis; University of East Anglia*

Volumetric growth factors of five aminium sulphate salts have recently been measured as a function of relative humidity (RH) by Zhang and co-workers (Environ. Sci. Technol. 2011, 46, 4474-4480). Using new data for solubilities and solution densities we have modeled the growth factors based upon the RH / concentration relationship (on a mole of water per mole of salt basis) of aqueous $(NH_4)_2SO_4$, on the assumption that aminium ions in aqueous solution will have similar interactions with water and other ions to those of NH_4^+. This is consistent with the observed behaviour of solutions of a number of aminium nitrates, for which water activities and solute activity coefficients are close to those of NH_4NO_3. Calculations were carried out using the Extended Aerosol Inorganics Model (E-AIM, http://www.aim.env.uea.ac.uk/aim/aim.php). Modelled growth factors agree very well with the data, although some trends in water uptake with aminium ion size are evident at low RH (high concentration). Measured solubilities have been used to obtain equilibrium solubility products that can be entered in E-AIM to predict properties of aerosol particles containing NaCl, acid ammonium sulphate and nitrate, and amines which will be neutralized to aminium ions in the same way as ammonia to NH_4^+.

10BA.1

Investigation of Bioaerosol Contamination in New Jersey Homes Affected by Hurricane Sandy. Leonardo Calderón, Huajun Zhen, Zuocheng Wang, Brian Buckley, Joan W. Bennett, Paul J. Lioy, GEDIMINAS MAINELIS, *Rutgers, The State University of New Jersey*

The storm surge from Hurricane Sandy flooded and affected more than 70,000 structures along the New Jersey shore in October 2012, leaving an unprecedented temporal and geographic cluster of water-damaged and mold-infested homes and businesses. Demolition and remediation of affected structures is underway and is anticipated to peak in late spring/early summer of 2013.

Because Sandy was a cold weather event, some of the short-term problems from molds, as seen in Louisiana after Hurricane Katrina, were initially obscured. Nonetheless, in anticipation of potential mold exposure issues we began collecting airborne samples of mold and bacteria in affected homes. The concentrations of culturable bacteria and mold were determined using SAS Super 180 portable sampler and culturing method. The total mold concentrations were determined using Air-O-Cell spores traps and microscopy. An initial set of samples was collected in December 2012-January 2013 in homes at different stages of remediation. The average concentrations of total airborne mold spores in homes without remediation or with remediation in progress ranged from ~10^4 to >10^5 spores/m^3, compared to approximately 1,000 spores/m^3 in re-mediated or minimally affected homes. Indoor mold was dominated by Penicillium species (>95%), while outdoor mold were mostly Ascospores, Cladosporium and some Penicillium (<10%). Concentrations of viable mold in remediated or minimally affected homes were below 1000 CFU/m^3, while these concentrations in homes without remediation or with remediation in progress reached close to 10^4/m^3 and samples were often overloaded. The levels of culturable bacteria in affected homes were not substantially higher than in minimally affected homes.

As the remediation efforts intensify during warmer weather, we expect to investigate more homes as permitted by access and funding. The results so far indicate that mold exposures could reach substantial levels in affected homes and that proper remediation is the key to reducing such exposures.

10BA.2

An Integrated Modeling Approach to Understand the Interaction between Air Pollution and Pollen Allergy in a Changing World. RUI ZHANG, Tiffany Duhl, Muhammed T. Salam, James House, Richard Flagan, Ed Avol, Frank Gilliland, Alex Guenther, Serena H. Chung, Brian K. Lamb, Timothy M. VanReken, *Washington State University*

There is growing evidence that air pollutants can interact with inhalant allergens carried by pollen grains to enhance the risk of allergic airway disease (AAD) for sensitive populations. Linking air pollutants, pollen levels, and human allergenic response using an integrated modeling approach is a key step toward quantifying the overall health impacts under current and future climate conditions. A regional-scale pollen release and transport modeling framework has been developed within the WRF/CMAQ air-quality modeling system. The Simulator of the Timing and Magnitude of Pollen Season (STaMPS) model was developed to estimate the daily pool of pollen available for release by wind. It is driven by species-specific meteorological threshold conditions and is flexible with respect to the representation of vegetation species and plant functional types. The hourly pollen emission flux is then parameterized using the pollen pool, friction velocity, and wind threshold values. Dry deposition for each species of pollen is estimated based on pollen grain size and density.

An evaluation of this new modeling framework was conducted during the 2010 pollen season for southern California. The simulation period coincided with observations by the University of Southern California's Children's Health Study (CHS), which included ozone, PM2.5, and pollen count, as well as measurements of exhaled nitric oxide in study participants. Two nested domains with horizontal grid cells of 12 km and 4 km were constructed and seven representative allergenic pollen genera were included: birch, walnut, mulberry, olive, oak, sagebrush, and grasses. The modeling framework tends to underestimate peaks in oak and overestimate grass pollen concentrations, but it shows reasonable agreement with observed concentrations for other species. For future work, the modeled pollen, ozone, and PM2.5 concentrations will be used to evaluate species-specific pollen allergen dose response functions to understand the interaction between air pollution, pollen level, and respiratory health outcomes.

10BA.3

Parameterizing the Humidity-Induced Rupture of Pollen to Produce Respirable Particles. QIAN ZHOU, Timothy M. VanReken, *Washington State University*

Many types of pollen contain allergenic material that has been linked to asthma and other respiratory ailments. However, the pollen grains themselves are too large to reach the lower airways where the asthma response occurs. Recent work has suggested a likely explanation. When exposed to high relative humidity, pollen has been observed to rupture and produce fine particles. The pollen rupture is likely the result of osmotic swelling; water from the surrounding environment is absorbed into the pollen grain until the grain wall fails and the cytoplasm is released. Previous studies have shown that the resulting particles are of respirable size (< 2 micrometers) and contain allergenic material that can trigger human immune response.

Our research has shown that there is a quantifiable dependence of pollen rupture on water vapor exposure. For a given species, we have found that raising the exposure relative humidity increases the overall fraction of pollen grains that rupture and decreases the time required for rupture to occur. Here we present a parameterization of that process. The pollen rupture model is based on the assumption of permeability-limited mass transfer of water through the pollen grain wall, taking into account both the osmostic and hydrostatic pressures of the pollen grain interior and the surrounding air. The performance of the pollen rupture parameterization will be evaluated against our existing results for wheat and pine pollens, and for an anticipated new ryegrass data set. Our ultimate goal is to build this pollen rupture parameterization into a recently developed regional modeling framework for estimating the release and atmospheric transport of allergenic pollens.

10BA.4

Automated Pollen Identification and Counting System (APICS). JAMES HOUSE, Gregory Griffin, Richard Flagan, *Caltech*

The process of counting pollen is laborious, slow, expensive, and of questionable accuracy. As a result, measurements are routinely made at fewer than 100 sites within the U.S. The available data are far too sparse to enable robust estimations of exposure. Moreover, data reporting from many of the present pollen counters is often restricted to coarse classes of pollen (e.g., grasses, trees, and weeds. Individual species counts are needed to assess health risks of allergic individuals. While other nations have national pollen counting networks that are operated by scientists, allergy clinics provide most of the documented pollen measurements in the U.S. Efforts to conduct epidemiological studies of the health impacts of pollen, and to elucidate the effects of climate change on pollen and allergic disease are confounded by the lack of historical trends on pollen, and by the lack of a robust pollen database that includes measurements from all regions with sufficient spatial resolution to assess geographic and local variations in concentrations, and that is accessible for scientific research. To enable such a network, the measurements must be made much more cost-effective and reliable.

We report on the development of an automated pollen identification and counting system (APICS) as a step in this direction. We have applied this system to the identification of pollen in samples that were collected using a conventional Burkard pollen sampler. The samples are affixed to microscope slides, each representing one day. A computer-controlled microscope, driven by software written in Java and using MicroManager, an open-source microscopy program, captures images from each slide. The images are processed to produce focused images of candidate objects within each field of view. The resulting candidate objects are then identified using computer-vision software that has been trained using a large library of labeled images. Using a desktop PC for the analysis, the system processes samples representing one week in less than 24 hours. We continue to work toward shorter analysis times.

The performance of APICS has been characterized in terms of its accuracy by comparison with human pollen counters. Initial measurements duplicated the scan procedures that are typically employed by human counters, i.e., a linear scan through the length of each slide. The automated system enables analysis of many more fields of view than can a human counter, including whole slide scans. Using these comprehensive scans, we have examined the biases associated with conventional methods, and explored alternate scan patterns that to reduce those biases. APICS has been used to provide daily pollen measurements for Pasadena, CA to reveal detailed patterns and trends in the pollen data that have not been possible with previous manual counts.

10BA.5

Effective Sampling of Infectious Viral Aerosols down to the Primary Virion Size. HOWARD WALLS, David S. Ensor, Lauren Harvey, Jean Kim, Ryan Chartier, Susanne Hering, Steven Spielman, Gregory Lewis, *Research Triangle Institute*

Airborne viruses represent a potentially significant health threat. The primary size of a viral particle can be very small, in the range of 20 nm to 300 nm. However, only recently have researchers begun to characterize the size and infectivity of viral bioaerosols in the submicron size range. We have developed a novel bioaerosol sampler using a laminar-flow water condensation method to efficiently sample viral aerosols to sizes well below 100 nm. The water condensation bioaerosol sampler provides a more gentle collection of the bioaerosols, maintaining their viability (infectivity) during the collection process. Using MS2 bacteriophage as a model system we performed size selected sampling from 300 nm down to 45 nm with both an all-glass impinger (4 mm; AGI-4) and the water condensation bioaerosol sampler. We demonstrated the existence of infectious viral particles below 100 nm and that the water condensation bioaerosol sampler collects viral aerosols more efficiently than an AGI-4 providing better preservation of infectivity. For example, for 45 nm diameter particles the water condensation bioaerosol sampler collected 10× more infective virions per liter of the same aerosol sampled and 20× more infective virions per collected particle compared to the AGI-4.

We also studied the amount of viral particle inactivation due to the aerosolization process using qRT-PCR. A large reduction in the percentage of infectious viral particles occurred upon aerosolization with a Collison nebulizer. With its ability to both collect aerosol particles down to the primary size of the smallest virus and maintain their infectivity, the water condensation bioaerosol sampler is a powerful laboratory tool that could elucidate the threat of submicron viral aerosols.

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10BA.6

Survival of Aerosolized Simulants of Bacillus Anthracis Exposed to Combustion Products of Novel Halogen-Containing Reactive Metals. SERGEY A. GRINSHPUN, Michael Yermakov, Reshmi Indugula, Xinjian He, Tiina Reponen, Edward Dreizin, Mirko Schoenitz, Shasha Zhang, Y. Aly, *University of Cincinnati*

If a bio-weapon facility is accidentally or intentionally targeted, a fraction of the released bio-agent (e.g., Bacillus anthracis spores) can remain viable and be subjected to a short- or long-range atmospheric transport representing significant threat. Novel halogen-containing reactive materials have been developed to inactivate viable microorganisms during their release to the atmosphere. A state-of-the-art experimental facility was used to investigate the survival of aerosolized spores of two well-established surrogates of Bacillus anthracis: Bacillus subtilis var. niger (also referred to as Bacillus atrophaeus or BG spores) and Bacillus thuringiensis (Bt spores). The spores dispersed in dry airflow were exposed for short time intervals (< 1 s) to the products originated by hydrocarbon flames seeded with Al powder (dispersion = 3-4.5 micron) regarded as the reference material and two novel powders, Al•I2 and Al•B•I2, which release iodine during their combustion. The bioaerosol particles interacted with the combustion products in a controlled high-temperature environment. When the estimated characteristic temperature in the cross-section of the exposure chamber was approximately 250–260°C (slightly below the threshold associated with a measurable heat-induced spore inactivation), both iodine-containing materials inactivated much more spores of both BG and Bt species than Al (by two to three orders of magnitude). The inactivation level provided by Al•B•I2 was significantly higher than that of Al•I2 for both species. The species effect on the spore survival was statistically significant ($p<0.05$) only for Al•B•I2. Similar tests performed at lower characteristic exposure temperatures (~180°C) also showed an iodine-enhanced inactivation although generating much lower inactivation levels (because only a small fraction of the released iodine remained in the gaseous phase in the exposure chamber). The results suggest a great biocidal potential of the two tested iodine-containing materials.

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10CC.1

Cloud-Aerosol Interactions in Deep-Convective Systems: Particle Mass, Number, and Composition Effects. BENJAMIN MURPHY, Ilona Riipinen, Annica Ekman, *Stockholm University*

The number, size, and composition of an aerosol population entrained into a cloud system can affect cloud physical features (e.g. updraft velocity or precipitation rate) while cloud properties can affect features of the aerosol population (e.g. through wet scavenging or aqueous-phase chemistry). In order to invesitgate these complicated feedbacks, we present a new three-dimensional cloud-resolving model, CRM-ORG, which accounts for the processing of inorganic and organic aerosol components in a fully-coupled, dynamic simulation. We apply this model to a case study of a deep convective cloud under clean conditions above the tropical Amazon.

Incorporating the Volatility Basis Set approach of Donahue et al. (2006) into the 3-D cloud resolving host model described by Ekman et al. (2006), the CRM-ORG model relies on a suite of lumped species to describe the oxidation products of biogenic VOCs. The mass transfer of these species to/from particles and cloud drops is treated dynamically along with aqueous-phase chemical reactions relevant to the production of low-volatility organic compounds that partition significantly to the particulate phase after cloud drop evaporation. The model accounts for particle nucleation and growth due to condensation of organic vapors. This work also probes the sensitivity of the results to both the nucleation mechanism formulation and condensable organic vapor volaitlity.

In order to gain a general understanding of cloud-aerosol interactions, we report the net effect of cloud processing on aerosol mass and number throughout the column. Of particular focus is the generation of new particles in the relatively clean background environment of the upper troposphere where substantial amounts of trace gases and particles are injected within the cloud outflow.

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10CC.2

Evaluating Aerosols, Clouds, and Their Interactions in Three Global Climate Models Using COSP and Satellite Measurements. GEORGE BAN-WEISS, Susanne Bauer, Ralf Bennartz, Xiaohong Liu, Kai Zhang, Yi Ming, Ling Jin, Jonathan Jiang,*University of Southern California*

Accurately representing the interaction of atmospheric aerosols and clouds is a great challenge in global climate modeling. This is in part because many aerosol and cloud physical processes operate on spatial scales that are much smaller than climate model grid cells. Thus, these processes are represented in climate models using parameterizations, making estimates of aerosol indirect forcing uncertain. To reduce uncertainty and improve parameterizations, signatures of aerosol indirect effects from climate models can be compared to those measured by satellites. These comparisons require special attention since aerosol and cloud measurements from satellites are inherently different than standard climatological output from climate models. In this work we compare signatures of how aerosols affect subtropical stratocumulus clouds in three climate models (NASA ModelE, NCAR CAM5, and GFDL AM3) to MODIS observations. We focus on near-coast marine areas near South Africa, South America, and Eastern Asia. These areas have persistent stratocumulus clouds and are subject to aerosol pollution from near-by land regions. Simulations are carried out for three years using prescribed SSTs. To maximize comparability to MODIS observations, cloud properties in climate models are diagnosed using the CFMIP Observations Simulator Package (COSP) and satellite overpass times are extracted. Aerosol-cloud interactions are analyzed using high frequency (3-hourly) climate model data. An algorithm is applied to determine cloud droplet number concentration (CDNC) from satellite observed and GCM simulated cloud optical depth and droplet effective radius. We find that the AM3 model matches well the observed CDNC in terms of spatial patterns, magnitude of the seasonal cycle, and sensitivity to aerosol loading. CAM5 overestimates the mean, seasonal cycle, and sensitivity to aerosol, while ModelE underestimates CDNC and cloud prevalence in the stratocumulus areas in general.

10CC.3

Combining Field and Laboratory Studies to Understand the Dominant Sources and Mechanisms of Cirrus Cloud Formation.DANIEL CZICZO, Sarvesh Garimella, Karl D. Froyd, Daniel Murphy, *MIT*

The formation of clouds is dependent on the availability of aerosols to initiate the condensation of water vapor. In the case of cirrus clouds, ice nucleation can occur homogeneously at low temperature and high saturation on the vast majority of particles or heterogeneously at high temperature and low saturation on the small fraction of atmospheric aerosols that are efficient ice nuclei (IN). The critical properties that make for a good IN are slowly being established. This work focuses on those particles which have been shown to be important IN through in situ studies: mineral dust and metallic particles are the dominant source of residual particles, whereas sulfate/organic particles are underrepresented and elemental carbon and biological material are essentially absent. We have conducted ice nucleation studies using the Droplet Measurement Technologies SPectrometer for Ice Nuclei (SPIN) on mineral dust and metallic aerosol and report ice nucleation conditions. A comparison to the types that are not observed in cirrus and to the onset of homogeneous freezing is made.

10CC.4

CCN and Vertical Velocity Influences on Droplet Concentrations and Supersaturations in Clean and Polluted Stratus Clouds. JAMES HUDSON, Stephen Noble, *Desert Research Institute*

Cloud microphysics and CCN measurements in two marine stratus cloud projects are presented and analyzed. Results show that the increase of cloud droplet concentrations (N_c) with higher CCN concentrations (N_{CCN}) rolls off for N_{CCN} at 1% supersaturation (S) ($N_{1\%}$) above 400 cm^{-3}. At such high concentrations N_c was no longer correlated with N_{CCN}, but is related to vertical velocity (W) or variations of W ($sigma_w$), which are more relevant to stratus clouds. This changeover from predominate N_c dependence on N_{CCN} to N_c dependence on W or $sigma_w$ is due to the higher slope (k) of CCN spectra that is typically found at lower S. The higher k at lower S becomes more relevant for determining N_c because of the reduction of cloud S due to greater competition among the higher droplet concentrations that are induced by high N_{CCN}. Higher k of input CCN spectra tends to increase the apparent influence of W or $sigma_w$ variations relative to the influence of N_{CCN} variations on N_c. This changeover at high N_{CCN} thus seems to put a limit on the indirect aerosol effect (IAE). Although these results appear to reduce the influence of the aerosol (CCN) on cloud microphysics this is really not the case because it is both the concentration and especially the shape (k) of the CCN spectrum that produces the conditions where the dynamics becomes more important for determining N_c and cloud microphysics.

On the other hand, in clean maritime air ($N_{1\%}$ <~ 200 cm^{-3}) stratus cloud N_c often exceeded $N_{1\%}$, which means cloud S > 1%, which considerably exceeds conventional wisdom that stratus cloud S is less than 0.3%. This means that smaller (i.e., 20 nm) more numerous CCN can produce stratus cloud droplets in the more susceptible clouds that are so important for IAE.

10CC.5

Observations of Sharp Oxalate Reductions in Stratocumulus Cloud Water at Variable Altitudes. Armin Sorooshian, ZHEN WANG, Matthew Coggon, Haflidi Jonsson, Barbara Ervens, *University of Arizona*

This work examines organic acid and metal concentrations in northeastern Pacific Ocean stratocumulus cloud water samples collected by the CIRPAS Twin Otter between July-August 2011. Correlations between a suite of various monocarboxylic and dicarboxylic acid concentrations are consistent with documented aqueous-phase mechanistic relationships leading up to oxalic acid production. Monocarboxylic and dicarboxylic acids exhibited contrasting spatial profiles reflecting their different sources; the former were higher in concentration near the continent due to fresh organic emissions. Concentrations of sea salt crustal tracer species, oxalate, and malonate were positively correlated with low-level wind speeds suggesting that an important route for oxalate and malonate entry in cloud water is via some combination of association with coarse particles and gaseous precursors emitted from the ocean surface. Three case flights show that oxalate (and no other organic acid) concentrations drop by nearly an order of magnitude relative to samples in the same vicinity. A consistent feature in these cases was an inverse relationship between oxalate and several metals (Fe, Mn, K, Na, Mg, Ca), especially Fe. By means of box model studies we show that the loss of oxalate due to the photolysis of iron oxalato complexes is likely a significant oxalate sink in the study region due to the ubiquity of oxalate precursors, clouds, and metal emissions from ships, the ocean, and continental sources.

10CC.6

Parameterization of In-Plume Aerosol Processing Effects on the Efficacy of Marine Cloud Albedo Enhancement from Controlled Sea-Spray Injections. Geoff Stuart, ROBIN STEVENS, Dominick Spracklen, Hannele Korhonen, Jeffrey Pierce,*Dalhousie University*

The intentional enhancement of cloud albedo via controlled sea-spray injection from ships has been proposed as a possible method to control anthropogenic global warming; however, there remains significant uncertainty in the efficacy of this method due to uncertainties in aerosol and cloud microphysics. A major assumption used in multiple recent studies is that all sea-spray was emitted uniformly into some oceanic grid boxes, and thus did not account for sub-grid aerosol microphysics within the sea-spray plumes. However, as a consequence of the fast sea-spray injection rates that are proposed, in the order of 10^{17} s^{-1}, particle concentrations in these plumes may be quite high and particle coagulation may significantly reduce the number of emitted particles and increase their average size. Therefore, it is possible that the emissions necessary to reach a desired cooling may be even larger than currently assumed.

Using a multi-shelled Gaussian plume model with size-resolved aerosol coagulation, we determine how the final number and size of particles depends on the emission rate and size of the emitted sea-spray plume and local atmospheric conditions, including wind speed and boundary-layer stability. Under the injection rates reported in Salter (2008) and typical marine conditions, we find that the number of aerosol particles is reduced by about 40%. This fraction decreases for decreasing emission rates or increasing wind speeds due to lower particle concentrations in the plume.

Based on the relations for expanding plumes from Turco and Yu (1997) and the results of our model, we develop a parameterization for the fraction of particles remaining based on the emissions rate, size distribution of emissions, wind speed, and boundary-layer stability. This parameterization should allow more accurate predictions of the aerosol number concentrations that would be produced by sea-spray geoengineering, and thus more accurate assessments of the efficacy and side-effects of this method.

10IM.1

Characterization of the Aerodyne Mini-Aerosol Mass Spectrometer. ANITA JOHNSON, J. Doug Goetz, Edward Fortner, Urs Rohner, Michael Cubison, Marc Gonin, Thorsten Hohaus, John Jayne, Douglas Worsnop, Peter DeCarlo, *Drexel University*

The Aerodyne mini-Aerosol Mass Spectrometer (mini-AMS) has been developed to facilitate size-resolved aerosol chemical composition measurements in a more compact space with lower power demands. Maintaining the high sensitivity of previous versions of the AMS was a key goal of this new development. The design of the mini-AMS has been updated with a more compact vacuum system utilizing new split flow pump technology and a smaller vacuum chamber. While the new compact design reduced the overall footprint of the aerosol mass spectrometer, other non-ideal characteristics arose. Higher air beam signal, and reduced particle transmission were seen with the original design. To optimize the sensitivity, reduce the airbeam signal, and improve the small particle transmission, laboratory experiments were performed. These included the detailed investigation of the optimal vacuum pressures in the differentially pumped system, and particle transmission experiments. Intercomparison with a Soot Particle-Aerosol Mass Spectrometer (SP-AMS) was performed during a field deployment to Lake Mokoma, Pennsylvania in the summer of 2012. The intercomparison showed similar measurements with the mini-AMS and the SP-AMS with the regression comparison of key aerosol species of sulfate and organics showing slopes of 0.949, and 0.615 and R2 of 0.81, and 0.71, respectively. Comparison of the mini-AMS calculated volume to a co-located Brechtel Scanning Electrical Mobility Sizer also showed similar agreement.

10IM.2

Aerosol Chemical Speciation Monitor (ACSM) Inter-Comparison Study for Ambient Fine Aerosol Measurements in Downtown Atlanta, Georgia. SRI HAPSARI BUDISULISTIORINI, Manjula Canagaratna, Philip Croteau, Karsten Baumann, Eric Edgerton, Nga Lee Ng, Vishal Verma, Wendy Marth, Stephanie Shaw, Eladio Knipping, Douglas Worsnop, John Jayne, Rodney Weber, Jason Surratt, *University of North Carolina at Chapel Hill*

Currently, there are a limited number of studies that evaluate ACSM performance in the field. In the present study, we report on the inter-comparison of the ACSM with collocated continuous and integrated species and mass measurements at the Jefferson Street (JST) site located in Atlanta, GA, over different seasons.

Correlations of two collocated ACSMs result in high correlation ($r^2 > 0.8$) for all chemical species, except for chloride ($r^2 = 0.66$), with slopes and 1-standard deviations (1.03–1.09 ± 0.005–0.02). The ACSM chemical constituents are linearly correlated with the continuous ($r^2 > 0.7$) and integrated ($r^2 > 0.6$) measurements from the JST site, but correlations of nitrate and chloride in the summer are weaker ($r^2 < 0.4$). Slopes of linear correlations of ACSM PM_1 versus JST $PM_{2.5}$ measurements for sulfate, ammonium, nitrate, and chloride are (0.87–1.12 ± 0.004–0.05), (1.05–1.31 ± 0.004–0.06), (1.73–2.79 ± 0.01–0.18), and (0.51–0.57 ± 0.04–0.07), respectively. OM/OC ratios from ACSM PM_1 OM with that of OC $PM_{2.5}$ from Sunset OC/EC Analyzer and filter measurements are (3.07–3.16 ± 0.01) and (2.81–2.77 ± 0.13–0.17), respectively. Large discrepancy found in nitrate measurements might be attributed to evaporation of nitrate from filter during warm periods and condensation of gas phase species on filters during cold periods. The possible contributions of organic nitrate signals to the measured ACSM nitrate concentrations are also investigated.

Correlations of the ACSM non-refractory PM_1 plus EC with TEOM $PM_{2.5}$ mass are strong ($r^2 > 0.7$) with slopes (1.14–1.80 ± 0.02–0.09). The ACSM NR-PM_1 correlations with FRM PM_1 are very high (r2 > 0.8) with slopes (0.7–1.30 ± 0.05–0.21). Estimation of aerosol density from correlation of ACSM PM_1 mass with SEMS-DMA-MCPC PM_1 volume concentration yields a density of 1.66 ± 0.3 g cmS^-3.

10IM.3

Development and Evaluation of a Laser Induced Incandescence - Mass Spectrometric Analyzer (LII-MS) for Online Measurements of Aerosol Chemical Composition. MIYAKAWA TAKUMA, Takeda Naoki, Koizumi Kazuhiro, Tabaru Masaya, Ozawa Yuya, Hirayama Noritomo, Takegawa Nobuyuki, *The University of Tokyo*

We have developed a new method to quantify chemical composition of aerosol particles depending on their mixing state with black carbon (BC): a laser induced incandescence – particle mass spectrometric analyzer (LII-MS). The LII-MS is a series of a LII chamber and a particle trap-laser desorption mass spectrometer (PT-LDMS) as reported by Takegawa et al. (2012). The LII chamber, which was designed and assembled by Fuji Electric Co. Ltd., is conceptually the same as a single particle soot photometer (SP2, Droplet Measurement Technologies Inc.) . The LII chamber does not only detect but also vaporize and/or decompose BC-containing particles and then the PT-LDMS measures the mass concentrations of sulfate, nitrate, and organic carbon in the sample air efficiently transferred from the LII chamber. The LII laser is turned on and off periodically, which enables the quantification of aerosol chemical composition with respect to their mixing state with BC. Performance of the LII-MS was tested in the laboratory by generating aerosol particles with various chemical compositions and mixing states, and the results have demonstrated the proof of concept. Preliminary data from ambient measurements in Tokyo are also presented and discussed.

10IM.4

Application of a SPAMS 3.0 Single Particle Aerosol Mass Spectrometer to Inhalational Pharmaceuticals and Real-time Microbiology. DAVID FERGENSON, *Livermore Instruments Inc.*

Several instruments capable of collecting a single laser mass spectrum from a single aerosol particle have been developed [1] and a trade-off typically exists between the simplicity of single laser tracking instruments such as the Rapid Single Particle Mass Spectrometer (RSPMS) [2] and the sizing accuracy of multi-laser tracking instruments such as the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) [3]. We describe the SPAMS 3.0, an instrument that combines the advantages of each type of instrument.

A SPAMS 3.0 uses a single laser which is square in profile to both determine the aerodynamic diameter of a particle and to actuate the ionization of that particle by a second laser, adjacent to the first. Like an RSPMS, under the right circumstances it ionizes all particles that it fires upon and degrades gracefully, even at very high particle concentrations. Like an ATOFMS, it determines the size of a particle aerodynamically. Ionization and data acquisition rates of up to 250 Hz are possible.

Data from two applications of the SPAMS 3.0 are presented. In the first application, a SPAMS 3.0 was used to determine the presence/co-presence of different active ingredients in inhalational pharmaceuticals as well as the sizes of the particles in which they were found. In the second application, a SPAMS 3.0 was used to determine the identities of individual microorganisms aerosolized from suspension in real-time.

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10IM.5

The Mass and Mobility Distributions of Ions Generated by a 10mCi Po-210 Alpha Particle Source as Measured by Differential Mobility Analysis-Mass Spectrometry. Mark Meredith, Carlos Larriba-Andaluz, Hui Ouyang, Ranganathan Gopalakrishnan, Derek Oberreit, CHRISTOPHER HOGAN JR., *University of Minnesota*

The unipolar diffusion charging rate and steady state bipolar charge distribution on aerosol particles are dependent on the mass and electrical mobility distributions of the charging ions. However, efforts to precisely determine these distributions have been scarce. We have used a parallel plate differential mobility analyzer coupled to a time of flight mass spectrometer (DMA-MS) to measure the two-dimensional mass-mobility distributions of both positive and negative ions produced by a 10 mCi Po-210 alpha particle source in dry air. In these experiments, ions were drawn into the DMA electrostatically, and the tubing involved was predominantly brass or stainless steel, with a small section of teflon tubing and delrin pastic housing the Po-210 source (keeping it isolated electrostatically from the DMA). The mass spectrometer had sufficiently high resolving power to enable clear identification of the atomic composition of detection ions. Overwhelmingly, both positive and negative ions are found to be ionized by protonation/deprotonation or electron addition/removal, and are composed of organic species from either tubing or which are commonly used in machining fluids (i.e. residues remaining on components after the manufacturing process), or from non-zero vapor pressure components of O-rings (polydimethylsiloxanes). The average masses and mobilities of negative ions are found to be less than those of their positive counterparts, and further narrower mass and mobility distributions are found for negative ions. Density functional theory (DFT) calculations were performed to determine candidate structures for the detected ions, with which gas molecule scattering calculations were applied to compare the predicted and measured mobilities for these ions. Generally, we find that scattering calculations with diffuse and inelastic reemission rules and considering the ion induced dipole potential, predict well the mobilities of ions.

10IM.6

Duty Cycle-Based Time of Flight Cross Section Measurement of Large Singly Charged Proteins. PETER T. A. REILLY, Gregory Brabeck, Vivek Jayaram, Rachit Singh, *Washington State University*

Duty cycle-based digital waveform manipulation is the enabling technology that has extended the working range of time-of-flight mass analyzers up to roughly m/z = 1,000,000. This technology allows millions of massive atmospheric sampled singly-charged ions to be trapped in vacuum at a point just before the end of a linear quadrupole ion trap and then axially ejected on demand in a tightly-collimated temporally-short plug into an awaiting orthogonal acceleration time-of-flight mass spectrometer for highly resolved mass analysis. The work presented here expands the use of duty cycle-based digital waveform manipulation for cross section measurement to characterize proteins and other large biomolecules and complexes. For this application, duty cycle waveform manipulation is important because it provides a method projecting millions of ions into the collision cell in a tightly focused kinetically controlled plug. This methodology allows a collection of ions to be separated as a function of size-to-charge ratio with the same experimental setup as was used to measure resolved mass spectra of singly-charged ions. This work uses ion trajectory simulations to develop the methodology for measurement of protein sizes by time of flight through a low pressure collision cell. The results were compared with kinetic energy based cross section analysis.

10NM.1

Barium Hexaferrite and Yttrium Iron Garnet Thick Films Formed by the Aerosol Deposition Method. SCOOTER JOHNSON, Shu-Fan Cheng, Ming-Jen Pan, Fritz Kub, Charles Eddy, *U.S. Naval Research Laboratory, Washington, D.C.*

The deposition of thick films of nano-crystalline barium hexaferrite (BaFe12O19) (BaM) and Yttrium Iron Garnet (Y3Fe5O12) (YIG) for application in high power passive rf electronic components by the aerosol deposition method (ADM) is presented.

The advantages of the ADM include the ability to form dense ceramic films up to hundreds of microns thick at room temperature and at a high deposition rate on a variety of substrates. Deposition is achieved by creating a pressure gradient that accelerates particles in an aerosol to a velocity up to 400 m/s. Upon impact with the target the particles fracture and embed. Continual deposition forms the thick compacted film.

BaM and YIG films are characterized for their structural, morphological and magnetic properties by scanning electron microscopy, profilometry, and vibrating sample magnetometry, respectively. For BaM, magnetic saturation of the film is 80 % of the bulk value of 68 emu/g, but a significant increase in coercive field suggests significant particle fracturing. All samples have a squareness value near 0.5 indicating randomized orientation of the magnetization. YIG and BaM films of 10 mm in length deposited for 5 minutes resulted in an approximately 200 micron thick film or a deposition rate of 40 microns/min.

10NM.2

Plasmonic Multipetal Flower Assemblies for Hot-spots Engineered SERS(Surface-Enhanced Raman Spectroscopy) Nanosensor. KINAM JUNG, Jungsuk Hahn, Sungjun In, Heechul Lee, Peter Pikhitsa, Kwangjun Ahn, Kyungyun Ha, Junhoi Kim, Jongkwon Lee, Sunghoon Kwon, Namkyoo Park, Mansoo Choi, *Seoul National University*

We fabricate four different arrays of 3D plasmonic multipetal flower (m-PF) assemblies composed of nanoparticles for SERS substrates using spark discharge and ion induced electrostatic focusing method. We demonstrate the control of SP hot-spots as a function of the petal number m (4, 6, and 8). With the increase of the petal number, both the numbers of hot-spots that are formed in 3D nanogaps located between adjacent petals, and the field intensity in the hot-spots show m-proportional increase, to consequently result in approximately m^2 dependencies in the SERS enhancement as a whole. The obtained SERS enhancement is 10^6 ~ 10^7, sufficient for the single molecule detection. Quantitative and qualitative optical behaviors of fabricated 3D multipetal flower assemblies are also studied by measuring dark field (DF) spectra. Enhanced excitation of non-radiative higher order SP modes for the higher m-petal flowers is also interpreted in terms of m-petal geometry, in agreement with the results of SERS, DF spectra, and rigorously calculated near field distributions.

10NM.3

Formation of 1.0-10 nm Ni Clusters in an Atmospheric Pressure DC Microplasma.

R. MOHAN SANKARAN, Ajay Kumar, Seungkoo Kang, Carlos Larriba-Andaluz, Hui Ouyang, Christopher Hogan Jr., *Case Western Reserve University*

Microplasmas are a special class of plasmas formed in geometries where at least one dimension is less than 1 mm. Plasma confinement leads to several unique properties, including high-pressure stability and non-equilibrium. Aerosol nanoparticles can be nucleated and rapidly quenched in a microplasma to obtain small (less than 10 nm) clusters. Using a high resolution differential mobility analyzer (1/2-mini DMA, Nanoengineering) coupled to a faraday cage electrometer, we have investigated the formation of Ni clusters through the decomposition of nickelocene (bis(cyclopentadienyl)nickel). Nickelocene vapor was introduced into the microplasma via a heated tube containing nickelocene powder upstream of the plasma electrodes. Prior to mobility measurement, produced clusters were brought to a steady-state charge distribution via diffusion charging with ions produced in a Kr-85 source (TSI, Inc.). Both positive and negative mobility distributions measured exhibited high intensity peaks around ~0.75 nm equivalent “mobility diameter”, corresponding to the ions produced by the Kr-85 source. The introduction of nickelocene vapor in the microplasma resulted in a lower intensity distribution of clusters, spanning from the peaks corresponding to Kr-85 generated ions to 10 nm in mobility size. Under all circumstances, the mobility distribution from the ion peak to the largest produced clusters was continuous, indicating the microplasma reactor can form stable entities below 2.0 nm in size. To obtain structure-mobility relationships, density functional theory and gas molecule scattering calculations were carried out. The clusters were also collected by electrostatic precipitation and further characterized by atomic force microscopy to confirm their size and distribution. These results demonstrate the ability of microplasma reactors to form stable sub-2.0 nm clusters for studies of particle formation in the vapor phase.

10NM.4

Evolution of Particle Size Distribution of Pristine and Doped Titanium Dioxide in a Flame Reactor: Role of Various Process Parameters.

JIAXI FANG, Yang Wang, Tandeep Chadha, MengMeng Yang, Pratim Biswas, *Washington University in St Louis*

Flame Aerosol Reactor (FLAR) technology is a single step widely utilized commercial methodology for synthesizing nanomaterials. Despite its commercial success, there is still a lack of complete understanding in the fundamental particle formation mechanisms in flames below 3 nm. Challenges in measuring particle size distributions in flames are partially due to difficulties in sampling caused by rapid timescales of aerosol processes such as nucleation, condensation, sintering, and coagulation. In addition particles below 3nm are difficult to measure due to previous limitations in instrumentation. Electrical mobility classification of sub 3nm particles suffer from particle losses due to diffusion and flow instabilities at higher sheath flow rates while condensation particle counters have low detection efficiencies below 3nm. It is widely known that size distributions below 3 nm are no longer continuous as particle diameters become discrete due to the presence of stable molecular clusters. Careful characterization of nanoparticles below 3 nm in a flame aerosol reactor has yet to be performed.

We report particle size distributions of TiO2 in a premixed methane-air flame aerosol reactor for both pristine titanium dioxide and the effects of adding copper dopants. Particles were classified with high resolving powers using a Half-Mini DMA and detected using a faraday cage electrometer. The Half-mini DMA was operated at extremely high sheath flow rates (up to 740 liters per minute) while maintaining laminar flow thereby minimizing diffusion losses during electrical mobility classification. The faraday cage electrometer enabled detection of singly charged particles below 2nm. The evolution of size distributions with respect to height in the flame was examined with respect to varying process parameters such as residence time, equivalence ratio, and precursor concentration. An understanding of these process parameters will be critical in the ability to commercialize and scale up flame aerosol reactors for new applications such as mixed component systems.

10NM.5

Spark Discharge Generator (SDG) – A Promising Tool for Generation of Sub-nanometer Atomic Clusters. ANNE MAISSER, Konstantinos Barmpounis, Michel Attoui, George Biskos, Andreas Schmidt-Ott, *TU Delft*

Clusters consisting of less than 100 atoms can lead to materials with unique properties. Although investigations of atomic clusters date back to the 1970s, their use has been restricted mainly due to limitations in their production. The spark discharge generator (SDG), which has been widely employed to generate airborne nanoparticles of well-defined size and composition, can in principle be employed to produce clusters of a few atoms in high enough quantities. In the SDG varpor clouds are formed as a result of the high temperatures associated with the electrical breakdown between two electrodes. Upon expansion and cooling of these clouds the vapors nucleate to form clusters of a few atoms, which subsequently grow to larger particles by coalescence and agglomeration.

In this work we show that with high dilution flows in the spark region, the applicability of the SDG can indeed be extended to produce atomic clusters down to two atom ions. Similar results have been reported by Peineke et al. (2008) using a glowing-wire generator. The electrical mobilities of the generated clusters are measured by a high-resolution/high-transmission differential mobility analyser (DMA) using helium as a carrier gas. The electrical mobilities of the clusters measured in this work are in agreement with mobilities determined by conventional low-pressure drift-cell experiments (Weis et al., 2002). Our measurements also show that for small numbers of atoms (< 5), the mobility distribution patterns for Al, Ga, Pt and Ag are similar, showing odd-even oscillations due to electron pairing.

The results of this study point out that the SDG is a promising tool for generating atomic clusters suitable for many applications.

Peineke, C., Attoui, M., Robles, R., Reber, A.C., Khanna, S.N., Schmidt-Ott, A. (2009), J. Aerosol Sci., 40, 423-430.
Weis, P., Bierweiler, T., Gilb, S., Kappes, M.M. (2002), Phys. Rev. Lett., 355, 355-364.

10NM.6

Photoassisted One-step Aerosol Fabrication of Zwitterionic Chitosan Nanoparticles. JEONG HOON BYEON, Jeffrey Roberts,*Department of Chemistry, Purdue University*

Zwitterionic chitosan nanoparticles (ZCNPs) were conveniently obtained by a one-step aerosol method, and their potential for the production of biocompatible materials was investigated. A low molecular weight chitosan was conjugated with a succinic anhydride to produce zwitterionic chitosan (ZC). Collison atomized ZC droplets were simultaneously UV irradiated and dried in a tube furnace as a one-step aerosol process to form particles. The zeta potential of the ZCNPs could be easily tuned from pH 4-9, and it was more reactive for UV irradiated cases. On the other hand, the ZCNPs showed a slightly higher cytotoxicity (~85% in cell viability) than that for chitosan nanoparticles (CNPs, ~88%), and the UV irradiation of ZCs further decreased (~83%) cellular viability. The present aerosol process was effective to modify the CNP properties in a facile manner, which can then be employed for a wide range of biomedical purposes.

10SA.1

Sensitivity of the Chemical Mass Balance Model to Different Molecular Marker Traffic Profiles. PALLAVI PANT, Jianxin Yin, Roy M. Harrison, *University of Birmingham*

Road traffic is one of the key sources of particulate matter (PM) concentrations in urban areas, and a good understanding of the contribution of traffic emissions to PM mass is imperative for policy action. The Chemical Mass Balance (CMB) model, based on the principle of mass balance, is routinely used for quantitative estimation of source contributions. However, the model requires locally-relevant profiles for reliable source contribution estimates (SCEs). The traditional approach for creation of source profile involves source sampling although ambient data can also be used. The aim of this study was to assess the response of the CMB-MM model to molecular marker profiles for traffic derived using different sampling approaches, i.e. dynamometer (USA), twin-site (UK) and road tunnel (France) sampling. The traffic estimates thus obtained were cross-compared using other proposed methods.

Ambient data collected at different sites in UK was analysed using the CMB8.2 software for attribution of $PM_{2.5}$ OC mass to different sources (vegetative detritus, wood combustion, coal combustion, natural gas, crustal dust and traffic).The marker species for the traffic profile across the profile runs were monitored and cross-compared to assess the influential species in the different runs. $PM_{2.5}$ estimates were obtained using previously published OC to $PM_{2.5}$ source conversion ratios.

Based on comparisons with estimates from the EC tracer method and mass closures, the ambient profile was found to estimate traffic source better than other profiles although higher standard errors were reported for this profile. It was also observed that selection of species for inclusion in the profile can determine the overall modelling output, both for estimation of traffic source and the overall estimations. It can be concluded based on preliminary analysis that ambient profiles can generate reasonable estimates for traffic source. Further analysis is currently underway using a UK tunnel profile and European dynamometer profiles.

10SA.2

ME-2 Analysis of Long-term On-line Mass Spectrometric Data of Non-refractory Submicron Aerosol in the City of Zurich.FRANCESCO CANONACO, Jay Slowik, Urs Baltensperger, Andre Prévôt, *Paul Scherrer Institute*

We present measurements of submicron aerosol composition from an aerosol chemical speciation monitor deployed in downtown Zurich. The ACSM yields quantitative mass spectra of the non-refractory aerosol component with an averaging period of 15 to 30 minutes. These are one of the first full-year measurements in Europe using this technique. The ACSM is capable of resolving inorganic species such as NH_4, SO_4, NO_3, Cl, and the organics. The data can be further deconvolved in order to identify and apportion the sources, in particular for the complex organic fraction.

There are several possible techniques for the deconvolution of a data set. Positive matrix factorization (PMF) has been extensively exploited for this type of data. However, the multilinear engine 2 (ME2) offers advantages compared to PMF, due to the fact that the user has the possibility to introduce a priori information in form of e.g. known factor profiles into the model.

The aim of this work is to make use of the multiple approaches available in ME2 on the obtained data from downtown Zurich during the full year 2011. For this purpose we implemented a user-friendly interface in the software IGOR Pro.

We will discuss identification and source apportionment of ACSM organic data at an urban site over the full year of 2011 with the ME-2 algorithm. In particular, partially constrained source profiles lead to a successful separation of different sources including traffic wood burning, cooking and more which could not be apportioned by PMF. Especially interesting are the separation of several semi volatile secondary organic aerosol species that could be partially assigned to specific precursor groups. Different techniques, like the a-value or the pulling approach have been tested. Moreover, studying and comparing the outcomes of these just mentioned techniques provides useful information for estimating of the model uncertainty.

10SA.3

Direct Measurements of Near-Highway Aerosol Emissions and Volatile Organic Compounds in a High Diesel Environment.

H. LANGLEY DEWITT, Stig Hellebust, Brice Temime-Roussel, Sylvain Ravier, Lucie Polo, Jean Luc Jaffrezo, Veronique Jacob, Aurelie Charron, Jean-Luc Besombes, Nicolas Marchand, *Aix Marseille Université, Laboratoire Chimie Environnement*

In France, the diesel passenger car market has grown rapidly since the 1980s. Recent data show that diesel vehicles now outnumber gasoline vehicles on the road by a factor of 2-3. While diesel-powered engines usually offer an advantage in fuel efficiency over gasoline-powered engines, there is some controversy over the role of each vehicle type's emission in both primary organic aerosol and volatile organic compounds (VOCs) that react in the atmosphere to form secondary organic aerosol (SOA). In this context, the fall 2011 Measuring and mOdelling traffic COngestion and Pollution (MOCOPO) field campaign was designed to measure aerosol directly affected by vehicular emissions in-situ while capturing parallel data on local traffic. From September 11-September 23 2011, an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS) continuously measured the aerosol and VOC chemical composition, respectively, beside a heavily trafficked highway on the outskirts of Grenoble (France). Black carbon measurements and 4-hr filter samples for offline chemical analysis were also collected. The Positive Matrix Factorization model was applied to the high resolution aerosol and VOC data (both with and without inorganic ions) to resolve chemically and temporally aerosol and VOC mixtures for source apportionment. Periods heavily influenced by vehicular emissions were compared with periods more influenced by regional SOA. Two factors were found to exhibit diurnal trends related to traffic peaks: a typical Hydrocarbon-like Organic Aerosol (HOA) factor, which correlated well with black carbon, and possibly a nitrogen-containing organic aerosol factor (NOA). While the concentration of diesel- and gasoline-powered vehicles on the highway largely co-varied, estimated emission factors from traffic data and aerosol concentration in this high diesel environment were calculated and smog chamber data from diesel and gasoline vehicular emissions were compared to these ambient measurements.

10SA.4

Examination of Airborne-Based Smoke Marker Ratios from Prescribed Burning.

AMY P. SULLIVAN, Taehyoung Lee, Gavin McMeeking, Sonia Kreidenweis, Sheryl K. Akagi, Robert J. Yokelson, Shawn P. Urbanski, Jeffrey L. Collett, Jr., *Colorado State University*

Biomass burning is one of the main sources of water-soluble organic carbon (WSOC) and organic carbon (OC) aerosols. Therefore, it is important to be able to determine the contribution of biomass burning to the WSOC or OC concentrations. The most common approach used to make this determination is through the use of smoke marker measurements. The key to this approach is that the ratio of the smoke marker to the total WSOC or OC concentration must be known at the source. However, there is still much uncertainty in these source ratios, especially from prescribed burning and wildfires. Therefore, in this work, we collected smoke marker data from aboard the Twin Otter aircraft as it flew through smoke from prescribed burning activities taking place in South Carolina in November 2011. Results were obtained by coupling a Particle-into-Liquid Sampler (PILS) with a Total Organic Carbon analyzer for real-time measurement of WSOC and a fraction collector to provide off-line samples for smoke marker analysis by high-performance anion-exchange chromatography with pulsed amperometric detection. Airborne results for smoke markers, including levoglucosan, mannosan, galactosan, and potassium, from a number of different prescribed burns will be presented. Smoke marker ratios from controlled laboratory burn source samples collected at the Fire Science Lab in Missoula, MT during the FLAME (Fire Science at Missoula Experiment) studies will be compared to the results from the airborne measurements. How parameters such as aging and fuel type might play a role will also be discussed.

10SA.5

14C-based Source Apportionment of Carbonaceous Aerosols in Switzerland for 2008 – 2012.

PETER ZOTTER, Gabriela Ciobanu, Yanlin Zhang, Imad El Haddad, Soenke Szidat, Lukas Wacker, Urs Baltensperger, Andre Prévôt, *Paul Scherrer Institute*

Radiocarbon (14C) analysis is a direct and quantitative tool for distinguishing fossil and non-fossil sources of carbonaceous aerosols (total carbon, TC), since 14C is completely depleted in fossil fuels whereas other sources have a contemporary 14C-level. This study presents source apportionment results using measurements of 14C in organic and elemental carbon (OC and EC) collected simultaneously at 16 air quality monitoring stations (11 north and 5 south of the Alps) across Switzerland, during 5 consecutive winters (2007/2008–2011/2012). The filter samples are also analysed for EC/OC, major ions and levoglucosan content. A newly developed approach enabling the analysis of filter samples by the aerosol mass spectrometer was also applied. Black carbon (BC) was measured at 4 stations by aethalometers and apportioned into a traffic and wood-burning fraction. This is an unprecedented dataset in terms of number of samples analysed and methodologies applied, providing unique insights into wintertime carbonaceous aerosol sources.

OC and EC account respectively for ~80% and ~20% of TC, the second largest component of PM during the measurement period after Nitrate (25%) contributing 23% of total PM. 14C-results indicate that carbonaceous aerosol is overwhelmingly non-fossil (83% of OC and 46% of EC), suggesting that wood burning is the major source of TC in Switzerland during winter smog episodes. The highest non-fossil values (100% and 87% for OC and EC, respectively) were registered for alpine valley sites and the lowest at highly traffic influenced sites (47% for OCNF and 15% for ECNF). The spatial and temporal trends of biomass burning contribution observed during 5 winters and at the different sites will be further discussed and related to the prevailing meteorological and wood combustion conditions.

This work was funded by the Swiss Federal Office for Environment, inNet Monitoring AG, Liechtenstein and the Swiss cantons Basel-Stadt, Basel-Landschaft, Graubünden, Solothurn, Valais and Ticino.

10SA.6

Long-Term Trend Analysis of Factors Contributing to PM2.5 in Toronto: What is this Elemental Carbon-Rich Factor?

CHEOL-HEON JEONG, Greg J. Evans, Dennis Herod, Ewa Dabek-Zlotorzynska, *SOCAAR, University of Toronto*

A previous source apportionment study of five Canadian cities using Positive Matrix Factorization (PMF) revealed an elemental carbon (EC)-rich factor, characterized by more thermally stable EC fractions, that was only present at the three sites in south-eastern Canada (Jeong et al., 2011). A follow-up study of five urban and rural sites across this 600 km region showed that this EC-rich factor exhibited similar temporal patterns at the both the urban and rural sites, with an increasing trend from 2005 (Jeong et al., 2013). On average, the EC-rich factor accounted for approximately 50% of the total EC and contributed 6~20% of the total PM2.5 mass concentrations in this region. A third source apportionment study was conducted using long-term PM2.5 chemical speciation data measured from 2004 to 2011 in Toronto to investigate the underlying causes for the reduction in PM2.5 mass that has occurred since 2005. The contributions of PMF-resolved factors associated with long-range transport, i.e., secondary sulphate and secondary nitrate factors were found to show similar decreasing trends. This finding suggests that a reduction of coal combustion may be the main reason for the PM2.5 improvement in this urban area. The 8-year trend of the EC-rich factor contribution will be discussed in detail and the characteristic of the factor will be presented.

Jeong et al. (2011) Atmos. Poll. Res. 2, 158-171.
Jeong et al. (2013) Environ. Sci. Technol. submitted.

11CA.1

Searching for Evidence of Aqueous SOA Formation in the Po Valley. AMY P. SULLIVAN, Natasha Hodas, Barbara Turpin, Kate Skog, Frank Keutsch, Stefano Decesari, M. Cristina Facchini, Jeffrey L. Collett, Jr., *Colorado State University*

Laboratory experiments and predictions suggest that water-soluble products from the gas phase oxidation of volatile organic compounds can partition into atmospheric waters where they are further oxidized forming low volatility products. These products can remain in the particle phase after water evaporation forming what is termed as aqueous secondary organic aerosol (SOA). A gap between model-predicted and observed SOA and a tendency for smog chamber experiments to form SOA that is less oxygenated and hygroscopic than atmospheric SOA both suggest that missing aqueous processing may be a key contributor to ambient SOA. To date, however, few studies have attempted to observe aqueous SOA formation in the ambient atmosphere. Here we report observations from the Po Valley, Italy during the PEGASOS (Pan-European Gas-AeroSols-climate interaction Study) campaign conducted in June-July 2012, a time of high pollution and humidity when aqueous SOA production is favorable. Measurements of light organic acids and inorganic anions/cations were made using a PILS-IC (Particle-into-Liquid Sampler – Ion Chromatography), water-soluble organic carbon (WSOC) using a PILS-TOC (Particle-into-Liquid Sampler – Total Organic Carbon), and gas phase glyoxal using a laser induced phosphorescence technique. Additional measurements at the study site included standard gases and meteorological parameters. The approach and results of the analysis on the combined data set to identify evidence of aqueous SOA will be presented. Parameters to be examined include observed concentrations of oxalate (a key product of postulated mechanisms for aqueous SOA production), sulfate (a secondary product with an important aqueous formation pathway), glyoxal (an important gas phase precursor for aqueous SOA production), and WSOC (a good proxy for SOA in the absence of biomass burning). Periods of WSOC increase will be examined to look for evidence of aqueous SOA production and how it depends on liquid water content, light, the availability of gas phase precursors, and photochemical oxidants.

11CA.2

Secondary Pollutant Formation in the Lake Tahoe Basin, USA. BARBARA ZIELINSKA, Andrzej Bytnerowicz, Alan Gertler, Mark McDaniel, Joel Burley, *Desert Research Institute*

Lake Tahoe, located at 6,225 ft. (1,897 m) in the Sierra Nevada mountain range, is the largest alpine lake in North America. Known for the clarity of its water and the panorama of surrounding mountains on all sides, Lake Tahoe is a prime tourist attraction in the California – Nevada area. However, the Lake Tahoe Basin is facing significant problems in air quality and declining water clarity.

In the summer of 2012, we conducted a study in the Basin designed to characterize the precursors and pathways of secondary pollutant formation, including ozone, secondary organic aerosol (SOA) and ammonium nitrate. Four strategic sampling sites were selected inside the Basin; two of these sites were located at high elevation (one each on the western and eastern sides of the Basin) and two were positioned near the Lake level. We collected canister samples for detailed speciation of volatile organic compounds (VOC), 2,4-dinitrophenylhydrazine (DNPH) impregnated Sep-Pak cartridges for analysis of carbonyl compounds and honeycomb denuder/filter pack samples for measurement of concentrations of ammonia, nitrous acid, nitric acid, and fine particulate ammonium nitrate with a resolution of several hours over a 6-day sampling period. We also collected $PM_{2.5}$ Teflon and quartz filter samples for measurements of mass, organic and elemental carbon (OC/EC) concentrations and speciation of organic compounds. Ozone and NO/NO_2 concentrations were continuously measured.

This presentation will discuss concentrations of volatile biogenic and anthropogenic secondary pollutant's precursors in the Basin and relate these concentrations to the measured SOA tracers.

11CA.3

Characterization of Secondary Organic Aerosols from Isoprene, Monoterpenes, β-Caryophyllene, Toluene, and Naphthalene at Three Sites in the Pearl River Delta, China. JIAN ZHEN YU, Wing Yi Wong, X. H. Hilda Huang, *Hong Kong University of Science and Technology*

Isoprene, monoterpenes, beta-caryophyllene, toluene, and naphthalenes are common volatile organic compound (VOC) precursors for secondary organic aerosol (SOA) in areas of significant biogenic and anthropogenic VOC emissions, such as the Pearl River Delta (PRD) in South China. Field measurements of their molecular tracers provide estimates of SOA specific to precursors that can not otherwise obtained through other SOA measurements. Tracers for SOA derived from isoprene, monoterpenes, beta-caryophyllene, toluene, and naphthalenes were quantified in $PM_{2.5}$ samples collected at two urban sites and one suburban site in the PRD in 2009. No clear urban-suburban gradient in SOC was observed in this data set consisting of two samples in each month of 2009 at each site. Average SOC levels from both biogenic and anthropogenic precursors at GZ (an urban location in Guangzhou) and NS (a suburban location of Guangzhou) were comparable while SOC at TW (an urban site in Hong Kong) was consistently lower (about 52-85% of those at GZ and NS). The average total SOC concentrations attributable to the target precursors were 1.54 $\mu gC\ m^{-3}$ accounting for 14% of OC at TW, 2.35 $\mu gC\ m^{-3}$ (16%) at GZ, and 2.08 $\mu gC\ m^{-3}$ (16%) at NS. On certain days, the percentage of SOC from these few precursors could explain as much as 39% of OC, highlighting the importance of these VOCs in contributing to SOA. Among the three biogenic VOC precursors, SOC by beta-caryophyllene contributes the most (average: 0.41-0.56 $\mu gC\ m^{-3}$). The average SOC from naphthalenes is 0.33-0.53 $\mu gC\ m^{-3}$, comparable to the SOC attributable to toluene and xylenes (0.48-0.73 $\mu gC\ m^{-3}$). This result suggests the need to characterize and quantify emissions of naphthalene and its methyl derivatives for the understanding of SOA formation in this region. It was found that the SOA tracers for beta-caryophyllene and naphthalene were strongly correlated (r^2: 0.70) despite their apparently distinct sources, possibly suggesting oxidants rather than the VOC precursors are the limiting factors for the formation of SOA from these sources.

11CA.4

Observational Constraints on High- and Low-NOx Aerosol Formation from Isoprene. DAVID WORTON, Allen H. Goldstein, Jason Surratt, Brian LaFranchi, Arthur Chan, Yunliang Zhao, Robin Weber, Jeong-Hoo Park, Jessica Gilman, Joost de Gouw, Changhyoun Park, Gunnar Schade, Melinda Beaver, Jason St. Clair, John Crounse, Paul Wennberg, Glenn Wolfe, Sara Harrold, Joel A. Thornton, Delphine Farmer, Kenneth Docherty, Michael Cubison, Jose-Luis Jimenez, Amanda Frossard, et al., *University of California, Berkeley*

Isoprene photooxidation in the atmosphere is an important source of secondary organic aerosol (SOA) and there is increasing evidence that anthropogenic emissions can enhance this SOA formation. In this work we use ambient observations of organosulfates formed from isoprene epoxydiols (IEPOX) and methacrylic acid epoxide (MAE), an oxidation product of methacryloyl peroxy nitrate (MPAN), and a broad suite of chemical measurements to investigate the relative importance of high- and low- NO_x SOA formation pathways at a forested site in California. Gas phase IEPOX and MPAN concentrations were present in substantial excess (> 100 times) over their particle phase organosulfate products indicating that precursor abundances were not the limiting factor for SOA formation. Concentrations of the IEPOX- and MAE-derived organosulfates were similar (~1 ng m^{-3}) under cooler conditions, while the IEPOX-derived organosulfates were much more abundant (~10 – 20 ng m^{-3}) under warmer conditions, consistent with larger isoprene emissions. In contrast to the IEPOX-derived organosulfates, the MAE-derived organosulfate concentrations were negligible at elevated temperatures as a result of the short thermolysis lifetime of MPAN, which competes with the aerosol-forming reaction of MPAN with the hydroxyl radical. As the majority of the high NO_x SOA from isoprene goes through MPAN, with the exception of aqueous processing of glyoxal, the strong anti-correlation between temperature-driven isoprene emissions and the thermal lifetime of MPAN suggests that the low NO_x SOA formation pathway via IEPOX is more important at the surface. However, in regions of high NO_x, high isoprene emissions and strong vertical mixing the longer MPAN thermal lifetime aloft could lead to a vertically varying isoprene SOA source.

11CA.5

Secondary Organic Aerosol Formation from the Emissions of Soil and Leaf Litter Collected in a Temperate Coniferous Forest. CELIA FAIOLA, Graham VanderSchelden, Miao Wen, Doug Cobos, B. Thomas Jobson, Timothy M. VanReken, *Washington State University*

In the United States, emissions of volatile organic compounds (VOCs) from natural sources are known to exceed all anthropogenic sources combined. VOCs participate in oxidative chemistry in the atmosphere and impact the concentrations of ozone and particulate material. The formation of secondary organic aerosol (SOA) is particularly complex and is frequently underestimated using state-of-the-art modeling techniques. We present findings that suggest emissions of important SOA precursors from soil and leaf litter are higher than current inventories would suggest.

Soil and leaf litter samples were collected at Big Meadow Creek from the University of Idaho Experimental Forest. The dominant tree species in this area of the forest are ponderosa and white pine, douglas fir, western larch, and cottonwood. Samples were transported to the laboratory and housed within a 0.3 cubic meter Teflon dynamic chamber where VOC emissions were continuously monitored. To generate aerosol, soil and leaf litter emissions were pumped into a 7 cubic meter Teflon aerosol growth chamber where they were oxidized with ozone in the absence of light. The evolution of gas-phase species and particle characteristics were monitored over the following eight hours. Gas-phase species were measured within the soil chamber and aerosol growth chamber with a GC-MS-FID and a PTR-MS. Particle size distribution, chemical composition, and hygroscopic properties were measured in the aerosol growth chamber with a SMPS, HR-ToF-AMS, and CCNc respectively. Monoterpenes dominated the emission profile with emission rates up to 283 micrograms carbon per meter squared per hour. These emission rates are higher than those presented previously from summertime measurements, but are consistent with other results from springtime measurements in Finland. The dominant monoterpenes emitted were beta-pinene, alpha-pinene, and delta-3-carene in descending order. SOA yields and compositional profiles have also been evaluated and compared to other SOA derived from biogenic precursors.

11CC.1

Modeling the Impact of Surface Adsorption of Organic Gases on Aerosol Surface Tension and Cloud Droplet Formation. V. FAYE MCNEILL, *Columbia University*

We recently showed experimentally that the adsorption of surface-active organic gases from the gas phase can depress aerosol surface tension, leading to enhanced cloud droplet formation (Sareen et al., Proc. Natl. Acad. Sci. USA, 2013). We have developed a general analytical approach for predicting aerosol surface tension based on gas-phase surfactant loadings, taking into account the effects of both bulk uptake and surface adsorption. These predictions allow calculation of the particle hygroscopicity and predictions of cloud droplet formation. This approach may be used alone or in conjunction with atmospheric chemistry models such as the McNeill Group model, GAMMA (McNeill et al., ES&T 2012). We will present results for atmospheric scenarios and highlight needs for additional experimental work.

11CC.2

Statistical Mechanics of Multilayer Sorption: Surface Tension. ANTHONY WEXLER, Cari Dutcher, Simon Clegg, *University of California, Davis*

Mathematical models of surface tension as a function of solute concentration are needed for predicting the behavior of surface processes relevant to the environment, biology and industry. Current aqueous surface tension – concentration models capture either solutions of electrolytes or those of organics, but a single set of equations has not yet been found that represents both in one unified framework. In prior work we developed an accurate model of the activity-concentration relationship over the full range of compositions by extending the BET and GAB isotherms models to multiple sorbed monolayers (Dutcher et al. JPC 2011, 2012, 2013). Here we employ similar statistical mechanical tools to develop a simple equation for the surface tension – composition relationship that differs remarkably from prior formulations in that it (1) works equally well for organic and electrolyte solutes and their mixtures, (2) does not contain any fac-tors representing the relative amounts of solute in the bulk or at the surface – this is captured by surface-bulk equilibria in the model, and (3) is accurate over the entire RH range.

11CC.3

Quantifying Aerosol Mixing State with Entropy Measures. NICOLE RIEMER, Matthew West, *University of Illinois at Urbana-Champaign*

The “mixing state” of a particle population is the distribution of the per-particle composition. To understand aerosol climate impacts, the mixing state is important because it governs optical properties and cloud condensation nuclei activity, for example. In discussions on mixing state the terms “external mixture” and “internal mixture” are frequently used to describe how different species are distributed over the particle population. In an external mixture the particle species reside in different particles, whereas in an internal mixture the particle species are present within one particle.

While these terms may be appropriate for idealized cases, it has long been realized from observational evidence that ambient aerosol populations rarely fall in these two simple categories. Here we present, for the first time, a metric for aerosol mixing state based on rigorous information-theoretic entropy concepts. This is based on the division of species diversity into average per-particle diversity versus bulk population diversity. We illustrate this new framework with model results from the stochastic particle-resolved model PartMC-MOSAIC. These results demonstrate how the mixing state metrics evolve with time for several archetypal cases, each of which isolates a specific process such as coagulation, emission and condensation. We additionally present an analysis of the mixing state evolution for a complex urban plume case, for which these processes occur simultaneously.

11CC.4

Aerosol Dynamics Simulation Using Sparse Particle Methods. ROBERT MCGRAW, *Brookhaven National Laboratory*

A new class of sparse particle representations for an aerosol population is presented. As defined here, "sparse particle representation" refers to the replacement of a typically continuous particle distribution function (pdf) by a small set of weighted delta functions in particle size and/or composition coordinates. Specifically, class members are defined here as solutions to a constrained optimization problem involving maximization or minimization of an aerosol property using linear programming (LP) methods. The quadrature method of moments (QMOM), in which a set of lower-order moments is evolved by mapping them to an equivalent set of quadrature abscissas and weights for closure, is shown to fall into this class. The new LP-based approach allows for a much broader class of aerosol properties to be used to generate the sparse particle distributions; whereas the QMOM is limited to moments. The new sparse distributions are shown to provide a set of abscissas and weights that can be used both for quadrature approximation of aerosol physical and optical properties and for closure of the dynamical equations governing evolution of the pdf. In the first case, approximation of aerosol properties, nested bounds on the property are obtained through the sequential addition of either model- or observation-based constraints, with the most relevant measurements providing the greatest reduction in uncertainty, quantified in LP as a reduction in the size of the feasible solution set. In the second case, aerosol dynamics, a generalization of the Jacobian matrix transformation (JMT) [McGraw and Wright, Aerosol Science 34, 189-209 (2003)] enables a closed set of equations for aerosol property evolution to be obtained directly in terms of the sparse pdf. As a result, JMT closure is extended to a much broader set of aerosol properties than moments.

11CC.5

Cloud Condensation Nuclei Closure Study for Transient Drive Cycles. DIEP VU, Daniel Short, Mark Villela, Georgios Karavalakis, Thomas D. Durbin, Akua Asa-Awuku, *University of California, Riverside*

Particles emitted in the exhaust may vary in composition under different driving conditions. This poses challenges when characterizing ephemeral changes in aerosol composition for vehicle-testing procedures conducted over transient cycles. Hence, cloud condensation nuclei (CCN) properties of the exhaust from vehicle studies with gasoline fuel blends are currently not well understood. In this study, the potential to activate as CCN and form cloud droplets in the atmosphere was investigated for aerosols derived from various biofuel/gasoline blends. Measurements were collected for gas direct injection passenger (GDI) vehicles using different blends of ethanol and iso-butanol in gasoline over the Federal Test Procedure (FTP) and California Unified Cycle (UC) on a chassis dynamometer. A Continuous Flow Streamwise Thermal Gradient CCN Counter was operated in parallel with two different sizing instruments; a Scanning Mobility Particle Sizer (SMPS) and an Engine Exhaust Particle Sizer (EEPS). The EEPS provides a full particle size distribution within each second. The SMPS has longer time resolution and provides size distributions every 2.25 min. All instruments are operated during transient driving cycles. This is the first study to combine fast resolution CCN activation information from both a continuous CCN counter and an EEPS (10Hz). Results show the critical diameter shifts throughout the cycle, thereby reflecting the sensitivity of aerosol composition to the transient nature of the cycle. Measured versus predicted values of CCN are presented with EEPS and SMPS data sets.

11CO.1

Detailed Characterization of Particulates Emitted by Pre-commercial High-Efficiency Gasoline Engines. ALLA ZELENYUK, Paul Reitz, Dan Imre, Mark Stewart, Paul Loeper, Cory Adams, Mitchell Hageman, Axel Maier, Stephen Sakai, David Foster, David Rothamer, Michael Andrie, Roger Krieger, Kushal Narayanaswamy, Paul Najt, Arun Solomon, *Pacific Northwest National Laboratory*

Aggressive fuel efficiency mandates drive development of advanced engine technologies, which blur the lines between traditional engine categories. Spark Ignition Direct Injection (SIDI) and Gasoline Direct Injection Compression Ignition (GDICI) are two gasoline engine technologies with potential to achieve very high fuel efficiency by operating more like diesel engines.

We present the results of a study, in which we characterized the size, composition, effective density, and mass of individual exhaust particles, which we use to calculate fractal dimension, average diameter of primary spherules (dp), and number of spherules, void fraction, and dynamic shape factors as function of particle size.

GDICI particulate matter (PM) properties varied markedly with engine load. Under low load conditions, PM is dominated by compact organic particles externally mixed with ~30% fractal soot aggregates comprised of primary spherules with dp=40 nm. Under high load conditions, all particles are fractal with dp=26 nm. Under both conditions fractal agglomerates contain ~55% elemental carbon and have fractal dimensions of 2.11.

Similar characterization of SIDI PM indicates that dp varies dramatically depending on engine operating condition and fuel, which is a marked contrast with diesel. Under some operating conditions, two distinct particle modes were observed: regions of rich air/fuel mixture in the combustion region lead to fractal agglomerates with smaller dp, while the larger primary spherules may be linked to wall/piston impingement. In addition, we find the SIDI PM to contain 40-60% organics tightly bound with the elemental carbon, making it impossible to remove by thermo-denuder.

These results point to significant differences between the properties of PM produced by diesel engines and that generated by SIDI and GDICI engines, requiring adaptation of existing after-treatment technologies used to reduce particulate emissions and their environmental impact.

11CO.2

Chemistry and Partitioning Behavior of Inorganic and Organic Particulate Matter Measured in Real-time from Light-duty Vehicles under Varying Conditions. SONYA COLLIER, Toshihiro Kuwayama, Sara Forestieri, Michael Kleeman, Christopher Cappa, Qi Zhang, *University of California, Davis*

We investigated the chemistry and partitioning behavior of inorganic and organic particulate species in the exhaust of 11 in-use vehicles, which included 8 gasoline light-emission vehicles with years ranging from 1997 to 2003 and 3 alternative vehicles consisting of an ultra-low emission vehicle, a passenger diesel vehicle, and a gas direct-inject vehicle. In this study, vehicle emissions were sampled into a custom-built secondary dilution system (SDS) while running on a chassis dynamometer under the California Unified Cycle (UC), where emissions were diluted to atmospherically relevant concentrations (5-30 micro-grams per meter cubed) under varying relative humidity. Here we present the results for the non-refractory submicron particles sampled by an Aerodyne High Resolution Time-of-Flight Mass Spectrometer (HR-ToF-MS) at high time-resolution (0.1 Hz). High relative humidity (>70%) tests resulted in high yields of ammonium sulfate during certain portions of the UC. The chemically resolved size-distribution derived from the HR-ToF-MS indicates that the ammonium sulfate particles were externally mixed with the organics, suggesting rapid particle growth in the SDS. One case-study shows that a high burst of ammonium sulfate particles affected the partitioning behavior of the organic species to the particle phase. Data from complimentary, collocated instruments are consistent with the results obtained by the HR-ToF-MS. The results of this study offer the vehicle emissions community a closer look at the chemistry of PM from gasoline LDV and how it is affected by the conditions it is emitted into. These results may have large impacts on future vehicle emission control standards and source apportionment modeling.

11CO.3

Real-time Characterization of Intermediate Volatilty and Semi-Volatile Organic Compound Emissions from a Diesel Engine. EBEN CROSS, Alexander Sappok, James Hunter, Victor Wong, Jesse Kroll, *MIT*

This paper presents experimental measurements of intermediate volatility and semi-volatile organic compounds (I/SVOCs) emitted from a medium-duty diesel engine under a range of operating conditions. Similar to VOCs, I/SVOCs can impact air quality and climate by serving as precursors to secondary organic aerosol (SOA), but a detailed understanding of such impacts remains incomplete due to a lack of fast, reliable measurement techniques that target I/SVOCs. Here we describe measurements of I/SVOC emissions using a recently-developed technique that combines cryogenic collection and electron-impact high-resolution time-of-flight mass spectrometry. This instrument provides measurements of volatility-resolved mass loading and chemical composition (elemental ratios) of I/SVOCs with ~5-10 minute time resolution. In this experiment, I/SVOC emissions from a dynamometer-controlled Cummins (5.9 L) 2002 ISB 300 engine were measured across a range of engine operating conditions. I/SVOC emissions were characterized during both steady-state and transient conditions to obtain a representative picture of the I/SVOC emission profile of the engine. Transient operating conditions included numerous cold starts as well as changes in engine speed and load representative of on-road driving cycles. Results underscore the importance of transient emissions to the overall I/SVOC emission profile. Analysis of the high-resolution mass spectra reveal evolving hydrocarbon and oxygenated hydrocarbon signatures as a function of engine block temperature (i.e. cold starts) and engine load. The engine test-bed also allowed for the characterization of the influence of a diesel particulate filter (DPF) on the I/SVOC emission profile. I/SVOCs were characterized downstream of the DPF during soot-loading and DPF-regeneration cycles. The sampling apparatus was also equipped with a burner system that was used to characterize the I/SVOC emissions resulting from combustion of ultra-low sulfur diesel (ULSD) fuel and biodiesel fuel.

11CO.4

Ethanol and Iso-Butanol Gasoline Blends Use in Light Duty Gasoline Direct Injection Vehicles: Real-time Measurements of Particle Number, Sizing, and Composition. DANIEL SHORT, Diep Vu, Georgios Karavalakis, Thomas D. Durbin, Akua Asa-Awuku, *University of California, Riverside*

Currently, the use of gasoline direct injection (GDI) vehicles is increasing rapidly and their penetration is expected to grow in the near future within the U.S. market. Recent research has shown that GDI vehicles have better fuel economy and emit less greenhouse gas emissions compared to the conventional port fuel injection (PFI) vehicle. However GDI vehicles emit 3 to 4 times more particles than the standard PFI vehicle. Butanol, compared to ethanol, has more energy content and a lower vapor pressure making it a more ideal mixture with gasoline. Changes in fuel composition can modify the emissions of particle and gas-phase compositions. Specifically, the aerosol composition may contain black carbon (BC) and other insoluble material that modify particle nucleating properties.

The goal of this study is to analyze the emissions of two light-duty GDI vehicles tested on a chassis dynamometer. These vehicles are driven on both the Federal Test Procedure (FTP) and the Unified cycle (UC) and at steady state conditions. The fuels used are E10, E15, and E20 ethanol and gasoline mixtures. In addition to ethanol blends, these vehicles used B16, B24, and B32 butanol and gasoline mixtures. Regulated emissions, particle number and sizing, BC concentrations, and fuel economy are measured. BC concentrations are measured real-time with a Multi-Angle Absorption Photometer (MAAP). The size distribution of particles is measured with a scanning mobility particle sizer (SMPS). Additionally, we exploit CPCs of different working fluids to infer real-time insoluble particle mass fractions. Results have shown decreasing particle number with increasing ethanol and butanol concentrations in gasoline on both the FTP and UC driving cycles. In addition, particle emissions from both GDI vehicles are mostly water-insoluble. The results of this study will enhance our understanding of alcohol fuel mixture effects on emissions from emerging vehicle technology.

11CO.5

Understanding the Affect of Biodiesel Fuels and Engine Mode on Primary Organic and Sulfate Aerosol Emissions from a Light Duty Diesel Engine. JOHN LIGGIO, Shao-Meng Li, Katherine Hayden, Jeremy Wentzell, Tak Chan, Gang Lu, Jeff Brook, *Air Quality Research Division, Environment Canada*

As the use of biodiesel in vehicles increases there is a need to understand the affect this alternative fuel will have on air emissions and primary PM mass specifically. Experiments were conducted as part of the Diesel Engine Emissions Research Experiment (DEERE) to study the affect of varying biodiesel fuel blends and engine operating mode on the mass of primary organic aerosol (POA) and sulfate emitted. These experiments were conducted utilizing a Volkswagen TDI light duty diesel engine equipped with an OEM diesel oxidation catalyst (DOC) and exhaust gas recirculation (EGR). The engine operated on ultra low sulfur diesel (ULSD) and biodiesel fuels including canola, soy and tallow which were blended with ULSD varying from 5-100% by volume. Engine operating modes used included idle and non-idle conditions which were based upon three transient drive cycles used for standard emissions testing. Primary organic aerosol and sulphate was measured in real time with a High Resolution Aerosol Mass Spectrometer (HR-ToF-AMS). The emitted exhaust was also systematically diluted by a factor of 20-1500 to examine POA volatility. Preliminary fuel based emissions factors (mg/Kg Fuel) were estimated, which indicated that the use of biodiesel generally results in reduced POA and sulphate emissions. POA emission factors were also dependent upon dilution level, indicating a degree of POA volatility. The POA volatility was evident for all fuel types, but did not exist under high engine load conditions. The current study demonstrates that (1) the use of biodiesel fuels may reduce POA emissions, (2) POA from this engine is somewhat volatile but is not significantly affected by the fuel used, (3) the volatility of POA from this engine is highly influenced by driving mode, and (4) even non-blended (B100) biodiesel results in a detectable sulfate PM emission. Aspects of these four points will be discussed.

11IA.1

Indoor PM2.5 at Santiago, Chile, 2012. HECTOR JORQUERA, Francisco Barraza, *Pontificia Universidad Catolica de Chile*

A simultaneous indoor and outdoor $PM_{2.5}$ campaign has been carried out at Santiago, Chile between mid-October and mid-December, 2012. Paired Partisol 2000i samplers (Thermo Scientific, USA, 16.67 L/min) were deployed on a building roof at Downtown Santiago, measuring urban background $PM_{2.5}$ concentrations in 24-h integrated filter samples. In the same period, paired TAS Minivol samplers (Airmetrics, Eugene OR, USA, 5 L/min) were used to sample indoor $PM_{2.5}$ concentrations for 48-h integrated filter samples. Paired samplers used teflon and quartz filters for measuring total and trace elemental masses and EC/OC and biological components (proteins, carbohydrates and endotoxins), respectively. A total of 47 households were analyzed in the campaign, that included three socioeconomic statuses. A household survey and continuous measurements of indoor temperature, relative humidity and carbon dioxide concentrations were carried out as well.

Average indoor/outdoor $PM_{2.5}$ ratios had a mean and standard deviation of 1.1 and 0.4, respectively, with no significant differences across socioeconomic strata. Average $PM_{2.5}$ concentrations were 23.9 and 21.7 micro-g/m^3 for indoor and outdoor samples, respectively. We present a multivariate analysis of the database to explain indoor $PM_{2.5}$ variability in terms of outdoor $PM_{2.5}$ and household features. Receptor model results for outdoor and indoor $PM_{2.5}$ samples are discussed as well.

11IA.2

Particle Concentrations in Retail Environments. Marwa Zaatari, JEFFREY SIEGEL, *The University of Toronto*

Particles in retail environments can have enormous consequences for the occupational health of retail workers, for infectious disease transmission, and for the energy costs associated with filtration and ventilation. We measured indoor and outdoor mass concentrations of PM10 and PM2.5 and number concentrations of submicron particles (>20 nm) and size-resolved 0.3 – 10 µm particles and ventilation rates in 14 retail stores in Pennsylvania and Texas, including several stores visited multiple times over a year to assess any seasonal changes. Overall, the results were generally suggestive of relatively clean environments when compared to other investigations of other building types, although concentrations exceeded outdoor regulatory limits in several stores. PM10 and PM2.5 mass concentrations (mean±sd) were 20±14 and 11±10 µg/m3, respectively, with indoor-to-outdoor ratios of 1.0±0.7 and 0.88±1. Mean submicron particle number concentrations were 7,220±7,500 particles /cm3 with an indoor-to-outdoor ratio of 1.18±1.30. Stores with high concentrations of particles were generally associated with cooking (PM2.5 and submicron particles), recent cleaning (submicron particles), large amounts of foot traffic (PM10 and PM2.5), as well as high outdoor concentrations (all sizes). The mean contribution to PM10 and PM2.5 concentrations from indoor sources (vs. outdoors) was 78% and 45%, respectively. There was no significant correlation between measured ventilation rates and particle concentrations of any size, which suggests the complexity of particle sources and sinks in these environments.

11IA.3

Ultrafine Particle Emissions from Desktop Three-Dimensional Printers. Parham Azimi, Zeineb El Orch, Tiffanie Ramos, Robert Zylstra, Julie Steele, BRENT STEPHENS, *Illinois Institute of Technology*

Three-dimensional printers that utilize additive manufacturing processes are gaining popularity as rapid prototyping devices. The development of low-cost desktop versions has made this technology widely accessible for use in home and office settings. The majority of commercially available 3D printers utilize an extrusion deposition technique whereby a plastic filament wound on a coil is unreeled to supply a computer-driven moving extrusion nozzle. The heated nozzle melts the plastic feedstock and deposits small extruded thermoplastic beads in thin layers across a baseplate. The material immediately hardens to form a three-dimensional shape. Despite their rapid uptake, little information exists on potential emissions from operation of these high temperature desktop devices indoors, particularly for aerosols.

Therefore, we measured particle emissions from two types of commercially available desktop 3D printers operating inside an office space using a TSI NanoScan SMPS logging at 1-minute intervals. First, two printers fed by PLA (polylactic acid) were operated together to print sample plastic products. Second, printing from these two printers was repeated in conjunction with three additional higher temperature printers fed by ABS (acrylonitrile butadiene styrene) to print the same plastic products.

The 3D printers were shown to have substantial aerosol emissions primarily in the ultrafine (<100 nm) size range. Peak emissions occurred in the 30-50 nm range. The mean UFP emission rate from the higher temperature ABS printers was estimated to be ~1.9×10^{11} #/min each compared to ~2.4×10^{10} #/min for each of the lower temperature PLA devices. With all five devices operating at the same time in the office, mean UFP emission rates were estimated as ~6.5×10^{11} #/min. These data represent some of the first known measurements of which we are aware of particle emissions from desktop 3D printers and suggest that caution should be used when operating these instruments in unvented indoor environments.

11IA.4

Elevated Levels of Respirable Antimony (Sb) and Other Trace Elements inside an Elementary School. BRIAN MAJESTIC, Joseph Turner, Aurelie Marcotte, *University of Denver*

The link between atmospheric particulate matter (PM) and respiratory and cardiovascular diseases such as exacerbated asthma and increased mortality is well-documented. It is becoming increasingly clear that respirable metals (metals contained in particles < 2.5 microns in aerodynamic diameter, PM2.5) contribute to the adverse health effects of PM, especially in young children with developing lungs. In this study, we explored the metal concentrations inside and outside of an elementary school in Flagstaff, AZ. A MOUDI sampler was used to collect 11 size fractions ranging from > 18 microns to < 56 nm. Metals analysis showed that, in the supermicron fraction, metal concentrations were roughly 13 times higher inside the school compared to outside. In the submicron (PM1) fraction, similar metal concentrations were seen both inside and outside the school, with the exception of antimony (Sb). Submicron Sb, a US-EPA hazardous air pollutant, was highly enriched inside the school at levels on par with or greater than high traffic urban centers in the US. Based on size-resolved data and Cu:Sb ratios, the excess submicron Sb does not appear to be a result of brake dust or coal fly ash, which are well-known Sb sources. We hypothesize that the elevated PM1 inside the school Sb is a result of Sb oxides embedded in the carpeting as a flame retardant, which become resuspended inside the school from foot traffic. If this is the source, then it would have significant implications on the contribution of flame retardants and related compounds to indoor air quality.

11IA.5

The Impact of Energy Efficiency Retrofits on Indoor PM Levels. SARAH FREY, Pierre Herckes, Matthew Fraser, *Arizona State University*

Retrofitting building for energy efficiency often entails improved sealing of the building envelope to decrease demand for air conditioning. As indoor sources of pollution often have a greater impact on exposure of residents than outdoor pollutant levels, this sealing of the building envelope could impact the indoor air quality. To investigate this, we conducted indoor air quality sampling before and after an energy efficiency retrofit of a senior living facility in Phoenix, AZ. At the same time, we also interviewed the residents about their health and any other behaviors (i.e. smoking) that would impact indoor air quality.

We report the indoor PM levels for SunnySlope Manor, an apartment complex for low income seniors run by the City of Phoenix. Initial sampling, before the energy efficiency retrofit, was conducted during the summer of 2010. Follow-up sampling, both immediately after the energy efficiency retrofit and a year after the retrofit, was conducted from June – August, 2011 and 2012, respectively. A total of 52 units were studied in all three panels.

Analysis of the data shows the important parameters that determine if particle concentrations increase as a result of the retrofit, the impact of indoor sources on PM levels, as well as relationships between apartment ventilation rates (measured by blower door tests) and indoor PM levels. We will reveal both the short term and long term trends of PM levels across the three year study.

11IM.1

Investigation of Flowrate-dependent Performance of Bipolar Diffusion Chargers. Meilu He, Matthew Brown, SURESH DHANIYALA, *Clarkson University*

Bipolar diffusion chargers are widely used for differential mobility analyzer (DMA) based measurements of submicron aerosol size distributions. The knowledge of the exact charging efficiency of particles is critical to accurate calculation of size distributions from DMA measurements. If the particles can be assumed to be charged to steady state, the particle charging efficiency can be calculated following the theory of Fuchs (1963) or Hoppel and Frick (1986). The assumption of steady state charging, however, may not always be accomplished. The final nature of the charge distribution depends on the ion concentration in the neutralizer, particle residence time, and design of the charger. In this study, the charging efficiency of popularly used commercial 85Kr neutralizers with source strengths of 2 mCi and 10 mCi (TSI 3077 and 3077A) and a 210Po neutralizer are determined as a function of particle size (10 - 50 nm) and flowrate (0.1 – 6 LPM). The experiments show that the charging efficiency of the 2mCi neutralizer for particles smaller than 50 nm in diameter is strongly dependent on the aerosol flow rates through the neutralizer, with a minimum charging efficiency at a flowrate of 1 LPM. The increase in particle charging efficiency with decreasing flowrates below 1 LPM is consistent with earlier findings (e.g., Ji et al. 2004), but the higher charging efficiency for flowrates larger than 1 LPM is a surprising finding. Theoretical description of the performance of the different neutralizers explaining their flowrate dependent nanoparticle charging behavior will be presented.

11IM.2

The Radial Opposed Migration Ion/Aerosol Classifier (ROMIAC). WILTON MUI, Andrew Downard, Daniel Thomas, Jesse Beauchamp, John Seinfeld, Richard Flagan, *Caltech*

The radial opposed migration ion/aerosol classifier (ROMIAC), a novel differential mobility analyzer (DMA) that is capable of high resolution of particles as small as 1 nm, is presented. We discuss the instrument design, particle trajectory simulations, and experimental validation of the ROMIAC as an aerosol classifier. The ROMIAC uses a radial geometry and an isopotential inlet and outlet design to minimize diffusive losses. Monte Carlo COMSOL simulations were used to further refine the design for successful transmission of sub–3 nm particles. Classification of tetra–alkyl ammonium halide, peptide, and protein ions, followed by detection of the ions by a linear trap quadrupole mass spectrometer demonstrated the successful use of the ROMIAC for selecting 1.16–2.14 nm particles with a resolution of ~20. The performance of the ROMIAC against the traditional DMA was assessed from dimensionless quantity analysis, revealing an extended domain of capability of the ROMIAC for classifying nanoparticles and gas ions that would otherwise be impossible with the DMA due to diffusional losses or turbulent flow conditions. The ROMIAC is a very compact (~10 cm in diameter and length), inexpensive instrument with low auxiliary pump requirements (<40 lpm) that can achieve high resolutions for classification of particles throughout the nanometer size range.

11IM.3

Development and Performance Evaluation of New Type Differential Mobility Analyzer (Hy-DMA). KANG-HO AHN, Gun-Ho Lee, Hong-Ku Lee, Hee-Ram Eun, *Hanyang University, R. of Korea*

Differential mobility analyzer (DMA) is an essential equipment for aerosol researchers. Several different types of DMA have been developed and widely used. Generally, DMA basically consists of two concentric cylindrical columns. In this configuration a long column is needed for a large size particle generation or measurement. To overcome this problem, we developed toroidal type DMA. With this configuration and height of 8 cm and width of 14 cm, the operating range becomes similar to a standard long DMA. More detailed performance characteristics of Hy-DMA will be presented at the conference.

This research was supported by the Korea Ministry of Environment as an "Eco-innovation project".

11IM.4

A Water-based Fast Integrated Mobility Spectrometer with Enhanced Dynamic Size Range. MICHAEL PIKRIDAS, Steven Spielman, Chongai Kuang, Thomas Tsang, Scott Smith, Andrew McMahon, Susanne Hering, Jian Wang, *Brookhaven National Laboratory*

The laminar flow water condensation technology (Hering and Stolzenburg, 2005) and the Fast Integrated Mobility Spectrometer (FIMS, Kulkarni and Wang 2006) have been combined to capture aerosol size distributions with 1-second time resolution. Using a parallel plate geometry, the FIMS separates particles based on their electrical mobility, and then grows them in a supersaturated environment to form supermicron droplets. The droplets are subsequently laser-illuminated and detected by a high speed CCD camera. The images captured by the camera provide not only the particle concentration, but also the particle position, which is used to derive particle electrical mobility. With the water-FIMS, a multistage condensational growth is used that introduces water vapor downstream of the separation zone, so that the mobility separation can be achieved for a variety of sheath relative humidity values. The multistage growth also limits the exiting water vapor concentration to below saturation levels at ambient temperature, thereby preventing condensation on the optics.

By measuring all spanned particles sizes simultaneously, the FIMS significantly increases measurement speed and counting statistics. With the adaptation to water condensation method it is an ideal instrument for measurements of aerosols with rapid population dynamics or onboard fast-moving platforms. By employing a non-uniform electric field as described by Wang (2009), we anticipate that particles of a wide range of electrical mobilities can be simultaneously classified. A water-FIMS employing the non-uniform electric field is being developed. The performance of this improved FIMS, including its dynamic measurement size range, size resolution, and counting statistics, will be presented.

References:

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11IM.5

Development of a Pulsed-Voltage Differential Mobility Analyzer for Measuring Shape Parameters for Non-Spherical Particles. MINGDONG LI, Rian You, George Mulholland, Michael Zachariah, *University of Maryland*

For a non-spherical particle, a DMA measurement in a static electric field can only be used to get an equivalent spherical diameter, but is not sufficient to obtain geometric shape information. The electrical mobility of nonspherical particles is dependent on the particle orientation. It was previously found that the orientation of such particles can be changed by varying the electric field strength. This method required changed the flow to change the peak voltage. Here we describe the operation of a pulsed differential mobility analyzer (PDMA) which enables one to change the peak E-field experienced by the particle, for an arbitrary period of time during the particle transit through the DMA. With this approach the particle can be partially oriented in the field thus changing its average mobility without changing the flow. By varying the peak voltage and frequency we show how one can obtain both the length and diameter of rods. Furthermore this approach can be used to separate spherical from non-spherical particles with the same average mobility.

11UA.1

Variation of Particle Number Concentration in a Street Canyon and an Urban Background Site. KAARLE HAMERI, Vanessa Dos Santos-Juusela, Tuukka Petäjä, Anu Kousa, *University of Helsinki, Department of Physics*

We measured spatial and temporal variation of ultrafine particles in a street canyon and an urban background site in Helsinki for six months. The particles were counted using condensation particle counters. In addition, we evaluated the effects of temperature, wind speed and wind direction on ultrafine particles, as well as the correlation with PM2.5, PM10 and black carbon inside the street canyon. The results show that the ultrafine particles in the street canyon were highly correlated with black carbon (R2 = 0.78) and weakly correlated with PM2.5 (R2 = 0.34) and PM10 (R2 = 0.05). Number concentrations in the street canyon were inversely proportional to temperature and wind speed, and highly dependent on wind direction. The highest concentrations occurred during northeastern winds while the lowest occurred during southeastern winds. As both of these directions are perpendicular to the street axes, the results are most likely influenced by the formation of wind vortices inside the canyon, as suggested by previous studies. Although the temporal correlation of particle number concentration between the sites was moderate (R2 = 0.50), the concentrations in the street canyon were 3 - 5 times higher than the urban background levels, depending on the time scale. This study estimates the levels of ultrafine particles observed in a typical busy air pollution hotspot, and suggests that urban microenvironments should be evaluated in epidemiological studies. Additionally, it reinforces that regulations based on PM2.5 and PM10 mass concentrations may be insufficient for preventing the adverse health effects of airborne particles, as these fractions are only weakly correlated with UFP concentrations.

11UA.2

Primary Emissions Measurements and Secondary Organic Aerosol Formation Experiments Provide Insight to the Atmospheric Burden of Particulate Matter from Mobile Sources.

ANDREW MAY, Timothy Gordon, Shantanu Jathar, Albert A. Presto, Allen Robinson, *Carnegie Mellon University*

Mobile sources such as gasoline cars and diesel trucks emit a complex array of gas- and particle-phase organic material into the atmosphere that may contribute substantially to air pollution. Emissions include primary organic aerosol (POA), elemental carbon (EC), and organic vapors. Measurements of primary emissions are relative straightforward during source testing, while apportionment of pollutants to gasoline and diesel sources has been a topic of debate. Incorporating the formation of secondary organic aerosol (SOA) into apportionment estimates introduces even more uncertainty. Recent work has established two competing hypotheses: either gasoline vehicles dominate ambient SOA production from mobile sources or diesel vehicles do. Source attribution of SOA is further complicated due to varying regulations and fleet composition. Through comprehensive source testing, we have measured primary particulate matter (PM = POA + EC) and SOA precursors from an in-use fleet of on-road gasoline and diesel vehicles. These tests were coupled with environmental chamber experiments that quantified SOA production rates. We input distributions of measured PM emissions and SOA production rates into a Monte Carlo simulation to estimate the relative importance of gasoline and diesel vehicles to total ambient PM (primary + secondary) as a function of fuel consumption. Through our simulations, we find that while on-road diesel vehicles are the major contributor to primary PM, SOA production from on-road gasoline vehicles based on our chamber-derived yield values dominates the SOA budget from these two sources. For example, gasoline vehicles will be the dominant source of atmospheric PM from on-road sources as long as the vehicle fleet is greater than 60% gasoline on a fuel-consumed basis. The widespread implementation of diesel aftertreatment technologies will significantly reduce both primary PM and SOA precursors from diesel vehicles,; consequently, we predict futuristic vehicle fleets have an even greater quantity of ambient PM attributed to gasoline vehicles.

11UA.3

On-Road Gasoline and Diesel Vehicle Contributions to Fine Particulate Black Carbon and Primary Organic Aerosol Emissions.

TIMOTHY DALLMANN, Thomas Kirchstetter, Robert Harley, *University of California, Berkeley*

Motor vehicles are an important source of fine particulate matter (PM2.5) emissions that include organic aerosol (OA) and black carbon (BC) as major components. Other recent on-road studies have highlighted the importance of gasoline engine-related contributions. However, separation of gasoline versus diesel contributions is a major source of uncertainty that has been discounted by other investigators. This issue arises even in settings where heavy-duty diesel truck traffic is not allowed or is present at very low levels. We measured emissions from thousands of in-use light-duty (LD) motor vehicles at the Caldecott tunnel in the San Francisco area. Measurements of PM2.5, OA, and BC, along with gaseous species, were made in tunnel lanes in which LD vehicles accounted for >99% of total traffic. Measured pollutant concentrations were apportioned between LD gasoline vehicles and diesel trucks. Fleet-average emission factors were then calculated for LD vehicles using a carbon balance method. Diesel trucks, while accounting for <1% of total vehicles, were responsible for 24 ± 4, 22 ± 5, and 45 ± 8% of the measured PM2.5, OA, and BC concentrations, respectively. These disproportionate emissions contributions from diesel trucks can result in significant bias in the on-road evaluation of LD vehicle emission factors unless analysts explicitly account for their presence. Fleet-average OA and BC emission factors for light-duty vehicles reported here are 10 and 50 times lower, respectively, than average heavy-duty diesel truck emission factors measured during the same field campaign. Emission factors and overall fuel consumption for gasoline and diesel engines were used to map out the relative importance of these sources to overall on-road vehicle emissions. In contrast to other recent studies, gasoline engines were found to be an insignificant source of BC, and a relatively minor source of POA emissions at urban, state, and national scales.

11UA.4

Development and Implementation of Low Level Biodiesel Blend Formulations to Help the Air Quality Standards in California Related to Diesel Fuel. MARYAM HAJBABAEI, Georgios Karavalakis, Kent C. Johnson, Alexander Mitchell, Jim Guthrie, David R. Cocker III, Thomas D. Durbin, *University of California, Riverside*

The reduction of emissions from diesel engines has been one of the primary elements in obtaining air quality and greenhouse gas reduction goals within California and throughout the nation. This will predominantly be achieved by introducing more renewable fuels to partially replace conventional fuels. Biodiesel is a renewable fuel with the potential for diesel fuel applications. However, there is a tendency for biodiesel to increase nitrogen oxides (NOx) emissions which remains an important issue with respect to implementing biodiesel especially within California. California Air Resources Board (CARB) in collaboration with University of California, Riverside and Davis conducted an extensive study on the emissions impacts of biodiesel use. This earlier work showed that biodiesel would likely increase NOx emissions when used in California-certified diesel fuel at levels above 20%. However, the results of this study did not show clear trends for biodiesels at 5% levels.

The goal of this study is to evaluate the possibility of using different feedstock 5% biodiesel blends as potential alternative diesel fuel formulations for use in California. Preliminary study was performed to find the suitable candidate fuels for the full certification testing. For this purpose, emissions from 5% blends of animal-based, waste-vegetable oil, and soy-based with CARB reference fuel were studied. All blends passed particulate matter (PM), total hydrocarbons (THC), and carbon monoxide (CO) emissions criteria of the certification testing protocol. However, only 5% animal-based biodiesel was successful in mitigating NOx emissions increase with biodiesel. For the second phase of the study, the full certification testing was performed on two of the candidate fuels using CARB protocols. The two B5 blends included animal-based and waste vegetable oil biodiesel with a CARB reference fuel. For both phases of the study, PM, NOx, THC, CO, CO2, and soluble organic fraction (SOF) emissions were evaluated. The results of this study provide the initial framework for the development of certified alternative diesel formulations for biodiesel blends that can be implemented into the California diesel fuel market

11UA.5

Analyses of Emission Measurements for a Heavy-duty Diesel Bus through Experiments and Simulations: The Comparison between On-road and In-lab Methods. ZHEMING TONG, Yan Wang, Bo Yang, Topi Ronkko, Jorma Keskinen, Liisa Pirjola, K. Max Zhang, *Cornell University*

The development of emission inventories relies on the emission testing. On-road chasing method can capture the real world vehicle emissions and establish a link between the atmospheric dilution and the undiluted exhaust; while the in-lab chassis dynamometer measurements are widely used for regulatory purposes because tests are made under well-controlled conditions. However, the differences between the on-road and in-lab methods have not been well studied; meanwhile, experimental and modeling results have indicated that particle emission measurements are sensitive to how dilution is conducted. The objective of this study is to investigate the impact of on-road and in-lab transport and transformation of aerosol particles on particulate emissions through experimental and modeling analyses.

For the on-road method, the turbulent flow field in the wake of a scaled diesel bus is studied in a wind tunnel using Particle image velocimetry (PIV) method and the numerical Large-eddy Simulation model. Aerosol dynamics in this diluting exhaust plume is simulated by a turbulent reacting flow model (CTAG) and evaluated by the corresponding on-road experiments. For the in-lab method, the turbulent flow field and aerosol dynamics inside a two-stage dilution system (a porous diluter followed by an ageing chamber and a Dekati ejector diluter) are modeled by CTAG and evaluated by in-lab experiments. The approach of in-lab experiments is based on exhaust sampling and dilution method developed in “Particulates” program of EU. In that method, the exhaust is mixing rapidly with the dilution air inside the porous diluter and near the entrance of the ageing chamber. A thorough understanding of these two methods is important for the ongoing effort to define a standardized sampling methodology for characterizing emissions from vehicles, especially with diesel engines.

12AC.1

Chemistry of New Particle Growth Events in Mixed Biogenic and Urban Emissions - Results from the CARES 2010 Campaign. QI ZHANG, Ari Setyan, Maik Merkel, Berk Knighton, Cody Floerchinger, Scott Herndon, Timothy Onasch, Douglas Worsnop, Chen Song, John Shilling, *Univeristy of California, Davis*

New particle formation and growth events were frequently observed over the Sacramento and western Sierra Foothills area in June 2010 during the Carbonaceous Aerosols and Radiative Effect Study (CARES). Using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) we investigated the evolution of the size-resolved chemical composition of new particles at the T1 site of CARES about 40 km northeast of Sacramento. The new particle events usually occurred in the morning with the appearance of an ultrafine mode centered at 10-15 nm (in mobility diameter, Dm) followed by the growth of this mode to ~ 50 nm in the afternoon. The events were generally associated with southwesterly winds which bring urban plumes from Sacramento and the San Francisco Bay Area to the T1 site. Our results indicate that the growth of new particles was driven primarily by the condensation of oxygenated organic species and, to a lesser extent, ammonium sulfate. The average increase of organic mass in the ultrafine particles during this period was approximately 7.5 times higher than that of sulfate. The chemical composition of organics in ultrafine mode during the growth events was very similar to that of anthropogenically-influenced secondary OA (SOA) identified in urban plumes. In addition, the concentrations of species representative of urban emissions (e.g., black carbon, CO and toluene) were on average 1.5 times higher during the new particle event days than during the non-event days, so were the concentrations of the photo-oxidation products of biogenic VOCs. These results indicate that the frequent new particle formation and growth events over the Sacramento and Sierra-Nevada regions were promoted by the interaction between biogenic emissions and transported urban plumes.

12AC.2

Nanoparticle Growth and Salt Formation - a Modeling Study. TAINA YLI-JUUTI, Kelley C. Barsanti, Lea Hildebrandt Ruiz, Antti-Jussi Kieloaho, Ulla Makkonen, Tuukka Petäjä, Taina Ruuskanen, Markku Kulmala, Ilona Riipinen, *University of Helsinki*

New particle formation through gas-to-particle phase transformation produces significant fraction of atmospheric aerosol particles. The climatic effect of these nanoparticles depends on whether they grow fast enough to survive to sizes of several tens of nanometers before being scavenged by coagulation to larger particles. Large fraction of the nanoparticle growth is known to be due to condensation of organic vapors, but not all the mechanisms related to the growth are yet identified. The compounds condensing on the nanoparticles need to be low-volatile, or transfer into low-volatile compounds in the particle phase. Recent observations of semi-volatile organic acids and amines in atmospheric nanoparticles suggest that particle phase processes may be important for the growth, as these compounds would not be expected to exist in the particle phase in large amounts based on simple gas-particle partitioning.

In this study we used particle growth model MABNAG to study the role of salt formation on the growth of 3-20 nm nanoparticles. MABNAG couples the condensation/evaporation of vapors to/from particles with the thermodynamics of particle phase acid dissociation and base protonation. Based on gas phase concentrations and initial particle composition the model predicts evolution of particle size and composition. System including sulfuric acid, organic acid, ammonia, amine and water as condensing vapors was studied. The effect of salt formation for the organic acid was predicted to be small at typical boreal forest conditions, but significant at base-rich environments. In all cases, all the particle phase amine and ammonia was predicted to be protonated, indicating the importance of the salt formation for the condensation of the bases. The relative roles of the two bases stayed rather constant through the growth between 3-20 nm and depended strongly on their relative gas phase concentrations.

12AC.3

Characterization of Chemical Composition of Fog Water and Interstitial Aerosol in the Central Valley of California: Influence of Aqueous Chemistry. HWAJIN KIM, Xinlei Ge, Jianzhong Xu, Yele Sun, Youliang Wang, Pierre Herckes, Qi Zhang,*University of California, Davis*

A measurement study was conducted in the Central Valley (Fresno) of California in January 2010, during which radiation fog events were frequently observed. Fog plays important roles in atmospheric chemistry by scavenging aerosol particles and trace gases and serving as a medium for various aqueous-phase reactions. Understanding the effects of fog on the microphysical and chemical processing of aerosol particles requires detailed information on their chemical composition. In this study, we characterized the chemical composition of fog water and interstitial aerosol particles to study the effects of fog processing on aerosol properties. Fog water samples were collected during the 2010 Fresno campaigns with a Caltech Active Strand Cloud water Collector (CASCC) while interstitial submicron aerosols were characterized in real time with an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a Scanning Mobility Particle Sizer (SMPS). The fog water samples were later analyzed using the HR-ToF-AMS, ion chromatography, and a total carbon analyzer. The chemical composition and characteristics of interstitial particles during the fog events were compared to those of dissolved inorganic and organic matter in fog waters. Our results indicate that aqueous phase chemistry modifies the chemical composition of condensed phase species significantly. In general, the Central Valley fog water is composed of a higher fraction of nitrate and organics than in interstitial aerosol. We also found that sulfate is formed more efficiently in fog water although its contribution to total mass is relatively low. The high resolution mass spectra of dissolved organic matter (DOM) in fog water and those of oxygenated organic aerosols (OOA) derived from multivariate analysis of the HR-ToF-AMS spectra are highly correlated ($R^2 = 0.92$). A main distinct difference between fog DOM and OOA is the substantially higher N/C ratio (~3.8 times) in the fog water, mainly due to the presence of the $C_xH_yN_2^+$ family ions. By comparing with previous investigations and NIST mass spectra, we propose that the main source of nitrogen compounds is imidazole. Details and the environmental implications of results will be discussed.

12AC.4

Stabilization of Sulfuric Acid Dimer Clusters by Various Basic Gases. COTY JEN, Peter McMurry, David Hanson, *University of Minnesota*

Nucleation rates depend on both the concentrations of sulfuric acid and of basic gases, such as ammonia and amines. Chen et al. (PNAS, 2012, doi: 10.1073/pnas.1210285109) proposed that this occurs, in part, because "more volatile" sulfuric acid dimer clusters react with basic gases to form stable (i.e. "less volatile") dimers, thereby leading to the high nucleation rates that are observed in the atmosphere. This study explores the stabilization of sulfuric acid dimer by several basic gases. Measurements were conducted using a glass flow reactor which was continuously operated with a steady flow of humidified nitrogen containing sulfuric acid at concentrations of 10^7 to 10^9 cm^{-3}. Sulfuric acid concentration was controlled by varying a flow over a bulk reservoir of 98 % sulfuric acid. Temperature was 295-299 K and humidity was ~ 30 %. A known molar flow rate of a basic gas was injected at various points along the flow reactor. The University of Minnesota Cluster CIMS was used to measure sulfuric acid vapor and cluster concentrations. It was found that, for a given concentration of sulfuric acid vapor (A_1), the dimer concentration (A_2) increases with increasing concentration of the basic gas, eventually reaching a plateau where cluster concentrations are close to the kinetically limited values (i.e. collision-controlled concentrations that would be expected if sulfuric acid did not evaporate from the dimer). One implication is that the dominant sulfuric acid dimer cluster is stabilized by the base and is still amenable to detection by the Cluster CIMS. Results for ammonia show a smaller effect on the stabilization of the dimer. The Cluster CIMS also detected aminated clusters of the sulfuric acid trimer at low base concentration (< 20 pptv).

12AC.5

The Role of Hydration in Formation and Reactivity of Sulfuric Acid Clusters Containing Ammonia and Amines. JOSEPH DEPALMA, Douglas Doren, Murray Johnston, *University of Delaware*

Our previous computational work on charged and uncharged sulfuric acid clusters containing ammonia and amines has elucidated chemical properties and processes which are important to new particle formation and growth, including: cluster free energy of formation, molecular binding within clusters, reactivity (amine substitution for ammonia in clusters), and neutralization (optimum number of ammonia/amine molecules for a given number of sulfuric acid molecules). Yet water is ever present in the atmosphere, and is expected to influence the structure and thermochemistry of these clusters. Ambient clusters containing water are difficult to study experimentally, making computational methods an indispensible tool for their characterization. In the work to be presented here, clusters of the form $[(BH^+)_x(HSO_{4-})_x(H_2O)_y]$, with B = NH_3, DMA, x = 4,5,6 and y = 1-10 were investigated using classical numerical sampling, varying levels of quantum chemistry, and Boltzmann averaging over stable populations. Preliminary results suggest that water increases the hydrogen bonding in these clusters, thereby decreasing the binding energy between acid and base molecules. The change in binding energy does not appear to have a cluster size dependence, and is more pronounced with ammonia than amines, as ammonium salts have higher solubility in water than alkyl amines. The increased solubility decreases the anion-anion interactions found in “dry” uncharged clusters containing ammonia. Water does not solvate the amine clusters well, so the effects on binding energy are not as great as ammonia. Amine substitution for ammonia appears to be favorable, with values comparable to “dry” positively charged clusters. Sulfate ions are not observed in clusters with either ammonia or amines, suggesting that bisulfate is the preferred cluster composition in this size range, with or without water. Computational results will be discussed in the context of likely cluster growth pathways in the atmosphere.

12AP.1

Study of the Unipolar and Bipolar Diffusion Charging of Arbitrary Shaped Aerosol Particles by Brownian Dynamics Simulations. Ranganathan Gopalakrishnan, CHRISTOPHER HOGAN JR., *University of Minnesota*

With knowledge of the diffusion charging rate, both the evolution of a time-dependent charge distribution on particles in unipolar ion environments, and the steady-state charge distribution on particles in bipolar ion environments can be determined. Discussed in this presentation, we have utilized a combination of Brownian dynamics (BD) simulations to examine (1) the collision rate between particles of arbitrary shape and ions, and (2) the steady state charge distribution on arbitrary shaped particles in the presence of realistic ion populations. In unipolar charging, the collision kernel, which defines the collision rate between particles and ions of known number concentrations, (when expressed in a dimensionless form H) depends upon the diffusive Knudsen number, Kn_D, the ratio of the ion mean persistence path to a well-defined particle length scale. This particle length scale is a combination of the orientation averaged projected area PA and the Smoluchowski (diffusion) radius R_s of the particle. In the transition regime (finite Kn_D), the dimensionless collision kernel is shown to be geometry independent using BD simulations for conducting particles, depending only on Kn_D whose definition incorporates the potential energy to thermal energy ratios for both the Coulomb and image potentials.

To study bipolar charging, a BD method is also employed, but which circumvents ion-particle collision rate calculation while still enabling direct determination of the steady state charge distribution. Non-spherical particles (aggregates, linear chains and cylinders), with a Projected Area (PA) to diffusion based surface area ($pi*R_s^2$) ratio close to unity have similar bipolar charge distributions to spheres sphere of the same mobility diameter. However, highly non-spherical particles ($PA/piR_s^2 < 0.5$) behave very differently from spheres, and the spatial distribution of charge on the particle surface is seen to have a strong effect in both the nano- and submicrometer size ranges.

12AP.2

Influence of Back Electrostatic Field on the Collection Efficiency of an Electrostatic Lunar Dust Collector. NIMA AFSHAR-MOHAJER, Chang-Yu Wu, Nicoleta Sorloacia-Hickman, *University of Florida*

Dusty environment of the lunar surface and deposition of the charged particles were troublesome in previous NASA explorations. An electrostatic lunar dust collector (ELDC) was demonstrated earlier as a highly efficient way of protecting exposed surfaces from the falling lunar particles. However, the ELDC collection plates attract particles continuously, and a layer of deposited particles carrying the opposite charge builds up on the plates. In this study, the effects of back electrostatic field on the performance of an electrostatic lunar dust collector (ELDC) were investigated.

First, the relationships between ELDC dimensions, collection efficiency and electrical properties of lunar dust particles were derived to develop a comprehensive model for any size of the ELDC. Then, a Lagrangian-based discrete element method (DEM) was applied to track particle trajectories, and sensitivity analyses were conducted for the concentration of the incoming particles and the number of the pre-collected particles at 50 V and 100 V. The obtained results from tracking particle trajectories confirmed the formation of eddies in proximity of the collection plate. The continuous particles introduced into the ELDC reduced the collection efficiency, and ultimately led to a suspended regime. The maximum duration the ELDC can run without significant loss in collection efficiency was estimated to be 10 days for the studied ELDC size and applied voltage. Since the electrical power consumption of the ELDC was found to be negligible, increasing the applied voltage was found to be the best option to counter the back electrostatic growth.

Keywords: Lunar dust, Particle collection, Electrostatic field

12AP.3

Modeling of Corona-Quenching in Tube-Wire Type Electrostatic Precipitators. CHRISTIAN LUEBBERT, Ulrich Riebel, *FAU Erlangen-Nuremberg, Germany*

The reduction of current uptake in electrostatic precipitators by particle attached space charge is known as corona-quenching. This effect occurs at the precipitator's inlet section for high dust concentrations. As a typical consequence the current up-take is locally reduced to values of less than a percent of the clean gas current uptake under conditions of strong quenching. At the same time the sparking voltage decreases due to the distortion of the electric field. The required reduction of the applied voltage will not only prevent sparking but also the precipitation efficiency in the whole precipitator section. Hence for critical aerosols a fundamental understanding of the quenched state as well as of the kinetics of the transition from the quenched regime to the normal operation regime is inevitable for an adequate design of the electrostatic precipitator.

The focus of this work is on the theoretical description of the corona-quenching process in a wet tube-wire type electrostatic precipitator for sub micrometer sized aerosols. The basis of the analytical description is a balance of particle attached space charge, whereby models of different complexity are discussed. The presented models range from simple but well-reasoned calculation of the maximum current suppression time by particle attached space charge to 1D simulations, which are in almost perfect agreement with the measured current up-take behavior. The calculation approaches allow designing and optimizing electrostatic precipitators for concentrated aerosols. Furthermore, interpreting the theoretical results, it is found that there is a geometry dependent upper limit for the precipitation rate, which is achieved in the quenched state. Due to the very low current uptake precipitation of particles is highly energy efficient in this regime. However it follows different rules that have to be considered.

12AP.4

Interpreting SAXS Spectra of Nonspherical Water/Nonane Nanodroplets Using a New Particle Form Factor. GERALD WILEMSKI, Abdalla Obeidat, Fawaz Hrahsheh, Harshad Pathak, Barbara Wyslouzil, *Missouri University of Science and Technology*

The structure of nanodroplets plays a critical role in many natural and technological processes involving nucleation and aerosol formation. Here, we review our theoretical efforts to interpret experimental measurements of small angle x-ray scattering (SAXS) from D_2O/nonane nanodroplets formed in supersonic nozzle expansions. The experiments yield a spectrum of intensity I(q) versus scattering vector q, where q depends on the scattering angle and x-ray wavelength. We used classical molecular dynamics (MD) to simulate water/nonane nanodroplets and found that they have a nonspherical Russian Doll (RD) structure consisting of a roughly spherical water droplet that is partially wetted by a large nonane lens. We have developed an exact analytical expression for the particle form factor P(q) of a lens-on-sphere RD droplet with sharp interfaces and uniform lens and sphere densities for use in fitting the experimental data. The model was validated by comparing it with exact numerical results for P(q) based on the MD simulations. Excellent agreement was found. The fits of the measured SAXS spectra generated with this model are good and generally much better than those based on simpler structural models, but the overall droplet composition derived from the fitting results does not agree with the composition measured from FTIR experiments. In particular, the predicted mass fraction of condensed D_2O is only half that measured by FTIR. Further work is needed to resolve this discrepancy. This work was supported by NSF Grants CBET 1033387 and 1033439.

12AP.5

Effects of Multiple Scattering on the Radiative Properties of Fractal Soot Aggregates. FENGSHAN LIU, Gregory Smallwood,*National Research Council Canada*

Optical diagnostics play important role in our understanding of black carbon (soot) formation in combustion and in obtaining quantitative information on the morphology of black carbon emitted from various combustion devices. The Rayleigh-Debye-Gans theory for fractal aggregates (RDG-FA) has often been used to interpret the detected scattering signals. One of the important assumptions in the development of RDG-FA is that the multiple scattering within aggregates is negligible. The validity of this assumption has been investigated previously and it has been commonly believed that multiple scattering within aggregates affects aggregate scattering more than absorption.

This study critically examines the effect of multiple scattering on the absorption and scattering properties of fractal soot aggregates. The numerical method used in this study is the generalized Mie-solution method (GMM) applied to numerically generated fractal aggregates of prescribed fractal dimension of Df = 1.4, 2.1 and prefactor kf = 2.3 for aggregate sizes up to Np = 800. GMM allows calculations with and without multiple scattering and the difference between the two results is attributed to multiple scattering. Calculations were conducted to three different incident light wavelengths of 532, 1064, and 2118 nm, while the primary particle diameter and remained fixed at dp = 30 nm, resulting in three different primary particle size parameters of $xp = \pi dp/\lambda = 0.177, 0.0886$, and 0.0445. Numerical results show that multiple scattering effect increases with increasing primary particle size parameter xp. Multiple scattering has a stronger influence on aggregate absorption than aggregate scattering. Even for aggregates of fairly open structure of Df = 1.4, multiple scattering on aggregate absorption is significant. The so-called ‘shielding effect’ in aggregate absorption is fundamentally due to multiple scattering.

12CA.1

Novel Smog Chamber Studies of Wood Burning Emissions at Low Temperatures. EMILY BRUNS, Imad El Haddad, Stephen Platt, Brice Temime-Roussel, Dogushan Kilic, Jay Slowik, Anaïs Detournay, Luka Drinovec, Grisa Mocnik, Nicolas Marchand, Urs Baltensperger, Andre Prévôt, *Paul Scherrer Institute*

Domestic wood burning is a significant source of atmospheric aerosols, particularly in winter, as it is a common heating method in regions with moderate and cold climate. Nevertheless, uncertainties remain in the magnitude and characteristics of wood burning emissions. Discrepancies exist between the organic mass to black carbon ratio (OM/BC), possibly because previous laboratory studies were conducted at higher-than-ambient winter temperatures. In addition to primary emissions, previous experiments show that oxidation of gas phase wood burning emissions produces compounds with sufficiently low volatility to partition to the particles and form secondary organic aerosol (SOA). However, relatively little is known about these secondary aerosols and the role of ambient temperature and humidity in their formation.

We report results from smog chamber experiments characterizing primary and secondary wood burning products performed at representative winter temperatures for the first time. Primary emissions were diluted to atmospherically-relevant concentrations and injected into the chamber, where OH photochemistry initiated the formation and aging of secondary products. Experiments were performed at 263K and 288K, and at 50% and 90% relative humidity. Effects of wood loading in the oven were also investigated. The non-refractory aerosol composition and quantities were determined by aerosol mass spectrometry. BC quantification and the effect of organic coatings on BC optical properties were determined using Aethalometers with and without a thermal desorber in the sampling line. Measurements of gas phase species were made with a suite of instruments, including a proton transfer reaction mass spectrometer.

Conducting experiments at lower temperature resulted in higher primary OM/BC, enhanced SOA/BC and better agreement with ambient measurements. High fuel loading generated significantly more polycyclic aromatic hydrocarbons (PAHs) compared to average loadings. As PAHs and their oxidation products have deleterious health effects, this is a significant finding to mitigate negative wood burning impacts by improving oven operation protocols.

12CA.2

Secondary Organic Aerosol Precursors in Biomass Burning Smoke. LINDSAY HATCH, Wentai Luo, James F. Pankow, Robert J. Yokelson, Kelley C. Barsanti, *Portland State University*

Biomass burning is the second largest source of volatile organic compounds (VOCs) worldwide, which may undergo photochemical processing leading to secondary organic aerosol (SOA) formation. As part of the fourth Fire Lab at Missoula Experiment (FLAME-4) in 2012, samples of VOC emissions from fires of 6 different globally-relevant, plant-based fuels were collected and analyzed by two-dimensional gas chromatography/time-of-flight mass spectrometry (GCxGC/TOFMS). Hundreds of compounds were identified, many of which are known SOA precursors, including more than 15 monoterpenes, 10 sesquiterpenes, phenols, and substituted aromatics. Further, smoke from the 6 fuels displayed widely different chemical characteristics, particularly regarding the presence and abundance of biogenic and oxygenated compounds, highlighting that the pathways to SOA formation will vary considerably with fuel type. These FLAME-4 measurements will inform the development of a model describing chemical evolution and SOA formation within smoke plumes in order to improve air quality predictions downwind of fire activity.

12CA.3

Secondary Organic Aerosol Formation Projection from Single-Ring Aromatic Tail Pipe and Evaporative Emissions from California Gasoline Vehicles.

ANTONIO MIGUEL, *University of California, Los Angeles*

Biogenic and anthropogenic reactive organic gases (ROG) produce secondary organic aerosol (SOA) through photochemical reaction and partitioning processes. It is now recognized that SOA accounts for a significant fraction of the atmospheric burden of organic particulate mass. SOA formation follows a series of complex reactions and is dependent on a number of parameters including ROG type and concetration, existing PM, NOx and free-radical concentration, aerosol water content and relative humidity, actinic flux, and primary and intermediate organic compound concentrations. Over 80% of the ROGs in California are emitted from a wide range of sources including on-and off-road motor vehicles and equipment, aircrafts and ocean vessels, fuel storage and solvent evaporation. We estimate the SOA formation potential from tailpipe emission rates of the single-ring ROGs toluene, ethylbenzene, o-Xylene, 1,2,4-Trimethylbenzene and benzene for the 1995 to 2003 in-use California light-duty gasoline vehicle fleets. SOA formation yield (Y) data were obtained from reported well controlled smog chamber studies. The total mass concentration of organic aerosol, ΔMo, produced for a given amount of ROG reacted, ΔROG, was calculated from Y = ΔMo/ΔROG (Odum et al., 1997; Ng et al., 2007). Relative to the 1995 fleet, we estimate that the 2003 fleet decreased SOA production by 86%, at an average annual rate of about 10%, for the target single-ring aromatics. Evaporative single-ring ROGs fleet average emission rates decreased 63 to 90% from the 1999 to the 2003 fleet. Factors that contributed to the observed tail pipe precursor reduction for the periods considered include the retirement of non-catalyst vehicles, the increased use of emissions control technologies, and the switch to Phase III gasoline.

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12CA.4

Fuel-based Fine Particulate and Black Carbon Emission Factors from a Railyard Area in Atlanta.

Boris Galvis, Armistead Russell, MICHAEL BERGIN, *Georgia Institute of Technology*

Railyards have the potential to influence local fine particulate matter ($PM_{2.5}$) concentrations through emissions from diesel locomotives and supporting activities. This is of concern in urban regions where railyards are in proximity to residential areas. Northwest of Atlanta, Georgia, Inman and Tilford railyards are located beside residential neighborhoods, industries, and schools. The $PM_{2.5}$ concentrations near the railyards is the highest measured among the state-run monitoring sites. The authors estimated fuel-based black carbon (BC) and $PM_{2.5}$ emission factors for these railyards, determined the impact of rail yard activities on BC and $PM_{2.5}$ concentrations and assessed the cost- benefit of replacing current locomotive engines with cleaner technologies. High-time-resolution measurements of BC, $PM_{2.5}$, CO_2, and wind speed and direction were used to determine emissions factors (i.e., the mass of BC or $PM_{2.5}$, per gallon of fuel burned). By the authors' estimates, diesel-electric engines used in the railyards have average emission factors of 2.8 plus or minus 0.2 g of BC and 6.0 plus or minus 0.5 g of $PM_{2.5}$ per gallon of diesel fuel burned. Railyard emissions appear to lead to average enhancements of approximately 1.7 plus or minus 0.1 micrograms/m^3 of $PM_{2.5}$ and approximately 0.8 plus or minus 0.01 micrograms/m^3 of BC in neighboring areas on an annual average basis. AERMOD simulation shows that railyards are responsible for 1.6 plus or minus 0.1 micrograms/m^3 $PM_{2.5}$ and 0.6 plus or minus 0.07 micrograms/m^3 of BC near the railyards. Retrofitting the engines of the switcher locomotives at the railyards with new generator sets could decrease $PM_{2.5}$ emissions by 10 plus or minus 1.5 ton/year reducing $PM_{2.5}$ concentrations between 0.4 plus or minus 0.1 micrograms/m^3 and 0.6 plus or minus 0.2 micrograms/m^3 north and south of the railyards respectively. BenMAP estimates show health benefits much greater than cost of implementation of cleaner technologies.

12CA.5

Brick Kiln Emissions Quantified with the Aerodyne Mobile Laboratory during the Short Lived Climate Forcing (SLCF) 2013 Campaign in Guanajuato Mexico. EDWARD FORTNER, Berk Knighton, Scott Herndon, Joseph Roscioli, Miguel Zavala, Timothy Onasch, John Jayne, Douglas Worsnop, Charles Kolb, Luisa Molina, *Aerodyne Research, Inc.*

Brick kiln emissions are suspected to be a major source of black carbon in developing countries and black carbons role as a short lived climate forcer is under investigation. The SLCF brick kiln study was conducted from 12-17 March 2013 in the Guanajuato state of Mexico and examines these black carbon emissions. Three different types of brick kilns were measured (MK-2, traditional campaign kiln, and traditional fixed kiln) giving insight to the effects of different kiln designs on particle and gas phase emissions. The emission of these kilns was measured both during the fire stage and the subsequent smoldering stage.

The Aerodyne Mobile Laboratory conducted these emission measurements utilizing tracer release technology placed adjacent to the brick kiln. Utilizing this method the evolution of the brick kiln plume can be examined as it transits downwind from the source. Particulate measurements conducted by the mobile laboratory included the multi angle absorption photometer (MAAP) to measure black carbon mass, cavity attenuated phase shift (CAPSext) monitor to measure extinction and soot particle aerosol mass spectrometer (SP-AMS) measurements of black carbon. The SP-AMS instrument combines the ability to measure black carbon with the ability to determine the chemical composition of the PM associated with black carbon particles. Gas phase measurements conducted included CO, CO_2, NO_X, SO_2, CH_4, C_2H_6 and a variety of VOCs (Acetonitrile, benzene etc.) measured with a PTR-MS instrument. All of these measurements will be examined to construct emission ratios evaluating how these vary with different kiln types and different fire conditions. The evolution of particulate matter and gas phase species as they transit away from the source will also be examined.

12IA.1

Rapid Size and Chemical Characterization of Outdoor and Indoor Particulate Matter, Implications for Transport and Environmental Influence. PETER DECARLO, Michael Waring, *Drexel University*

The size, concentration, and chemical composition of submicron particulate matter (PM) was measured with an Aerodyne Aerosol Mass Spectrometer (AMS) in the winter of 2013. Utilizing a custom inlet switching system, PM was alternatively measured indoors and outdoors with a time resolution of 2 minutes. AMS measurements were conducted in Drexel Air Resources Research Laboratory in downtown Philadelphia. The unique set-up of this experiment allows the interrogation of the chemical and physical changes of PM as it is transported from the outdoor to the indoor environment. Lag time between changes in outdoor concentrations and reflected changes in indoor concentrations is clearly observed and the implications of air exchange in a mechanically ventilated building can be assessed. PM loss processes upon outdoor to indoor transport from deposition and/or volatilization are determined by the relative changes to non-volatile and semi-volatile species (e.g. ammonium sulfate and ammonium nitrate). Detailed changes in submicron size distributions are a combination of the same depositional and volatilization losses. The influence of different sources is investigated using mass spectral features, and factorization techniques such as positive matrix factorization (PMF). The influence of food trucks located on campus are clearly observed in the dataset using the ratio of m/z 55 and m/z 57 in the AMS measured mass spectra. These and other results will be presented.

12IA.2

Direct Measurements of Particle Decay Rates for Fine and Ultrafine Particles in 74 Residences in Edmonton, Canada.LANCE WALLACE, Jill Kearney, Morgan MacNeill, Warren Kindzierski, Marie-Eve Heroux, Amanda Wheeler, *US EPA (retired)*

Particle deposition rates are a fundamental determinant of indoor particle concentrations. However, these rates are not well known due in part to the difficulty of untangling the concurrent effects of infiltration, exfiltration, filtration by furnace fans and portable or in-duct air cleaners, and (for ultrafine particles (UFP) in particular) coagulation. Previous studies in multiple homes generally have been unable to determine deposition rates for individual homes, and have only provided an average rate for all homes in the study. In this large-scale study in Edmonton, Canada, a new method of separating indoor-generated from outdoor-infiltrated particles was developed.

Indoor and outdoor fine particles (FP) and UFP were measured for 7 consecutive days in both summer and winter in 50 residences per season. Continuous 1-minute average measurements were made by DustTraks (Model 8520, TSI, Inc., Shoreview, MN) equipped with 2.5 micrometer inlets and P-Traks (TSI, Model 8525). Air exchange rates were determined using the perfluorotracer (PFT) method. A censoring algorithm was developed to identify and remove peaks due to indoor sources. The remaining indoor concentrations were assumed to be due to infiltration of outdoor particles. The daily average infiltration factor could thus be determined. The product of this factor with the outdoor concentration provided the time-resolved estimate of the background concentration to which the indoor concentration was trending. For “well-behaved” (R^2>90%) indoor peaks, background-corrected decay rates could be determined. Subtraction of the air exchange rates provided an estimate of the deposition rates. About 400 (300) decay rates for UFP (FP) were determined in 60 (58) homes. On average, deposition and filtration accounted for about 75% of the total decay rates, the remainder being due to air exchange. These decay and deposition rate estimates for individual homes will allow a better estimate of distributions of rates across homes for modeling total indoor exposures.

12IA.3

Dynamic Modeling Study for In-cabin Ultrafine Particle Transport: Evaluation of Infiltration and Passive Ventilation in a Wide Range of Driving Speed. EON LEE, Michael Stenstrom, Yifang Zhu, *University of California, Los Angeles*

A few recent studies have proposed in-cabin ultrafine particle (UFP) models. However, these models did not incorporate infiltration and passive ventilation as a function of driving speed. This study presents a zero-dimension pseudo-steady-state model coupled with two sub-models describing infiltration and passive ventilation. The infiltration term was formulated using vehicle envelope leakage parameters (i.e., flow coefficient and pressure exponent) to address the dynamic behavior of infiltration as a result of the two competing processes: aerodynamic pressure on moving vehicle surface and mechanical cabin pressurization. The passive ventilation term was empirically derived from extensive field measurements. This model allows infiltration and passive ventilation to affect in-cabin UFPs at any driving speed in time. Model predictions agreed well with the experimental measurements in 12 different vehicle models as well as previously published data in the literature. In outdoor air (OA) mode, UFP I/O increases at increasing driving speed due to mechanical ventilation, passive ventilation, and infiltration. While mechanical ventilation dominantly controlled the I/O, passive ventilation and infiltration could also increase the I/O by 0.45 under fan off. In this case, surface deposition mechanism reduced the I/O in driving speed up to 60 and 90 km/hr in sedan and minivan, respectively. Above these driving speeds, passive ventilation and more importantly infiltration increased the I/O. When operating fan in OA mode, mechanical ventilation reduced the effects from infiltration and passive ventilation. Thus, in-cabin UFP concentration significantly changes by different particle gain/loss mechanisms and the magnitude of change depends on driving speed, ventilation condition, and vehicle type.

12IA.4

Outdoor and Indoor Exposure to Traffic Aerosols at Schools: Effect of Anti-idling Campaign. SERGEY A. GRINSHPUN, Jin Yong Kim, Michael Yermakov, Tiina Reponen, Chris Schaffer, Patrick Ryan, *University of Cincinnati*

Exposure to traffic aerosols may be elevated at schools because of the emission from cars and buses transporting students daily. Vehicle idling within school proximity is expected to increase the outdoor concentration of fine particulate matter, which may consequently affect the indoor aerosol concentration in schools. In this study, the impact of an anti-idling campaign on outdoor and indoor air quality was evaluated at four urban schools in Cincinnati (Ohio, USA), which exhibited different levels of exposure to school bus and car emission. At each school, Harvard-type PM2.5 impactors operated in parallel – two indoors and two outdoors; each station was equipped with one Teflon filter and one with quartz filter. The samples were analyzed gravimetrically (for PM2.5), using X-ray fluorescence analysis (for elements, including Si, S, Ti, V, Mn, Fe, Cu, Zn, Br, Pb) and with thermal-optical transmittance (for elemental and organic carbon: EC and OC). The outdoor concentrations of most of the elements were significantly reduced as a result of the anti-idling campaign. The decrease in outdoor concentrations was followed by a corresponding decrease in indoor concentrations for most of the relevant elements. In contrast to elemental concentrations, the anti-idling campaign did not have a definitive effect on PM2.5. Decreases in outdoor PM2.5 were not always followed by similar decreases in indoor PM2.5. Given that the traffic emission is represented primarily by ultrafine particles, PM2.5 may not serve as a good indicator of changes in traffic aerosol exposures. The findings suggest that changes in outdoor air quality in the school vicinity produced by an anti-idling campaign are capable of reducing the children’s traffic aerosol exposures inside the schools.

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12IA.5

Application of High Efficiency Cabin Air Filter for Simultaneous Control of Ultrafine Particles and Carbon Dioxide in Passenger Vehicles. EON LEE, Cha-Chen Fung, Yifang Zhu, *University of California, Los Angeles*

Modern passenger vehicles are commonly equipped with cabin air filters, but the filtration efficiency is only at 40-60% for ultrafine particles (UFPs). Although setting the vehicle ventilation system to recirculation (RC) mode can reduce in-cabin UFPs by 80-95%, carbon dioxide (CO_2) from exhaled breath of passengers can build up quickly inside the cabin. To avoid the CO_2 build-up issue, the vehicle needs to be operated under outdoor air (OA) mode to allow sufficient air exchange. This study investigated in-cabin UFP removal under OA mode using high efficiency particulate air (HEPA) filters. UFP concentrations were simultaneously monitored inside and outside of 12 different vehicles under three different driving conditions: stationary, local roadway, and freeway. Under each experimental condition, data were collected with no filter, in-use original equipment manufacturer (OEM) filter, and two types of HEPA filters. The HEPA filters were found to reduce in-cabin UFP number concentration by 93% on average, much higher than in-use OEM filters (i.e., 41-65% on average). Using the HEPA filters also made the in-cabin environment more independent from the changes of driving speed and the fluctuation of UFP concentrations on different roadways. Throughout the measurements the in-cabin CO_2 concentration remained at 626-816 ppm, a significant reduction from a typical in-cabin CO_2 concentration range of 2500-4000 ppm in recirculation mode.

12IM.1

Validation of New Fast Scanning Mobility Particle Sizing System. JAMES FARNSWORTH, Brandon Detmer, Nathan Birkeland, Fred Quant, Hans-Georg Horn, Brian Osmondson, *TSI Incorporated*

Differential mobility classification has become the measurement principle of choice for making aerosol size distribution measurements in the 1 nanometer to 1 micron range, especially since the scanning concept was introduced by Wang and Flagan in 1990. In order to met the need for faster measurements while leveraging the reliability of differential mobility classification, a new classifier (TSI Model 3082) has been developed to enable scan times down to 5s.

The 3082 classifier retains the functions of the 3080 classifier with additions such as a dual polarity, high voltage (HV) controller for the DMA with 50 ms response time for faster scanning; 50 Hz data sampling for higher time resolution (Erickson et al 2012); increased sheath flow for improved size resolution; and integrated, removable accessories (x-ray neutralizer and impactors).

Validation testing of the new fast scanning SMPS and classifier has been completed. A comprehensive review of our validation test results is presented, including measurement results obtained from scan times down to 5s, high voltage control accuracy, sheath flow rate control and accuracy, and size measurement accuracy using standard reference materials (such as PSL spheres) in compliance with the ISO 15900 Standard which recommends test methodology for differential mobility devices. Equivalence data comparing SMPS measurements using the new 3082 classifier versus the 3080 classifier will also be presented; these data demonstrate good agreement of both classifiers at traditional scanning rates as well as the advantages of the new model at reduced scan times.

Additional testing was completed to understand limitations of the device in high stress environments. Data from environmental testing such as operation in high humidity environments and stress tests such as Highly Accelerated Life Testing (HALT) will be presented.

12IM.2

Highly Size- and Time-Resolved Particulate Matter Characterized by Novel Optical Analysis. NICHOLAS SPADA, David Barnes, Shankar Chellam, Thomas A. Cahill, *University of California, Davis*

Aerosols may have a large impact on the atmospheric radiative balance by means of heating or cooling, both directly and indirectly. In spite of the myriad optical devices and techniques currently in use, aerosols have the greatest uncertainty in the global radiative budget by far. New techniques for studying their interactions with light radiation are necessary to increase comprehension of global climate change.

In response to this, a high-resolution technique for quantifying optical parameters of size- and time-resolved particulate matter (PM) samples was developed. Total extinction is directly measured while scattering is resolved from absorption via application of beta-attenuated mass measurements and calibrated mass scattering efficiencies. In this way, absorption in inverse megameters is achieved in eight size modes spanning 10 to 0.09 micrometers with up to one hour time resolution. The large number of wavelengths (n = 120, lambda = 350 – 800 nm) monitored enables precise determination of Angstrom exponents, which may be useful in identifying major aerosol types. Good correlations with a collocated Aethalometer provided validation of black carbon monitoring and were most correlated with the 0.26 – 0.09 micrometer size mode. The current products of this technique include size and time profiles for extinction, absorption, single-scattering albedo, and Angstrom exponents for both extinction and absorption. In this way, a comprehensive understanding of PM optical parameters can be collected expeditiously.

This technique was applied for specific studies targeting those with interesting optical profiles: namely the largest rail yard in the western United States, the petrochemical industrial area of the Houston ship channel, and a unique automotive tunnel restricted to single-axle vehicles. The optical results of these studies highlight the importance of concurrent size and time resolution while showcasing the elevated clarity of ambient pollution profiles. These results, including the system geometry and calibration results, will be presented.

12IM.3

Towards Accurate Calculation of Particle Size Distributions from Fast-SMPS Measurements. ISHARA JAYASURIYA, Meilu He, Suresh Dhaniyala, *Clarkson University*

The Scanning Mobility Particle Sizer (SMPS) is one of the most popular instruments for aerosol experimental research. The SMPS enables measurements at very high resolution and accuracy and over a reasonably broad size range. While the SMPS can theoretically provide size measurements with an uncertainty of ~1%, such accuracies are difficult to obtain during practical operation. In particular, when the SMPS is operated over a finite scan-time, the non-idealities in the behavior of the scanning-DMA, the response of the CPC, and the transport of particles between the DMA and the CPC must be accurately accounted for. While several theoretical approaches for the above identified non-idealities have been proposed, the practical deployment of these approaches requires experimental identification of critical system parameters. In this study, the response of a fast scan SMPS system is modeled to understand the importance of different system parameters on the instrument performance, and experimental approaches to obtain the necessary system parameters are established. The system modeling approach and related experiments will be discussed and the implications for accurate sizing of ultrafine particles with fast scanning will be detailed.

12IM.4

Aerodynamic Aerosol Classifier. Farzan Tavakoli, Jonathan Symonds, JASON S. OLFERT, *University of Alberta*

A new aerosol particle classifier, the Aerodynamic Aerosol Classifier (AAC), is presented with some of its applications. The instrument uses a centrifugal force and sheath flow between two concentric rotating cylinders to produce a monodisperse aerosol classified byaerodynamic diameter. Since this instrument does not requirechargedparticles, it produces a true monodisperse aerosol without artefacts caused by multiply-charged particles like other classifiers. This work reports the theoretical and experimental results of the new instrument with some of its applications.

Two diffusion models and two non-diffusion models have been used to predict the performance of the AAC.The limiting trajectoryand particle streamline models are analytical methods and do not include particle diffusion. To demonstrate the diffusion effect, a convective diffusion model has been developed by solving the convective-diffusion equation for the AAC which has been solved using the Crank-Nicolson method. The diffusing particle streamline model is an analytical model which models particle diffusion as a Gaussian cross-stream profile about the corresponding non-diffusing particle streamline.The transfer functionswere obtained as a function of the particle relaxation timeand the particle aerodynamic diameter. The transfer function has been studied for different flow rates. PSL (polystyrene latex) particles and DOS (DioctylSebacate) along with a differential mobility analyzer (DMA) were used to verify the instrument and to obtain the experimental transfer function.

A DMA and the AAC were used in tandem to measurethe effective density, dynamic shape factor, and the mass of soot particles emitted from an inverted burner. The measured DMA-AAC mass–mobility exponent was 2.17 for a flame equivalence ratio of 0.67, which agrees well with DMA-CPMA measurements. The effective density was found to vary between 0.18–0.86 g/cm3and the dynamic shape factor was calculated to be 1.5–2.6 over the range of 90 to 630 nm in mobility diameter.

12IM.5

Merging Multiple Instrument Measurements of Aerosol Size Distributions into a Best Estimate Aerosol Size Distribution.JASON TOMLINSON, Fan Mei, Don Collins, Gunnar Senum, Stephen Springston, Chen Song, Jacqueline Wilson, Alla Zelenyuk, Jennifer Comstock, John Hubbe, John Shilling, Duli Chand, Mikhail Pekour, Beat Schmid, Larry Berg, *Pacific Northwest National Laboratory*

The Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Aerial Facility (AAF) utilizes three optically based aerosol probes, mounted on under-wing pylons, to measure the aerosol ambient size distribution aboard the DOE AAF G-1 aircraft. The Ultra High Sensitivity Aerosol Spectrometer – Airborne (UHSAS-A), Passive Cavity Aerosol Spectrometer (PCASP), and the Cloud Aerosol Spectrometer (CAS) each measure a subset of the ambient aerosol size distribution from 0.06 micro-meter to greater than 10 micro-meter at a sampling frequency of 1 Hz. These optically-based instruments are used aboard an aircraft because they provide the desired sampling rates. However, the instruments have known problems stemming from poor collection efficiency at certain sizes, noisy data, and difficulty in accurate sizing of the aerosol if its composition is different from the calibration aerosol. In addition, the merging of size distributions is not always straightforward. These problems can lead to difficulty when conducting closure studies or in modeling studies.

The DOE AAF has recently released a Best Estimate Aerosol Size Distribution to remedy the aforementioned problems. Errors in the measured size distributions are quantified and the size distributions for the three probes are recovered, merged, and smoothed using a kernel-based Twomey algorithm. The fidelity of the merged size distribution will be presented through lab studies, comparison with vacuum aerodynamic size distributions measured by single particle mass spectrometers (SPLAT II and mini-SPLAT, and a comparison with ground based measurements during the Two-Column Aerosol Project intensive operation periods in July 2012 and February 2013.

12UA.1

Scooter Emissions Dominate Urban Organic Aerosol. IMAD EL HADDAD, Stephen Platt, Alessandro Zardini, Jay Slowik, Michael Clairotte, Covadonga Astorga, Peter Barmet, Josef Dommen, Urs Baltensperger, Andre Prévôt, *Paul Scherrer Institute*

In urban areas, where the health impact of pollutants increases due to higher population density, traffic is a major source of ambient organic aerosol (OA). A significant fraction of OA from traffic is secondary, produced via the reaction of exhaust precursor gases with atmospheric oxidants. Secondary OA (SOA) has not been systematically assessed for different vehicles and driving conditions and thus its relative importance compared to directly emitted, primary OA (POA) is unknown. 2-stroke (2S) scooters are inexpensive and convenient and as such are a popular means of transportation. However, as the European regulations for scooters are less stringent than for other vehicles, current estimates suggest that 2S scooters may emit more POA and SOA precursors than all other vehicles combined.

Here, we assess POA emission factors (EFs) and potential SOA production from 2S scooters. 2S scooters were run in idle or simulated low power conditions and on a chassis dynamometer, during regulatory ECE47 driving cycles. Emissions was introduced into smog chambers, where primary emissions and SOA formation were monitored using a suite of instruments including a high-resolution time-of-flight aerosol mass spectrometer and a proton transfer time-of-flight mass spectrometer.

We show that the oxidation of VOCs in the exhaust emissions of 2S scooters produce significant SOA, exceeding by up to an order of magnitude POA emissions. We show that SOA formation from 2S scooter emissions essentially stems from the condensation of aromatic oxidation products. Further, we demonstrate that replacing the standard gasoline with an aromatic-free fuel mitigates SOA production, underlining the major role of aromatic compounds from 2S exhaust on SOA production. POA and potential SOA EFs determined here from 2S scooters will be presented and compared with EFs from other vehicles (4S scooters, gasoline cars and diesel cars) to assess the contributions of 2S scooters in urban atmospheres.

12UA.2

Spatial Variation of Pollutants in the Near-Road Environment. NICHOLE BALDWIN, Philip K. Hopke, Stuart Batterman, Suresh Raja, *Clarkson University*

Exposure to traffic-related air pollutants such as black carbon (BC), fine particulate matter (PM2.5), and NO2 can exacerbate asthma and other respiratory problems. Cities such as Detroit, MI have high volumes of local traffic combined with long-haul trucking which contribute to air pollution and thus, respiratory problems of nearby residents. Of particular interest are diesel engine emissions, which consist of ultrafine particles (UFP) that are deposited in the lungs and aggravate disease.

To assess exposure in the vicinity of major roadways, this study aims to characterize pollutant evolution in the near-road environment with respect to time and distance from highways. Sites at varying distances from Detroit highways were sampled for 5 minutes each during mornings and afternoons for 7 consecutive days in two seasons. The concentrations of BC, UFP, PM2.5, PM10, SO2, and NOx were measured. Concentration differences due to time of day, day of the week, distance from highway, wind speed and direction, and season were studied.

Concentrations decreased with distance from the highway with NO and BC showing the largest changes; PM10 changed the least. NO levels decreased 53%, from 25 ppb at 50 m from the highway to 12 ppb at 500 m. BC concentrations decreased 25%. UFP diameters increased from 49 nm to 55 nm. Pollutant levels were usually highest in the morning, a result of meteorological conditions, e.g., diminished dispersion and lower mixing heights. Concentrations at locations 50 and 150 m downwind of highways were usually elevated relative to upwind locations and approached background levels at 500 m downwind.

Traffic-related air pollutant concentrations decrease with distance from highways, thus, people living or working closest to highways receive the highest pollutant exposures. Further analysis of the spatial variation will allow an improved understanding of exposure, advancing health impact assessments.

12UA.3

Characterizing Urban Roadside Environments through Long-Term Monitoring: Particle Mass, NOx, Traffic and Signal Phasing. CHRISTINE M. KENDRICK, Linda A. George, *Portland State University*

Roadside monitoring of nitrogen dioxide (NO_2) will begin in the United States over the next several years due to recent changes in the Clean Air Act. Urban roadside environments also have elevated particle mass, number concentrations and nitric oxide (NO) from traffic emissions. Daily commuter populations experience frequent short-term exposures of increased pollution as drivers, vehicle occupants, bicyclists, and pedestrians. Populations living, working, and attending school in close proximity to roadways experience long-term exposures. This presentation describes the unique opportunity of establishing a continuous, long-term roadside monitoring station at an intersection on SE Powell Boulevard in Portland, Oregon beginning in fall 2012. The station measures PM_{10}, $PM_{2.5}$, NOx and meteorological variables. Through a partnership with the City of Portland, traffic volumes and timing of adaptive signal phases are also collected. SE Powell is a major, urban arterial corridor with a high compositional mix of traffic (buses, freight, cars, pedestrians). The intersecting road, SE 26th, also includes bicycles. While higher average PM_{10} and $PM_{2.5}$ concentrations were expected for winter compared to fall due to lower mixing height and other meteorological conditions, data collected to date shows the upper ranges of PM_{10} and $PM_{2.5}$ to be three times higher in winter than fall, even at 10 and 15 minute aggregations. The continuous monitoring is showing the type of frequent, elevated, short-term exposure concentrations that exist at a roadside while also providing a starting point to document long-term, seasonal trends in the Pacific Northwest. Preliminary modeling shows some expected patterns such as PM_{10} and $PM_{2.5}$ inversely correlated with wind speed. However, low wind speed days show particulate mass concentrations to follow diurnal traffic patterns and correlations with NO and NO_2. Identification of such conditions alongside measured roadside concentrations help to piece out the meteorological and traffic contributions to the roadside environment.

12UA.4

Effects of Diesel Particle Filters on Heavy-Duty Diesel Truck Emissions at the Port of Oakland. CHELSEA PREBLE, Timothy Dallmann, Steven DeMartini, Nathan Kreisberg, Susanne Hering, Robert Harley, Thomas Kirchstetter, *University of California, Berkeley*

To accelerate pollutant emission reductions from heavy duty-diesel trucks around ports and rail yards, the California Air Resources Board’s Drayage Truck Regulation required replacement of trucks with pre-1994 engines and retrofit with diesel particle filters (DPFs) of trucks with newer engines. Previous studies at the Port of Oakland monitored the pollutant emission effects of initial phases of this regulation. New measurements in March 2013 were made after all trucks in the fleet had either been replaced with newer filter-equipped engines or retrofit with DPFs. Pollutants were measured in the exhaust plumes of individual heavy-duty trucks at high time resolution (1-2 Hz) as the trucks drove by a mobile lab that was parked on a bridge above the traffic en route to the Port. We measured ultrafine particle number concentration and size distribution, black carbon concentration, and concentrations of nitrogen oxides (NO_X and NO). These emissions were linked on a truck-by-truck basis to detailed information about each engine and installed emission control equipment. This analysis examines the change in the distribution of pollutant emissions across all Port trucks as a result of the Drayage Truck Regulation and the emissions characteristics of various truck subpopulations based on engine model year and types of emission controls. In addition, the ultrafine particle and NO_2 emissions impacts of retrofit and new-engine DPFs and selective catalytic reduction systems are examined. These results are significant as California is now requiring a similar cleanup of nearly all on-road heavy-duty diesel trucks and buses operating in the state and other states are likely to follow California’s lead.

12UA.5

Short-lived Increases in Particle Concentration Disproportionately Influence Exposure to Roadway Air Pollution and Health Outcomes. ROBY GREENWALD, Priya Kewada, Fuyuen Yip, Jeremy Sarnat, *Emory University*

The concentration of particulate pollutants on roadways can rapidly change in response to traffic conditions, meteorology, or the proximity of high-emitting vehicles. These changes are not apparent when performing integrated pollutant measurements. Previous investigation has found that the maximum concentrations of several pollutants are stronger predictors of observed health outcomes than integrated concentrations, and it is biologically-plausible that health effects may be driven by short-lived exposure events. To investigate the influence of transitory concentration spikes, the time series of continuously measured in-cabin pollutants from the Atlanta Commuters Exposure (ACE) study were analyzed to determine the frequency and magnitude of events. Measured pollutants include fine particulate matter (PM2.5), particle number concentration (PNC), black carbon (BC) and particle-bound PAHs. If pollutant levels exceeded a threshold value defined as the mean plus one standard deviation (SD) for the entire study and the pollutant concentration increased with a slope exceeding a one SD increase in one minute, an event was triggered. The event was terminated when the concentration reached a local minimum or fell below the threshold value. All pollutants averaged 4-5 events per commute except PM2.5, which averaged less than one. PNC events frequently occurred at different times than BC and PAH events. In many cases, the source(s) of an event could be determined from study data. Although a typical event lasted only a few minutes, the fraction of commute exposure that occurred during an event was double the fraction of time that was during an event. Cumulative event exposure approached 50% of the total and was closely associated with observed health outcomes.