Plenary I

Can We Tame the Aerosol Uncertainty Monster?

KEN CARSLAW, Lindsay Lee, Kirsty Pringle, Carly Reddington, Leighton Regayre, *University of Leeds*

Aerosol science has made enormous steps in understanding fundamental processes and in making measurements that probe ever more complex particle properties. But how much of this new knowledge is being translated into better models of how aerosols affect climate? From the third to the fifth IPCC assessment report, aerosols have remained the largest radiative forcing uncertainty. In this presentation I address two questions: firstly, whether we are working on the right processes and secondly, how we can use models and observations to slowly reduce the persistent uncertainty. Using fairly well established statistical techniques it is possible to perform essentially a Monte Carlo simulation with a complex global aerosol model. This enables the contribution of all important processes to the overall prediction uncertainty to be quantified and mapped. The list of key processes turns out to differ substantially depending on whether you want to understand the uncertainty in present-day aerosol or its effect on radiative forcing. The properties of biomass burning particles are important for present-day global CCN uncertainty, but are less important for the uncertainty in forcing, although big questions remain about how these particles interact with clouds. The list also depends on whether you want to understand the sources of uncertainty in forcing since the pre-industrial period or over recent decades. Natural aerosols tend to dominate forcing uncertainty when referenced back to the pre-industrial, but uncertain anthropogenic emissions are the most important factor for recent changes in forcing, with aerosol microphysical processes being less important. Regardless, the list of most uncertain parameters enables us to begin to constrain the model uncertainty using well-chosen measurements. In this direction, I will describe a methodology that could be used to define an optimum measurement strategy if the reduction in model uncertainty is the objective.

Plenary II: AEESP Lecture

Fine Particulate Air Pollution and Human Health: Science, Public Policy, and Controversy.

C. ARDEN POPE, *Brigham Young University*

There is increasingly compelling scientific evidence that breathing fine particulate air pollution contributes to human morbidity and mortality. Epidemiologic evidence suggests that short-term exposure exacerbates existing pulmonary and cardiovascular disease and increases the risk of becoming symptomatic, requiring medical attention, or even dying. Long-term repeated exposures increase the risk of chronic pulmonary and cardiovascular disease. There appears to be multiple mechanistic pathways that link exposure with adverse health outcomes including, pulmonary/systemic oxidative stress and inflammation, enhanced initiation and progression of atherosclerosis, and altered cardiac autonomic function. A recent integrated study of factors that contribute to burden of disease suggest that exposure to fine particulate air pollution contributes substantially to global burden of disease, especially in much of the developing world. There is also evidence that public policy efforts to reduce fine particulate matter air pollution can be successful, can improve air quality, and can contribute to enhanced human health. Pollution abatement efforts, however, can also be costly, challenging and controversial. This presentation will focus on the air pollution health science that motivates the public policy and will briefly discuss the most recent controversy regarding the use of “secret science” to inform public policy.

Plenary III: Friedlander Lecture

Linking Tailpipe to Ambient: Atmospheric Evolution of Combustion Emissions. ALLEN ROBINSON, *Carnegie Mellon University*

Emissions from motor vehicles, wildfires, and other combustion processes are major contributors to atmospheric fine particle mass. These emissions are a complex mixture of organic and inorganic species. Some of these species are directly emitted as particles, but the vast majority of the emissions are gases and vapors. Upon entering the atmosphere, emissions are exposed to oxidants and sunlight, which causes them to evolve chemically and physically, generating secondary particulate matter. To develop effective control strategies one must understand the overall contribution of emissions from combustion processes to ambient particulate matter -- both direct particle emissions and particle mass formed in the atmosphere. This talk will synthesize results from source testing, tunnel experiments, ambient measurements and chemical transport modeling to investigate the atmospheric evolution of emissions from combustion processes, focusing on organic aerosols. The results reveal a dynamic picture in which secondary organic aerosol formed in the atmosphere dramatically exceeds the direct particle emissions, especially for low emitting sources. Both speciation data and mass closure analysis indicate that low-volatility vapors are an important class of secondary organic aerosol precursors. The talk concludes with a brief discussion of the implications of these findings on human exposures, climate, and the design of regulations to control pollutant emissions.

Plenary IV

Climate, Biofuel Emissions, and the Quest for Relevance.
TAMI BOND, *University of Illinois at Urbana-Champaign*

Over the last 25 years, the climate research community has acknowledged that direct and cloud-related aerosol radiative forcing is one of the greatest uncertainties in understanding the trajectory of future climate. Understanding of present-day and historical aerosol forcing assists in determining climate sensitivity. I will discuss what is known about the historical evolution of burning biofuel to provide energy, the characteristics of emitted particles, and how these particles change with combustion technology. I'll review how emission measurements made in controlled situations differ from those in real, in-use settings. I will also look forward to changes expected during the next 25 years, when aerosol concentrations will decrease or remain the same. The growing greenhouse-gas forcing is quite likely to overwhelm aerosol forcing, leaving aerosol science as a less important player in the climate arena. Nevertheless, stresses on well-being via climate and health are likely to persist, increasingly concentrated among sensitive and low-income populations. I argue that aerosol scientists will have a transformed but equally relevant role to play in the coming world.

1AC.1

Secondary Organic Aerosol Formation from Acylperoxynitrates (APNs) of Biogenic Aldehydes. TRAN NGUYEN, Kelvin Bates, Matthew Coggon, Xuan Zhang, Zhenfa Zhang, Avram Gold, Jason Surratt, John Crounse, Paul Wennberg, John Seinfeld, *California Institute of Technology*

Biogenic aldehydes, such as methacrolein and pinonaldehyde, are first generation compounds produced in high yields from the tropospheric oxidation of unsaturated hydrocarbons. Their OH-oxidation under typical ambient conditions generates acylperoxynitrates (APNs). These APNs are efficient precursors to secondary organic aerosol (SOA), although the SOA production mechanism is still unclear. We present new results from chamber studies on the photooxidation of methacrolein, pinonaldehyde, and other structurally-specific aldehydes. Chemical species and SOA are monitored with online techniques such as chemical ionization mass spectrometry, gas-chromatography with flame-ionization detection, and aerosol mass spectrometry. The importance of each previously-proposed mechanism (e.g., via the lactone, dioxoketone, or epoxide intermediates) for SOA formation from APNs will be explored. Mechanistic differences in the OH abstraction vs. addition channels in APN chemistry, and their influence toward the production of SOA intermediates, will be discussed.

1AC.2

SOA Formation from the Aqueous-phase Reactions of Phenolic Compounds. QI ZHANG, Lu Yu, Jeremy Smith, Cort Anastasio, Alexander Laskin, *University of California, Davis*

Phenolic compounds are emitted in significant amounts from biomass burning and can undergo fast aqueous-phase reactions to form secondary organic aerosol (SOA) with mass yields of ~ 100% (Smith et al., ES&T, 2014). In this study, we investigate the aqueous-phase reactions of three phenols (phenol, guaiacol and syringol) with two oxidants - excited triplet states of carbonyls (3C*) and hydroxyl radical (OH) under atmospheric relevant conditions. The low volatility products of these reactions were thoroughly characterized using high-resolution aerosol mass spectrometry (HR-AMS), ion chromatography (IC), and high resolution electrospray mass spectrometry (ESI-MS). The evolution of phenolic SOA as a function of photochemical age was studied using a newly developed online experimental approach. Our results indicate that aqueous-phase reactions of phenols mainly involve polymerization, hydroxylation, carbonylation, esterification, and various fragmentation processes including aromatic ring opening and loss of methoxy groups. The atomic oxygen-to-carbon ratio (O/C) of the SOA increased over the course of phototransformations, more rapidly at the beginning, and achieved a value of 1 - 1.2 after simulated sunlight illumination equivalent to multiple days of tropospheric exposure. The first generation products included dimers and hydroxylated monomers, which were later transformed to higher-order oligomers and highly oxygenated monomeric and oligomeric derivatives. As the photoreactions continued, ring opening processes became more dominant and the fragmentation was accompanied with a gradual decrease of SOA mass.

1AC.3

SOA Potential Formation from Whole Gasoline. CHIA-LI CHEN, Ping Tang, Lijie Li, David R. Cocker III, *University of California, Riverside*

The objective of this study is to investigate the SOA potential formation from whole gasoline vapor under varying NO_x conditions. Odum et al. (1997) performed chamber experiments with 12 different reformulated gasolines, and their results showed that SOA formation from atmospheric oxidation of these fuels was dominated by the aromatic content of the fuel. However, these experiments were conducted at relatively high concentrations of VOC and NO_x. Further, the U.S. EPA and CARB has continued to promulgate standards for reformulated and conventional gasolines including increasing oxygenate content while reducing sulfur, olefins, and aromatics. The SOA formation impact from gasoline vapor is expected to differ from previous studies as the chemical composition and our understanding of the relationship between particle formation and atmospheric reactivity has evolved. In this work, chamber experiments are designed with series of aromatics and n-alkanes from gasoline to evaluate the atmospheric potential of SOA formation with emissions from whole gasoline vapors. Winter and summer fuel blends representative of Southern California are selected to be evaluated from the SOA formation from whole gasoline at the UCR CE-CERT environmental chamber. The characteristics of SOA formation are identified by Volatility Tandem Differential Mobility Analyzer (VTDMA), Aerosol Particle mass Analyzer (APM)-SMPS and High-Resolution Time-of-Fight Aerosol Mass Spectrometry (HR-ToF-AMS) for particle volatility, density, and chemical composition, respectively. The SOA yields of different blend gasolines are evaluated with the PM-SAPRC model, two-product model and volatility basis set. Preliminary result shows that the SOA yield from winter gasoline photoxidation is 5.8% ~8.5% at aerosol mass loading less than 10 $\mu g/m^3$. This presentation will discuss the ability of these approaches of estimate SOA formation from fuel mixtures from chamber results of individual SOA precursors.

1AC.4

Effect of Temperature and Dilution on SOA Derived from Reaction of Beta-pinene with Nitrate Radical. CHRISTOPHER BOYD, Lu Xu, Javier Sanchez, Xiaoxi Liu, Wing-Yin Tuet, Greg Huey, Nga Lee Ng, *Georgia Institute of Technology*

Secondary organic aerosol (SOA) is a major component of atmospheric aerosol, which has important implications on health, climate, and visibility. Studies have shown that nighttime chemistry can account for about 20-50% of biogenic precursor oxidation in polluted urban areas. The primary nighttime oxidant is the nitrate radical (NO3) formed by reaction of ozone and anthropogenic NO2. The interactions of biogenic VOCs with NO3 radical represent a direct way for positively linking anthropogenic and biogenic emissions. Since reaction with nitrate radical is predominant at night, it often reacts at colder temperatures and at a time when the boundary layer height is at its lowest. Beta-pinene is an important biogenic precursor in nighttime aerosol chemistry because of its relatively high abundance and high SOA yields when oxidized by NO3. However, the temperature effects on SOA formation from NO3 oxidation of beta-pinene at lower temperatures have not been quantified. In this study, chamber experiments with beta-pinene are performed at the Georgia Institute of Technology Environmental Chamber facility, which has the capability to perform reactions in the range of 4-40 degrees C. Reactions are carried out at lower temperatures to simulate lower nighttime temperatures of the ambient environment. N2O5 is injected into the chamber by pre-reacting NO2 and O3 in a flow tube to initiate beta-pinene oxidation. Aerosol chemical composition is characterized by a High Resolution-Time of Flight-Aerosol Mass Spectrometer (HR-TOF-AMS) with corresponding gas-phase oxidation products measured by a Chemical Ionization Mass Spectrometer (CIMS). Aerosol products formed at lower temperatures have different compositions when compared to higher temperature experiments of similar mass loading. Preliminary results show that the SOA yield of beta-pinene with nitrate radical increases by about 25% for every increase in 10 degrees C. More detailed analysis will discuss the influence of reaction temperature and dilution on gas-phase and aerosol composition.

1AC.5

Photoactivated SOA Formation: Mechanistic Insight from Modeling and Experiments.

V. FAYE MCNEILL, Andrew Sumner, Joseph Woo, Wanyi Li, Nabil Khan, Yi Rao, *Columbia University*

Reactions in or on aerosol particles involving the participation of light-absorbing organic aerosol species as photoactivators have been suggested as pathways for the photochemical processing of volatile organic species (Yu and Keutsch, 2012; Monge et al., 2012; Aregahegn et al., 2013, Rossignol et al. 2014), leading to the efficient formation of secondary organic aerosol (SOA) material. Additional insight into the mechanisms and kinetics of these processes is required so that we may evaluate their importance on the regional and global scales via atmospheric chemistry modeling. We have used a combination of bulk phase and surface-specific spectroscopy, density functional theory, and box modeling to this end. Bulk flash photolysis kinetics studies, along with the surface-active nature of many likely photoactivator species, show that this chemistry most likely occurs at the gas-aerosol interface. Results from surface-specific nonlinear optical studies of photoenhanced VOC oxidation will be presented. Analysis of published aerosol chamber data using our photochemical box model, GAMMA, shows evidence for SOA formation from glyoxal via photoenhanced fulvic acid and, to a lesser degree, particle-phase products of glyoxal SOA formation. Finally, density functional theory provides insight to candidate photoactivator-VOC pairs, demonstrating the general nature of this phenomenon.

1AC.6

Instantaneous NO Effect on Secondary Organic Aerosol Formation during m-Xylene Photooxidation.

LIJIE LI, Ping Tang, Chia-Li Chen, David R. Cocker III, *University of California, Riverside*

SOA formation from aromatic hydrocarbon photooxidation is highly sensitive to NO concentration. Instantaneous NO effect on SOA formation from m-xylene photooxidation has been investigated in this work by data mining 10 years of aromatic hydrocarbon chamber experiments conducted in the UCR chamber. First, sub-ppb level NO effect on SOA formation is studied by modifying classical aromatic SOA growth curves based on NO_2/NO ratio. Relationships among SOA growth rate, hydrocarbon consumption, HC/NO, absolute NO concentration, NO_3 radical concentration and OH radical concentration are demonstrated. Second, five NOx injection schemes are applied to chamber photooxidation experiments to simulate continuous NO sources in urban areas. Radical concentrations are estimated using the SAPRC-11 photochemical model. Influence of NO_x injection schemes on radical concentrations (OH, HO_2 and RO_2), SOA formation, aerosol volatility and aerosol density is explored. An mz43 ($C_2H_3O^+$)/mz44 (CO_2^+) ratio determined by ToF-HR-AMS is used to explore SOA chemical composition differences arising from these injection schemes. It is expected SOA formation was suppressed at high NO concentrations as reported by many studies. Interestingly, however, enhanced SOA formation is also observed when low NO levels (~1ppb) were artificially maintained by continuous or step-wise injection. A mechanism for promoting SOA formation at ~1ppb NO concentration is proposed. This study facilitates the understanding of NO effect on SOA formation under atmospherically relevant conditions.

1AC.7

Incremental Secondary Organic Aerosol Formation at Simulated Atmospheric Reactivites. MARY KACARAB, William P. L. Carter, David R. Cocker III, *University of California, Riverside*

A surrogate mixture of anthropogenic and biogenic volatile organic compounds (VOCs) was developed to study the effects of individual compounds on secondary organic aerosol (SOA) formation in simulated urban atmospheres with biogenic influences. Environmental chamber simulations were designed to enable the study of the incremental aerosol formation from select anthropogenic (aromatic) and biogenic (terpene) precursors under chemical conditions created by the surrogate mixtures. The surrogate reactive organic gas (ROG) mixture used was based on that used to conduct experiments to study incremental effects of VOCs on O_3 formation. Multiple surrogate experiments (with and without the SOA precursor) were performed in the University of California Riverside (UCR) College of Engineering Center for Environmental Research and Technology (CE-CERT) dual 90m^3 environmental chambers. SOA incremental aerosol yields and aerosol properties such as density, volatility, and elemental chemical composition (from elemental analysis of high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) data will be presented. Incremental yields, SOA characteristics, and O_3 formation will be compared with data from previous single VOC studies conducted for these aerosol precursors following traditional VOC/NOx chamber experiments. Comparison between the incremental effects of VOCs on SOA formation and properties are important when evaluating how to best extrapolate environmental chamber observations to the ambient atmosphere and provides useful insights into current SOA formation models.

1AP.1

Light Scattering by Thickened Percolation Aggregates. WILLIAM HEINSON, Chris Sorensen, Amit Chakrabarti, *Kansas State University*

Light scattering by random shapes is of major importance in understanding the effects that atmospheric dust has on climate change. We present a model to create random shapes that mimic some atmospheric dusts. We start with an on-lattice percolation aggregate of fractal dimension 2.5, then thicken the cluster by filling in the nearest neighbors till it reaches a fractal dimension of 3. Next we use a discrete dipole approximation algorithm to solve for the light scattering and apply Q-space analysis to explore patterns as the phase shift parameter, rho, increases. The scattering displays power laws with q with exponents that evolve with rho.

1AP.2

Wavelength Resolved Polarized Elastic Scattering Measurements from Single Particles. Jozsef Czege, VASANTHI SIVAPRAKASAM, Jay Eversole, *Naval Research Laboratory*

We provide an update on the progress of our project to investigate the polarimetric scattering signatures of aerosol particles. Our goal is to search for correlations of angular and polarimetric elastic scatter patterns with morphological categories based on individual particle structure and composition, and to evaluate application of these types of correlation for discrimination between man-made and naturally occurring aerosol particles. In order to implement this type of capability, we have developed an experimental arrangement to measure multi-angle, multi-wavelength polarized scatter from single aerosol particles suspended in a sample flow in essentially real-time. Our experimental approach is based on a super-continuum light source, an array of optical fibers, an imaging spectrometer and camera to simultaneously acquire a two-dimensional snapshot of scattering data. Preliminary Mueller matrix measurements have been made from individual particles held in an optical trap (at 405 nm), or on particles that slowly drift into the collection volume. We have done modeling for these measurements at specific angles and the comparison with experimental measurements shows good agreement. Initial measurements were conducted in the visible region, 450 nm to 900 nm, but recently we have extended the range of the measurements to encompass the IR region, 1000 to 1700 nm as well. We are currently making polarimetric measurements on larger 2 to 4 µm particles held in an optical trap and these measurements will be discussed. We plan to investigate scatter correlations for non-spherical particles and agglomerates in the near future and will include the most recent results.

1AP.3

Bounds on Aerosol Physical and Optical Properties Using Linear Programming-based Extension of the Quadrature Method of Moments. ROBERT MCGRAW, *Brookhaven National Laboratory*

Moment methods have rich mathematical connections that embody orthogonal polynomials, continued fractions, and quadrature. In the quadrature method of moments (QMOM) a sequence of e.g. radial moments of a particle distribution function (pdf) is inverted using such methods to obtain a small set of quadrature abscissas and weights that can be used to accurately estimate aerosol physical and optical properties. The pdf itself is not required; only values for a, typically small, set of its moments are required. For the present study a new approach to moment inversion is presented that is not based on moment methods or limited to moments. The new approach can be applied to arbitrary kernels over the pdf with the result that many aerosol properties and/or measurement, i.e. those linear in the pdf, can be accurately represented. These new inversions, which like the QMOM lead to sparse representations for the aerosol, solve the constrained optimization problem in which of various physical and/or optical properties of the aerosol are either maximized or minimized subject to various constraints using optimization theory. The QMOM, recovered as a special case, falls into this class. The method is shown to yield nested sequences of rigorous upper and lower bound pairs that constrain a selected aerosol physical or optical property, e.g. light extinction coefficient, particle surface area, etc., based on a Bayesian-like input sequence of independent measurement/model constraints.

1AP.4

Linear Electrodynamic Quadrupole Trap for Single Particle Studies. MATTHEW HART, Erin M. Durke, Jason Edmonds, Jay Eversole, *Naval Research Laboratory*

Advantages of using a linear electrodynamic quadrupole trap (LEQ) include the relative ease, or increased efficiency of particle capture and control. The stability region of the LEQ is along the symmetry axis defined within four parallel, equally spaced rods, and can be many centimeters in length. Within this region one, or multiple, charged, micron-sized particles can be captured and confined at ambient atmospheric pressures. Although similar to the established mechanism used for the quadrupole mass filter in ion mass spectroscopy (IMS), the lack of vacuum in the LEQ creates a damping effect on the particles which broadens the conditions of stability with respect to an IMS quadrupole mass filter. We have trapped particles ranging in size from 0.5 um to 10 um with only small adjustments in the operating parameters such as LEQ frequency. Trapped particles can be held stationary or controllably conveyed along the axis by using a combination of airflow along the length of the device and properly placed electric potentials. Multiple optical measurements can be made along the length of the LEQ. We report the modeling of particle trajectories, stability limits and trapping within a LEQ together with experimental data obtained from liquid and solid particles for model validation. Recent experimental results pertaining to evaporation rates and light scattering phenomena will be presented.

1AP.5

Radiative Properties of Soot Fractal Aggregates Formed by Polydisperse Point-Touch Spherical Particles. FENGSHAN LIU, Jerome Yon, *National Research Council Canada*

Optical diagnostics play an important role in our understanding of black carbon (BC), also known as soot formation in combustion and in obtaining quantitative information on the morphology of black carbon emitted from various combustion devices. It is highly desirable to predict the radiative properties of BC particles in order to accurately estimate their role in the Earth's radiation budget. The Rayleigh-Debye-Gans theory for fractal aggregates (RDG-FA) has often been used to interpret the detected scattering signals and predict the radiative properties of soot fractal aggregates. RDG-FA has been formulated for aggregates formed by point-touch monodisperse primary particles. In reality, however, BC particles in general comprise polydisperse primary particles with a certain degree of overlapping or bridging.

In this study fractal aggregates formed by polydisperse primary particles are numerically generated using a diffusion limited cluster-cluster aggregation (DLCA) algorithm. The mean and standard deviation of primary particles are 34.2 nm and 6.85 nm, respectively. The aggregate size range considered is 1 to 1006. The fractal dimension and the prefactor are 1.78 and 1.44. Radiative properties of these fractal aggregates, including absorption cross section, scattering cross section, and the asymmetry factor, were calculated for $m = 1.6 + 0.6i$, a typical value of soot in the visible spectrum, and at wavelengths of 532 and 1064 nm using RDG-FA and the generalized Mie-solution method (GMM). Through a direct comparison between the GMM and RDG-FA results, the accuracy of the RDG-FA theory can be assessed. To evaluate the effect of polydispersity in primary particle size on the radiative properties of soot fractal aggregates, additional calculations were calculated for aggregates formed by monodisperse primary particles whose sizes are such that the aggregate volume is conserved.

1AP.6

High Intensity X-ray Scattering of Nanosized Ice Particles Formed in a Supersonic Nozzle. ANDREW AMAYA, Viraj Modak, Harshad Pathak, Michael Bogan, Hartawan Laksmono, Claudiu Stan, Duane Loh, Raymond Sierra, Anders Nilsson, Jonas Sellburg, Trevor McQueen, Sebastien Boutet, Garth Williams, Marc Messerschmidt, Barbara Wyslouzil, *The Ohio State University*

Supersonic nozzles with cooling rates of about 10^5 K/s are able to probe both vapor-liquid and liquid-solid phase transitions at extreme nucleation rates of up to 3×10^{17} $cm^{-3}s^{-1}$ for vapor-liquid and up to 6.6×10^{22} $cm^{-3}s^{-1}$ for liquid-solid. The ice formed by the liquid-solid phase transition in this process is thought to be cubic. To examine the structure of the nanometer sized ice crystals, x-ray diffraction experiments are needed with a range of scattering vectors, q, between 1.0 A^{-1} and 3.5 A^{-1}. These experiments should be possible using either the Free Electron Laser at the LCLS (CXI beamline) or the conventional synchrotron radiation at the APS (BESSRC 12-ID). The advantage of using CXI is that the high intensity of the beam can potentially provide high resolution imaging of single isolated particles, and using the LCLS to probe aerosol produced in a supersonic nozzle has never been attempted before. Using the Free Electron Laser at the LCLS in the supersonic nozzle generated a 2-D x-ray scattering pattern with concentric rings located at q values of 1.74 A^{-1}, 2.82 A^{-1}, and 3.28 A^{-1}. The relative intensities of the peaks suggest that the nanometer sized ice crystals created in a supersonic nozzle have a crystal structure that is close to pure cubic ice.

1AP.7

Divine Proportion Shape Invariance of DLCA Fractal Aggregates: An Analytical Theory. William Heinson, Amit Chakrabarti, CHRIS SORENSEN, *Kansas State University*

This paper reconsiders an analytic theory, the restricted hierarchical model (RHM, Sorensen and Oh, Phys. Rev. E58, 7545 (1998)), for Diffusion Limited Cluster Aggregates (DLCA) that accurately predicts the fractal dimension of the aggregates. However, a three parameter description involving the fractal dimension, prefactor and aggregate shape is both necessary and sufficient for a complete description of fractal aggregate morphology. We show that aggregate shape is poorly described by the principal radii of gyration and best described by side length ratios of circumscribing rectangular solids with side directions determined by the principal radii of gyration. We find for simulated clusters in three spatial dimensions the side lengths are related in a geometric manner. The RHM yields accurate values for these ratios and the fractal dimensions of the aggregates via a simple analytic calculation. Simulations of the RHM yield accurate predictions for the prefactor of the aggregates. Hence the RHM provides a complete three parameter description of DLCA aggregates. Finally, and remarkably, we find that aggregate shape is described by the Divine Proportion in $d = 2$ and its generalization in $d = 3$.

1CC.1

Optical Properties of Suspended Mineral Dusts from Desert Source Regions. Johann Engelbrecht, HANS MOOSMULLER, Samuel Pincock, David Campbell, Rajan K. Chakrabarty, R.K.M. Jayanty, Gary Casuccio, *Desert Research Institute*

On a global scale, mineral dust aerosol has the largest mass emission rate, average column mass burden, and average optical depth of all aerosol types, with its single scattering albedo (SSA) determining the sign (heating or cooling) and influencing the magnitude of its radiative forcing. Previously, we had suspended surface soil samples from ten desert sites and characterized their optical properties, especially SSA at two visible wavelengths, concluding that mineral dust SSA was controlled by iron content (Moosmüller et al.; 2009). Here we have extended this work to 65 samples, including sample locations in Africa, Arabian Peninsula, Asia, North and South America, and Australia.

A sieved fraction of each sample was suspended in an entrainment facility, from which the airborne particulate matter (PM) was sampled and analyzed. Instruments integrated into the entrainment facility included PM filter samplers, a beta attenuation gauge for the continuous measurement of PM mass fractions, an aerodynamic particle size (APS) analyzer, and a three-wavelength (405, 532, 781 nm) photoacoustic instrument with integrating reciprocal nephelometer for monitoring aerosol absorption and scattering coefficients of suspended PM2.5. Filter sample media included PTFE membrane and quartz fiber filters for chemical analysis (71 species), and nucleopore filters for individual particle analysis by scanning electron microscopy (SEM). Sieved fractions were also analyzed by X-ray diffraction for their mineral content and further mineralogically characterized by optical microscopy.

We will be presenting results on the optical measurements, showing the relationship between PM optical properties including SSA at different wavelengths and chemical as well as mineralogical properties of the entrained dust samples.

References

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1CC.2

In-situ Measurement of the Aerosol Absorption Spectrum as a Function of Particle Size: Implications for Climate Change. CHRISTOPHER ZANGMEISTER, James Radney, *National Institute of Standards and Technology*

he absorption spectrum of any material is a direct function of its underlying chemical and physical properties, with the absorption strength at a specific wavelength depending upon the amount of material present and the complex refractive index. We will present visible spectrum (500 nm to 825 nm) absorption measurements of weakly absorbing atmospherically relevant aerosol using a supercontinuum phot acoustic spectrometer. We show that the aerosol absorption spectrum depends on both the material and particle size. Using these results, we'll illustrate the sensitivity of radiative forcing predictions on these underlying spectral dependences.

1CC.3

Effects of Global Climate on Photochemical Pollutant Levels Using Climate Downscaling Meteorology and Chemical Transport Model. HONGLIANG ZHANG, Jianlin Hu, David Rasmussen, Zhan Zhao, Shu-Hua Chen, Michael Kleeman, *University of California, Davis*

Exposure to particulate matter (PM) has adverse effects on human health that may change in response to altered climate and emissions. A recent study that downscaled GCM predictions over multiple years predicted that climate change may increase future extreme PM events in California. In this study, calculations are summarized from a second downscaling exercise using improved models to contribute to the ensemble of emerging results concerning global change and air quality. Predictions from the Community Climate System Model (CCSM) are downscaled for both present (year 2001-2010) climate and future (year 2046-2055) climate periods. The Weather Research and Forecasting (WRF) model is used to downscale results to 4km spatial resolution and hourly time resolution. The UCD/CIT chemical transport model is used to predict pollutant concentrations and source apportionment in both present and future climate. Present emissions are obtained from the California Air Resources Board (CARB) while future emissions are based on projections from CARB and the South Coast Air Quality Management District (SCAQMD). PM (primary and secondary) and ozone concentrations are analyzed under three scenarios: (i) present emissions with present meteorology, (ii) present emissions with future meteorology, and (iii) future emissions with future meteorology. Results from 20 years of simulation from the three scenarios are compared to ensure statistical significance in the presence of natural inter-annual variability. The effects of global climate on future average and extreme PM & ozone concentrations and human exposure are discussed.

1CC.4

Multi-year Analysis of Aerosol Optical Depth and its Impact on Cloud Properties over a Coastal-urban City of South Africa as Retrieved from MODIS. A. JOSEPH ADESINA, Venkataraman Sivakumar, K. Raghavendra Kumar, *University of Kwazulu-Natal, Durban, South Africa*

Clouds that are formed in a polluted environment tend to have smaller droplets which can bring about suppression of precipitation and temporal variation in cloud life time. Aerosols, a significant component of air pollution may lead to an increase in cloud optical thickness due to a combination of reduction in cloud droplet radius and increased water content. Its semi direct effect can inhibit cloud formation and evaporation of existing cloud so that aerosol – cloud interaction presents a major research area in atmospheric science. We have used the Terra Satellite onboard of the Moderate Resolution Imaging Spectroradiometer (MODIS) to investigate the spatial and temporal relationship between aerosol optical depth (AOD) and cloud parameters namely, water vapor (WV), cloud optical depth (COD), cloud fraction (CF), cloud effective radius (CER), cloud top temperature (CTT) and cloud top pressure (CTP). A seasonal variation of aerosol optical depth over Cape Town was found to be highest during the spring (September to November) and using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model we were able to trace the origins of the air masses. Our analysis of the temporal variation based on 5years (2008-2012) of dataset showed a strong positive correlation between AOD and WV. The correlation between AOD and COD, CF showed similar pattern of negative correlation from January to July and thereafter, positive for the remaining months of the year. The AOD and CER only showed positive correlation from March to July and then October to December. There is a noticeable positive correlation between AOD and CTT, CTP in all the months of the year, except from July to September. The co-variation of CTT and CTP may be due to large scale meteorological variation.

1CC.5

Ice Nucleating Particle Emissions from Biomass Combustion and the Potential Importance of Soot Aerosol.

EZRA LEVIN, Gavin McMeeking, Paul DeMott, Christina S. McCluskey, Christian Carrico, Shunsuke Nakao, Chelsea Stockwell, Robert J. Yokelson, Sonia Kreidenweis, *Colorado State University*

Ice nucleating particles (INP) are required for ice crystal formation at temperatures warmer than -36 ºC and thus play a crucial role in cloud and precipitation formation. Soot, or black carbon (BC), is a potential INP, although laboratory and field studies suggest highly varied and sometimes little efficacy of different BC sources. Biomass burning has been found to be a source of INP in previous studies, and is also a major contributor to atmospheric BC concentrations. This study focuses on isolating the BC contribution to INP from biomass combustion sources. Measurements of the emissions from a number of globally relevant biomass fuels were made during the fourth Fire Lab at Missoula Experiment (FLAME 4). Concentrations of INP active in the immersion-freezing mode were measured using a Colorado State University Continuous Flow Diffusion Chamber (CFDC). For a subset of the burns, the contribution of refractory black carbon (rBC) to INP concentrations was determined through the use of laser induced incandescence (LII) for removing rBC particles. For these experiments, the sample was passed through an LII device, the Single Particle Soot Photometer (SP2; Droplet Measurement Technologies) placed in series ahead of the CFDC. By alternating the SP2 laser power on and off, the contribution of rBC to INP concentrations was determined. Over all, combustion emissions from 13 of 22 different biomass fuel types produced measurable INP concentrations for at least one burn. On average, all burns which produced measureable INP had higher combustion efficiency, which is associated with higher BC emissions, than those that did not produce measureable INP. Reductions in INP of 0 – 70% were observed when the SP2 laser was turned on, indicating the important contribution of rBC particles to INP concentrations for some burns.

1CC.6

Adjoint Analysis of Ice Crystal Sensitivity to Heterogeneous Nucleation Spectrum.

SYLVIA SULLIVAN, Benjamin Sheyko, Athanasios Nenes, *Georgia Institute of Technology*

An adjoint model of the 2009 Barahona and Nenes ice cloud parameterization (ABN09) is used to understand the changes in cirrus sensitivity caused by different heterogeneous ice nucleation spectra. Input updraft velocity; temperature; and sulfate, black carbon, and dust numbers and sizes come from the Community Atmosphere Model version 5.1, and the parameterization gradient is calculated with respect to these variables. We evaluate the importance of including aerosol description in the nucleation spectrum with a default scheme from Meyers et al. 1992, which contains only supersaturation dependence. Crystal number sensitivities are also calculated with the Phillips et al. 2008 and, for the first time, updated Phillips et al. 2013 spectra within the ABN09 framework. These two empirical spectra depend strongly on aerosol profile, and several input parameters and correlations have changed value or form between the two. Differences in their sensitivity, then, show where the formulation of different ice-nucleating aerosol groups can be most influential. We focus on the importance of aerosol surface area available for nucleation, classification of organics, and the functional representation of black carbon. Attribution plots point to the geographical regions where the results for each of these factors may have the largest impact. This attribution analysis also indicates whether more variability in output crystal number comes from inherent nucleation spectrum biases or from natural aerosol fluctuations.

1CC.7

Droplet Activation Parameterization for Climate Models: The Population Splitting Concept Revisited. RICARDO MORALES BETANCOURT, Athanasios Nenes, *Georgia Institute of Technology*

Aerosol-cloud interactions constitute one of the most uncertain aspects of anthropogenic climate change estimates. The magnitude of these interactions as represented in climate models strongly depends on the process of aerosol activation. This process is the most direct physical link between aerosols and clouds properties. Calculation of droplet number in GCMs requires the computation of new droplet formation (i.e., droplet activation), through physically based activation parameterizations. Accurately determining the size of the droplets when exposed to the maximum supersaturation is crucial to compute the condensation rate onto the growing droplets and ultimately, to determine the number of activated droplets, Nd. Given that aerosol particles larger than about 200 nm do not grow in equilibrium with the ambient supersaturation, computation of its condensation rate is particularly challenging. In this work we postulate, implement and evaluate modifications to the ``population splitting" concept introduced in the activation parameterization of Nenes and Seinfeld (2003) for calculation of water condensation rates in droplet activation parameterizations. These changes aim to achieve a more physically consistent representation of the condensation rate on the largest aerosol particles during the activation process. The modifications introduced here lead to an improved accuracy and precision of the parameterization-derived Smax and Nd as determined by comparing against those of detailed numerical simulations of the activation process. A numerical computation of the first-order derivatives of the parameterized Nd to input variables was performed, and compared against the corresponding parcel model derived sensitivities, providing a thorough evaluation of the impacts of the introduced modifications in the parameterization ability to respond to aerosol characteristics. The proposed modifications require only minor changes for their numerical implementation in existing codes based on the population splitting concept.

1HA.1

Health Implications Of Aerosols from Asbestos-Bearing Road Pavements Traditionally Used in Southern Brazil. RICARDO H. M. GODOI, Sérgio J. Gonçalves Jr., Célia Sayama, José M. Reis Neto, László Bencs, Bálint Alföldy, René Van Grieken, Carlos A. Riedi, Ana Flavia L. Godoi, Guillherme C. Borillo, Yara S. Tadano, *Federal University of Parana - Curitiba, PR, Brazil*

Asbestos is worldwide recognized as a public health problem due to its carcinogenic potential and for this reason many countries have banned their industrial processing and usage. Many localized communities worldwide are continuously exposed to Naturally Occurring Asbestos (NOA), in areas for which the potential health hazard is still unknown. Chemical characteristics and composition of atmospheric aerosols (bulk, size-segregated and single particle) were assessed in a specific exposure area of Piên, Paraná State, Southern Brazil, where a large amount of ultramafic rocks (NOA, bearing serpentinite belts and their associated soils) have been used for decades as road paving in rural areas, without awareness of their adverse environmental impact. Inhalable particulate matter was continuously collected at two sites (Crispins' Meadow and Maias' Meadow) over the most traffic demanding countryside road during two-week-long sampling campaigns. The elemental composition of individual particles and bulk PM was analysed by means of electron probe microanalysis and energy-dispersive X-ray fluorescence, respectively. A large number of the analyzed single particles (~700), were identified as the microfibrillar morphology, consistent with the mineral chrysotile (white asbestos). A lung deposition model estimated the deposition of asbestos at various parts of the human respiratory airways. Calculations revealed that most particles gather in the extrathoracic region. Due to the occurrence of inhalable suspended chrysotile near local roads and the long-term exposure, it can apparently trigger an increased risk of lung cancer development in the population of the studied region. This finding indicates that NOA should be recognized and treated as a large-scale environmental health problem, which affects the life-quality and health of the population in developing as well as developed countries. Government authorities need to take geological factors into account to reduce the likelihood of unplanned disturbance of environments containing natural asbestos-bearing materials.

1HA.2

An Analysis of Air Pollution Effects On Health In São Paulo City Through Health Impact Assessment Approach.

SIMONE MIRAGLIA, Karina Abe, Ricardo Popescu-Junior, *Universidade Federal de Sao Paulo, Sao Paulo, Brazil*

Air pollution is a problem of growing importance in urban centres all over the world, but it has a special concern in developing countries. Several epidemiological studies have consistently shown an association between particulate air pollution and not only exacerbations of illness in people with respiratory diseases but also increase in the numbers of deaths from cardiovascular and respiratory diseases.

Sao Paulo is the world's third largest city and the largest in South America with over 10 million inhabitants. In this study, we investigated the population of Sao Paulo over 30 years old exposed to particulate matter with diameter less than 2.5microgram (PM2.5) from 2009 to 2011. The total of studied population was 6 millions people and the respiratory and cardiovascular mortality avoided in two scenarios of pollutants' decrease was conducted in terms of health impact assessment, through APHEKOM software. The period between 2009 and 2011 registered a mean of PM2.5 of 21.39 microgram /m^3 + 10 SD. The maximum was 78 microgram/m^3 and the minimum was 5 microgram/m^3. The first scenario has considered the mortality avoided if the PM2.5 annual mean concentration could decrease 5 microgram/m^3 and in the second scenario a decrease of 10 microgram/m^3 was considered.

As a result, the first scenario has avoided 1,724.8 annual deaths or 28.7 deaths avoided per 100,000 inhabitants over 30. It represents a gain of 5.2 years in life expectancy. The second scenario revealed a better projection. The 10 microgram/m^3 decrease in annual mean concentration of PM2.5 could avoid 3,856.6 annual deaths or 64.2 deaths per 100,000 inhabitants, meaning a 12 years in life expectancy gain.

In conclusion, Health Impact Assessment approach is valuable for showing health gains concerning air pollution improvements in developing countries, orientating the public policies for diminishing air pollutants.

1HA.3

Air Quality Assessment of Indoor Brazilians Elementary Schools Nearby Petrochemical Industry.

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Air pollution has been framed as a basic requirement in environmental analysis of indoor and outdoor environments, given its steady increase in recent times. The mitigation of pollution released to the environment originating from the industrial sector has been the aim of all policy-makers and its importance is evident if the adverse health effects on the world population are considered. Although this concern is controversial, petroleum refinery has been linked to some adverse health effects for people living nearby. Apart from home, school is the most important indoor environment for children and there is increasing concern about the school environment and its impact on health, also in developing countries where the prevalence of pollution is higher. As most of the children spend more than 40% of their time in schools, it is critical to evaluate the pollution level in such environment. In the metropolitan region of Curitiba, South Brazil, five schools nearby industries and highways with high density traffic, were selected to characterize the aerosol and gaseous compounds indoor and outdoor of the classrooms, during 2009-2011. Size segregated aerosol samples were collected for analyses of bulk and single particle elemental profiles. They were analysed by electron probe x-ray micro-analysis (EPXMA), and by energy-dispersive x-ray fluorescence (EDXRF), to investigate the elemental composition of individual particles and bulk samples. The concentrations of benzene, toluene, ethylbenzene, and the isomers of xylenes (BTEX); NO2; SO2; acetic acid; and formic acid were assessed indoor and outdoor using passive diffusion tubes. BTEX were analyzed by GC-MS and other collected gasses by ion chromatography. Individual exposition of BTEX was assessed by personal passive diffusion tubes. Results are interpreted separately and as a whole with the specific aim of identifying compounds that could affect the health of the scholars.

1HA.4

Estimating Climate and Health Costs from Emissions of On-road Gasoline and Diesel Vehicles.

SHANTANU JATHAR, Allen Robinson, *University of California, Davis*

On-road gasoline and diesel vehicles account for more than three-quarters of the fuel used by the transportation sector and therefore are a significant source of greenhouse gases, air toxics and ozone- and aerosol forming precursors. Transportation research and policy analysis studies lack a nuanced treatment of air pollutants. For example, these studies focus on emissions at the ‘tailpipe’ that often ignore the distinction between primary (directly emitted like carbon monoxide or elemental carbon) and secondary pollutants (chemically formed in the atmosphere like ozone or sulfate), which have different spatiotemporal patterns and therefore different climate and health effects. Further, to the best of our knowledge, these studies have ignored the atmospheric formation for secondary organic particulate matter.

In this work, we used two large datasets, one that measured primary pollutants (Kansas City PM characterization Study) and the other that measured both primary and secondary pollutants (May et al., 2014; Gordon et al., 2013a,b) to build distributions of emission factors for primary and secondary, gas- and particle-phase pollutants for on-road vehicles. We used these distributions to characterize the inherent vehicle-to-vehicle variability. Using a Monte-Carlo simulation and published cost estimates for climate and health effects, we estimated pollutant-resolved marginal climate and health costs in cents-per-mile for on-road gasoline and diesel vehicles as a function of engine emissions standard and/or control technology. Light-duty gasoline vehicles, medium-duty uncontrolled diesel trucks and diesel particulate filter equipped diesel vehicles have marginal climate+health costs of 0.9 to 2.2, 5.2 to 19.7 and 3.9 to 5.0 (5th to 95th percentile) cents-per-mile respectively. We find that for all vehicles, climate costs, which are dominated by CO2, outweigh health costs. Health costs are dominated by secondary organic particulate matter formation for gasoline vehicles, by elemental carbon emissions for uncontrolled diesel vehicles and appear to be negligible for diesel particulate filter equipped diesel vehicles.

1HA.5

Aerosol Emissions from Ships Using Heavy Fuel Oil or Diesel Fuel: Composition and Biological Effects on Human Lung Cells.

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In the framework of the virtual Helmholtz Institute HICE, health effects of emissions from ships are addressed. A ship diesel engine was operated either with heavy fuel oil (HFO) or diesel fuel (DF). The emissions were comprehensively characterized (chemical composition and physical properties). Simultaneously human lung cell-cultures (human alveolar basal epithelial cells, A549 and BEAS2B) were ex-posed at the air-liquid-interface (ALI) using a special ALI mobile exposure system and a custom-built transportable S2-biological laboratory-container. The fresh ship engine aerosols were diluted (DF~1:40, HFO ~ 1:100) before exposure. The 4 h exposed cells subsequently were toxicologically and molecular-biologically characterized (transcriptomics, proteomics and metabolomics). Although the HFO-exhaust was more diluted, the deposited PM-dose on the cell layer was still higher for HFO- than for DF-exposure. Stable isotope labeling technologies (13C-Glucose/metabolomics; 2H-Lysine/SILAC-proteomics) were applied for high detection sensitivity and accuracy for molecular-biological effect at sub-acute toxicity dose levels. The chemical analysis results on HFO- and DF-ship diesel PM depict much more particle mass, organic mass, polycyclic aromatic hydrocarbons (PAH) and oxidized-PAH, aliphatic compounds and transition metals (V, Ni, Fe) for the HFO case. DF-PM in the contrary contained more elemental carbon (EC) and black carbon (BC). The comprehensive investigation of the biological effects of DF- and HFO-ship emissions on the human lung cells gave a surprising result: Although for HFO-experiments the PM-dose was higher and the concentration of known air toxics as PAH and transition metals were much higher, the PM DF-experiments induced broader toxic- and biological-effects in the cells. Monitoring of the cellular response for HFO-emission revealed biological effects such as inflammation and oxidative stress, DF-emission particles induced a broader general reaction including basic cellular pathways. This is suggesting that both, DF- and HFO-PM emission can evoke harmful health effects. In conclusion the currently promoted switching from HFO to DF without precipitation of elemental carbon-emissions may be insufficient from a public-health perspective. This work/HICE (www.hice-vi.eu) is supported by the Helmholtz Association (HGF).

1HA.6

Characterization of Atmospherically Important Organic Radicals in the Gas and Particle Phase. STEVEN CAMPBELL, Chiara Giorio, Markus Kalberer, *University of Cambridge*

When volatile organic compounds are oxidized in the atmosphere less volatile compounds form which partition into the condensed phase and contribute to organic aerosol mass. The formation and composition of secondary organic aerosol (SOA), is poorly understood (Hallquist et al., 2009).

Epidemiological studies showed close correlations between exposure to ambient aerosol and adverse health effects, although toxicological mechanisms are largely unknown. It is likely that particle-bound reactive oxygen species and especially organic radicals play a key role by promoting oxidative stress which can lead to various pulmonary diseases (Donaldson et al., 2003). In addition, the role of organic radicals in SOA formation and composition is entirely unknown. The analysis of these species represents an analytical challenge due to their characteristic high reactivity and low concentrations.

The aim of the present work was the development of a method to characterise atmospherically important organic radicals in the gas and the particle phase by stabilisation with spin traps (5,5-dimethyl-pyrroline N-oxide, DMPO and N-tert-butyl-alpha-phenylnitrone, PBN) to facilitate chemical analysis.

Gas phase and particle-bound organic radicals were generated in a flow tube by reacting oleic acid or alpha-pinene (two SOA model systems) with ozone and OH radicals. The radical intermediates formed during these reactions were then scavenged and stabilized in impingers containing the spin trap and characterised via Ultra-High Resolution Mass Spectrometry. A number of radical-spin trap adducts have been identified in the gas and particle phase. In the most simple system, the ozonolysis of alpha-pinene, only one radical-spin trap adduct was identified which is identical to the expected product.

The reaction with OH yields more complex mixtures of radical-spin trap adducts, which will be discussed and compared with theoretically expected radical formation.

References

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1HA.7

Factors Controlling the Pulmonary Bioaccessibility of Trace Elements in Atmospheric Fine and Ultrafine Particles Near an Industrial Site. LAURENT ALLEMAN, Saliou Mbengue, Esperanza Perdrix, Aude Pascaud, Pascal Flament, *Mines Douai, SAGE, F-59508 Douai, France*

Exposure to metals from fine and ultrafine particles (UFP, < 100 nm) is of major health concern, especially in heavily industrialized areas. This study aims to better characterize the metal fraction of fine (PM2.5) and UFP emitted in an industrial-marked urban context (Dunkirk harbour, France) and to determine their lung bioaccessibility, in relation with their health impact. UFP and PM2.5 have been collected in specific environments: (i) in an urban area influenced by traffic and industrial emissions and (ii) at the stacks and in the vicinity of a ferromanganese plant, characteristic of the industrial activity in Dunkirk. Metals pulmonary bioaccessibility was determined using a synthetic lung fluid (Gamble solution), and compared to a 4-step sequential extraction method, in order to infer metal speciation. In the urban area, UFP elemental concentrations are primarily related to local sources (traffic and domestic heating), while larger submicronic particles (100 nm to 1 µm) are mainly affected by industrial sources, especially metallurgical plants, the main source of particulate metals in this area. Metal-rich (and low bioaccessible) UFP high concentrations (60% of the total PM2.5 mass) are observed in stack flues and then decrease rapidly in the vicinity of the plant, due to fast changes in temperature and humidity. In parallel, this low metal bioaccessibility increases quickly in the near field, mostly due to mixing processes with other particles sources. This bioaccessibility varies also according to the particle properties (metals chemical speciation and particle size distribution), their origin and formation processes. Far from the industrial zone, the metal bioaccessibility may also be affected by physicochemical transformations of fine particles occurring during atmospheric transport (mixing/agglomeration, aggregation, oxidation or reduction processes). The in-vitro bioaccessibility assessment is of interest to better understand the metal bioavailability and thus for a better appreciation of the health impact of toxic metals.

1IA.1

Relative Contributions of Self-Pollution and On-Road-Pollution to Children's Exposure in School Buses. EON LEE, Yifang Zhu, *University of California, Los Angeles*

Previous studies have shown children are exposed to high levels of $PM_{2.5}$, black carbon (BC), and ultrafine particle (UFP, diameter <= 100 nm) inside school buses. Both surrounding vehicle emissions from the roadway (i.e., on-road-pollutions) and school bus' own emissions contribute to the exposure levels. While many studies have reported the presence of self-pollution in schools buses; the relative contributions between on-road-pollution and self-pollution is unknown. This study investigated under what conditions and to what extend self-pollution becomes more important than on-road-pollution. We estimated self-pollution rates inside six school buses and assessed the associated changes of spatial concentration distributions at increased driving speeds. The selected school buses include a wide range of model year, passenger capacity, cabin volume, and engine/exhaust tail-pipe locations. We measured the number concentration and size distributions of UFPs, $PM_{2.5}$, BC, CO_2, and CO levels concurrently in and out of school buses. In-cabin measurements were conducted at breathing zones in the front, center, and back of school buses. Statistical regression analyses were conducted to estimate self-pollution rates for UFPs, $PM_{2.5}$, and BC. This study found high self-pollution rates of UFPs, $PM_{2.5}$, and BC in the school buses. On local streets, self-pollution makes in-cabin/on-road concentration (I/O) ratios as high as ~1.5 for UFPs and slightly less for $PM_{2.5}$ and BC. In comparison, on freeways, the I/O ratio was ~1.0 because of high air exchange rates and the infiltration of high-concentration of pollutants. Self-pollution dominates spatial concentration distributions of in-cabin pollutants. The spatial concentrations were substantially decreased at all three monitoring points at high driving speeds due to increased air exchange rates. The findings in this study suggest that self-pollution in school buses depends on self-pollution source strength, ambient concentration, and driving speed.

1IA.2

Commuters' Exposure to PM2.5 and CO2 in Metro Carriages of Shanghai Metro System. HAO GU, Bin Xu, *Tongji University*

A comprehensive measurement campaign was conducted to examine the commuters' exposure to PM2.5 (diameter<=2.5 micro-meter) and CO2 in metro carriages under different conditions. The average PM2.5 and CO_2 concentrations inside all the measured five metro lines were found to be 0.084 ± 0.042 mg/m^3 and 1253.1 ± 449.1 ppm (parts per million), respectively. The factors that influence the PM2.5 and CO_2 concentrations were quantitatively investigated. The in-carriage PM2.5 concentrations are greatly affected by the ventilation systems, out-carriage PM concentrations and the passenger number. The largest in-carriage PM2.5 and CO_2 concentrations at 0.132 mg/m^3 and 1855.0 ppm were observed inside the carriage equipped with the oldest ventilation systems. The average PM2.5 and CO_2 concentrations increase up to 24.14% and 9.93% as the metro driving from underground to overground. The average in-carriage PM2.5 and CO_2 concentrations increase 17.19% and 26.97% as the metro drives from urban to the suburban area. It was observed that PM2.5 concentration is proportional to the on-board passenger number at a ratio of 0.0004 mg/m^3 per passenger. A mathematical model that incorporates all the above parameters is established to estimate the in-carriage PM2.5 concentration.

1IA.3
Feasibility of Partial Air Recirculation for Vehicle HVAC System. HEEJUNG S. JUNG, Michael Grady, *University of California Riverside*

On roadways, in-cabin exposures to ultrafine particles have been shown to be 10 times higher than ambient levels and contribute to approximately 50% of total daily ultrafine particle exposure among Los Angeles commuters. These results can apply to most of urban areas where high traffic volume exists. The high exposure at previous studies is because air on the roadway is entrained into the vehicle cabin. Scientists found cabin air-recirculation can reduce particle concentrations in the vehicle cabin significantly and effectively. However, their findings could not be applied to the cars in the market because of simultaneous increase of CO2 concentrations in the cabin. Partial recirculation of cabin air (as opposed to full recirculation and off/off control) suppresses the increase of cabin CO2 concentrations while taking advantages of air recirculation to reduce cabin particle concentrations. The study showed cabin CO2 concentration is determined by the balance between source strength and vehicle body leakage rate. This balance is influenced by multiple parameters: vehicle speed, cabin volume, fan speed, and number of passengers. The study demonstrated to control cabin CO2 concentrations at a certain target level by adjusting openings of the recirculation door angle. This method is a cost effective way of maintaining clean air quality of the cabin and can be applicable to new cars at a minimum cost. The presentation includes results and discussion from 1) feasibility test: proof-of-concept, 2) characterization of vehicle HVAC system, 3) influence of vehicle speed, 4) input parameters to control cabin CO2 concentration, and 5) mathematical modelling.

1IA.4
Physical Characteristics of Ultrafine Particles Generated by Electronic Cigarettes. CHA-CHEN FUNG, Zhongshu Li, Mei Zheng, Yifang Zhu, *UCLA*

Recent studies have shown the electronic cigarettes (ECs) generate a substantial amount of ultrafine particles (UFPs). A variety of factors, such as puff duration and ingredients, may contribute to the characteristics of emitted UFPs. Tobacco and Menthol flavored ECs at 0 mg/ml and 24 mg/ml nicotine strengths from one brand were tested to determine the effect of puff duration, EC flavor, and nicotine concentration on UFP characteristics. The puff duration (from 2 to 5 seconds) had a strong positive linear relationship (R^2=0.99) with the total particle number concentration (PNC) generated for all the different flavor and nicotine combinations tested. The effects of EC flavor and nicotine concentration on PNC and particle size distribution were more complicated. The tobacco EC generated higher PNC and smaller particle mode (25 nm) compared to menthol EC (33 nm). The 0 mg/ml nicotine concentration generated lower PNC than the 24 mg/ml for the tobacco EC. This effect was reversed for the menthol EC. There are clear interactions between EC flavor and nicotine concentration that affect the UFPs generated. More detailed chemical analysis is needed to understand these interactions.

1IA.5

Investigation of the Reactivity of PAHs Present in Model Indoor Surfaces. SHOUMING ZHOU, Matthew Forbes, Jonathan Abbatt, *University of Toronto*

It is well known that indoor surfaces are covered by semi-volatile organic and inorganic substances that arise from deposition of aerosol particles, primary and secondary gas-phase species, as well as skin oils; however, it is not clear whether this semi-volatile surface layer (SVSL) affects the reactivity of the substances either mixed with it or embedded under it. Given that these substances can be transferred to humans through dermal contact, via inhalation of both volatile components and aerosol particles, or by hand-to-mouth ingestion, it is important to understand the reactivity of SVSLs as a function of indoor environmental conditions.

In this work, we have developed quantitative analytical technique using direct analysis in real time-mass spectrometry (DART-MS) for chemical study of the heterogeneous oxidation of SVSLs. Using a polycyclic aromatic hydrocarbon (PAH) as a surrogate reactive species, the reactivity of the PAH towards gas-phase ozone is investigated by mixing the PAH with different SVSL substances, e.g. cooking oil (liquid), secondary organic aerosol (SOA) collected from ozonolysis of α-pinene (viscous liquid/glass), and meso-erythritol (solid), as well as aerosol substances collected in authentic indoor environments. The effects of the phase of the SVSL, the relative humidity, and exposure light on the reactivity will be systematically investigated.

1IA.6

How Air Quality Metrics and Wireless Technology can Maximize the Energy Efficiency of HVAC in a Working Auditorium. ANNA LEAVEY, Yong Fu, Mo Sha, Andrew Kutta, Chenyang Lu, Wei-Ning Wang, Bill Drake, Yixin Chen, Pratim Biswas, *Washington University in St Louis*

HVAC is the single largest consumer of energy in commercial and residential buildings. Reducing its energy consumption without compromising occupants' comfort or indoor air quality would have environmental and financial benefits. This measurement study assesses the sources of indoor aerosols in a university auditorium, and evaluates whether a particle number metric could supplement the current CO_2 and temperature sensors in informing occupancy times and subsequent HVAC control. A wireless testbed consisting of a retrofitted wireless Condensation particle counter (CPC), 25 wireless temperature sensors, 2 HVAC-embedded temperature and CO_2 sensors, and a web camera was deployed in the working auditorium, to monitor the air quality, temperature, and occupancy of the room. The main objectives were to identify particle sources using the retrofitted CPC, map the temperature variability of the room and select the most optimally located sensors for HVAC control using clustering algorithms, and examine possible energy savings by operating the HVAC only during periods of occupancy using 1) calendar-based scheduling, and 2) air quality indicators, including a particle number metric, as proxies of occupancy. All air quality metrics increased with higher occupancy rates, although HVAC-modes changes were also identified as a source of particle numbers. Clustering analysis identified an alternative temperature sensor location for optimal HVAC control. Operating the HVAC using calendar-based scheduling resulted in energy savings of between 8 and 79%, increasing if occupancy events were scheduled close together. Finally, CO_2 was the strongest predictor of occupancy counts with an R^2 of 0.62 ($p < 0.001$) during simple regression analysis. Incorporating particle numbers and temperature improved estimates of occupancy only slightly ($R^2 = 0.67$), however incorporating a particle metric may enable the general air quality to be monitored, and identify when filters should be replaced.

1IA.7

Indoor and Outdoor Endotoxins at Santiago, Chile: Spring 2012 Results. HECTOR JORQUERA, Francisco Barraza, Gonzalo Valdivia, Lupita Montoya, *Pontificia Universidad Catolica de Chile*

Endotoxins are biopolymers belonging to the cell wall of Gram-negative bacteria and as such are present in indoor and outdoor environments as part of airborne particulate matter (PM); they are thought to induce inflammatory response to inhaled PM and have been found associated to asthma, lung inflammation and oxidative stress.

We carried out a simultaneous indoor and outdoor PM2.5 campaign at Santiago, Chile between mid-October and mid-December, 2012. We used Partisol 2000i samplers (Thermo Scientific, USA, 16.67 L/min) and TAS Minivol samplers (Airmetrics, Eugene OR, USA, 5 L/min) to sample outdoor and indoor PM2.5 for 24-h and 48-h integrated filter samples, respectively. Endotoxins in PM2.5 were measured following a kinetic chromogenic LAL assay. We measured a total of 44 households, including three socioeconomic statuses, and conducted a household survey as well.

Average endotoxin concentrations were 0.12 and 0.10 [EU/m^3] for indoor and outdoor samples, respectively. Indoor endotoxin concentrations showed no significant differences across socioeconomic status ($p=0.783$). Average indoor/outdoor ratios had a mean and standard deviation of 1.56 and 1.59, respectively. When we plot indoor against outdoor concentrations we find that roughly half of the households present indoor sources of endotoxins while the other half do not.

We analyzed the database to understand indoor endotoxin variability in terms of household features such as presence/absence of pets, moisture, ventilation, cleaning and cooking practices and the ratio of indoor to outdoor endotoxin concentration. The presence of household pets explained the largest I/O ratio of 12, but median endotoxin concentrations did not show a statistically significant difference between pets/no pets households ($p=0.563$). We also found that as household ventilation increases (measured by the time windows are kept opened) I/O ratios decrease, as expected.

1UA.1

Assessment of In-cabin Human Exposure to Ultrafine Particles under Different Conditions of Urban Traffic in Salvador, Bahia, Brazil. Egídio Guerreiro, Paulo Pinho, Márcio de Carvalho, Danilo Leão, João Marçal, José Róbson de Luna, Rodrigo Vieira, Lílian Guarieiro, Jailson de Andrade, ANTONIO MIGUEL, *University of California, Los Angeles*

In large urban centers commuters, are exposed to toxic ultrafine particles (UFP, aerodynamic diameters, dp<100 nm, and nanoparticles (NP, dp < 50 nm) under a variety of weather and traffic conditions. Limited information is currently available on commuter exposure to freshly emitted UFP and NP while driving on major roads and freeways. As commuters are spending more time on the road, it is important to know their exposure levels to harmful pollutants in microenvironments. The major goal of this study was to evaluate passenger in-cabin exposure to UFP under different traffic conditions in the urban area of Salvador, Bahia, Brazil. UFP number concentrations (100 nm nominal) were measured using a TSI model 3910 particle counter placed on the center of the back seat of a model year 2010 Toyota Hilux 3.0 light duty 4x4 diesel car in five sites, under different traffic conditions: (A) high traffic volume (HTV) and no building corridors; (B) HTV with high impact of marine spray; (C) low flow of vehicles; (D) HTV with building corridors; and (E), a Tunnel with HTV.

In-cabin UFP concentrations show that the commuters can be exposed to high concentrations of UFP in roads with both HTV, under low airflow conditions (sites D and E). As expected, with windows open, the highest 300nm particle concentrations were observed in site E (990 particles/cm3). With closed windows, the lowest concentration was observed in Site C (40 particles/cm3). Roads without building barriers favor particle dissipation resulting in lower number concentrations. Ambient temperature appeared to influence particle number concentrations, suggesting that passenger exposure to UFP may be higher under higher solar radiation conditions. Taken these data together, commuters are advised to close the vehicle’s windows while driving in places with high traffic and low road airflow in order to reduce their exposure to vehicle exhaust and resuspended air pollutants.

1UA.2

Assessing the Impact of Driving Pattern on Emission Factor Variability Using a Gasoline Direct Injection Light-duty Passenger Vehicle. NAOMI ZIMMERMAN, Jon M Wang, Cheol-Heon Jeong, Nathan Hilker, Kelly Sabaliauskas, Robert Healy, Greg J. Evans, *SOCAAR*, *University of Toronto*

Real-world vehicle emission factors (EFs) provide valuable insight into the impact of environmental factors, such as meteorology, driving patterns, and traffic conditions, on actual vehicle emissions; measurement of these environmental factors is not possible in laboratory studies. The variability of real-world EFs is an open question, particularly for near-road EF measurements where the environmental factors vary to a larger extent. Near-road EF measurements are distinct in that they can capture large numbers of vehicles and measure their emissions on a vehicle-by-vehicle basis, thus despite their variability they remain important contributors to the development of EFs for emission models and inventories.

To assess the impact of environmental factors on near-road EF variability, a light-duty 2013 Ford Focus SE sedan, equipped with a gasoline direct injection (GDI) engine, was driven past a near-road field sampling site located in downtown Toronto, Canada under a series of driving conditions, in early to mid-2014. Similar to diesel engines, GDI engines produce a strong particle signal, making them high emitting vehicles. Three driving conditions were assessed: 1) engine idle, 2) cruising at 40 km/h, and 3) hard acceleration to 50 km/h. The vehicle was equipped with a GPS logger to record precise vehicle location and speed. The high meteorological variation characteristic of seasonal changes in Toronto enabled measurements across a broad temperature spectrum.

As the vehicle drove past the field site, measurements of CO2, CO, NOx, black carbon, VOCs, and particle number concentration and size distribution were recorded and fuel-based emission factors were calculated. For each emission factor detected, wind speed, wind direction, and temperature were also recorded. Preliminary study findings indicate that near-road EF variability is minimized for engine idle or cruising conditions as compared to driving conditions involving acceleration or braking. The methodology and implications of this study will be discussed in this presentation.

1UA.3

Seasonal and Multi-Year Trends in Vehicle Emissions Measured in a Traffic Tunnel. ALBERT A. PRESTO, Xiang Li, Timothy Dallmann, *Carnegie Mellon University*

Even after multiple decades of regulation, emissions from motor vehicles remain a major source of urban air pollution. Thus a nearly constant need exists to characterize and better understand vehicle emissions and their changes over time. In recent years, several key regulatory changes and scientific advances have shifted traditional views of motor vehicle emissions. Notably, strict regulations for emissions of particulate matter (PM) and nitrogen oxides (NOx) from diesel engines are changing the characteristic emissions profile of diesel vehicles. Emissions of PM, NOx, and CO from gasoline-powered automobiles are also declining due to increasingly strict regulations.

In order to explore emissions from a current on-road vehicle fleet we measured the emissions of particulate (e.g., PM mass, OC, and EC) and gaseous pollutants (e.g., NOx, CO) from motor vehicles in a traffic tunnel in Pittsburgh, PA. Pollutant emissions data are reported as a function of the percentage of diesel fuel use in the tunnel, which allows for the estimation of separate emission factors for gasoline and diesel vehicles. Fuel- and fleet-averaged diesel emission factors are supplemented by measurements of emissions from plumes created by individual heavy-duty diesel vehicles. Measurements have been ongoing since January 2013 and are designed to capture seasonal and multi-year temporal trends in vehicle emissions. Seasonal trends are largely driven by changes in ambient temperature, while multi-year trends reflect the impact of turnover in the vehicle fleet.

Emissions of OC, EC, and NOx are 40-50% lower than similar measurements conducted at a nearby tunnel in 2001-2002. Initial results indicate that particulate OC emissions display slightly negative temperature dependence, with higher emissions at lower temperatures, while EC emissions are temperature independent. OC emissions data will be analyzed to determine if the temperature dependence is consistent with OC partitioning as predicted by measured volatility distributions of vehicle emissions.

1UA.4

Real-World Vehicle Emission Factors of Gaseous and Particle Phase Pollutants from High Time Resolution Near-Road Measurements.

JON M WANG, Cheol-Heon Jeong, Naomi Zimmerman, Nathan Hilker, Robert Healy, Greg J. Evans, *SOCAAR, University of Toronto*

Vehicles are an important contributor to outdoor urban air pollution. Exposure to traffic-related pollutants has been associated with negative impacts to human health and the environment. Emission factors (EFs) compiled from engine dynamometer studies are often used to model the impacts of vehicle emissions on air quality. However, dynamometer studies are limited, making it difficult to predict the variability of fleet emissions, especially for atypical heavy emitters. In order to better assess the representativeness of dynamometer-based EFs in real-world settings, EFs must be measured under ambient conditions for the in-use vehicle fleet.

The aim of this study is to apply near-road region measurements at a field site in downtown Toronto, Canada to calculate fuel-based EFs of passing vehicles for traffic-related pollutants. The selected pollutants and their respective instruments include ultrafine particles (FMPS 3091, TSI Inc), black carbon (PASS-3, DMT), volatile organic compounds (PTR-TOFMS 8000, Ionicon Analytik), and gaseous pollutants – NOx, CO, CO2 (42i, 48c, 410i, Thermo Scientific) all measured at high time resolution (0.5-1 Hz). The high time resolution allows for analysis of pollutant emissions on a plume-by-plume basis. Additionally, the climate in Toronto allows for comparison of EFs measured in vastly different seasons.

This study has provided EFs for both regulated and unregulated vehicle-related pollutants. The underlying methodology will be described along with associations of the EFs observed with local meteorology and vehicle classification (e.g. cars and trucks).

1UA.5

Characterization of Black Carbon and Polycyclic Aromatic Hydrocarbon Plume Events in Near-Source Microenvironments Using a Mobile Sampling Platform.

TIMOTHY DALLMANN, Peishi Gu, Yi Tan, Allen Robinson, Albert A. Presto, *Carnegie Mellon University*

In some urban microenvironments dominated by traffic or point source emissions, short time duration plume events spanning intervals ranging from seconds to tens of minutes can result in elevated air pollutant concentrations and disproportionately impact exposures for nearby populations. Central monitoring networks, generally designed to obtain hourly and daily average pollutant concentrations representative of a regulatory airshed, may not be well suited to assess these short term, localized events.

To explore the importance of source plume events, we conducted over 200 hours of sampling at 36 sites in Allegheny County, Pennsylvania in summer 2013 and winter 2013-2014 using a mobile measurement platform. Site selection was stratified according to three control variables: elevation, proximity to traffic, and proximity to point sources, allowing for investigation of a broad range of source influences. In-situ measurements of black carbon (BC) and particle-bound polycyclic aromatic hydrocarbons (PAH) were conducted using continuous instrumentation. Supporting measurements of gas phase species including nitrogen oxides, carbon dioxide (CO2), and volatile organic compounds were also made. Most instruments were operated with a time resolution of less than 10 seconds, allowing for the characterization of source related plume events.

Preliminary results indicate small numbers of plume events can heavily influence hourly average BC and PAH concentrations, with strong local source contributions particularly evident at sampling sites in close proximity to diesel sources (e.g. near roadways and rail lines). For example, intermittent plume events contributed greater than 80% of the total PAH measured at several high traffic sampling locations. In these cases, where PAH concentrations can vary over several orders of magnitude, hourly average concentrations do not provide an adequate representation of short term exposure conditions. Pollutant ratios (e.g. PAH/BC) and ratios of pollutants to CO2 for individual plume events provide further information on emission profiles for the various source types encountered.

1UA.6

Lead Impacts from General Aviation Airports: A Weight of Evidence Approach. STEPHEN FEINBERG, Jay Turner, *Washington University in St. Louis*

In 2008 the USEPA revised the National Ambient Air Quality Standard for lead (Pb). The more stringent standard has drawn attention to the need for refined emissions estimates and approaches to identify Pb concentration hot spots. Nationwide, piston engine aircraft are the single largest emission source of airborne Pb with emissions concentrated at general aviation (GA) airports. This study was performed to refine the Pb emission inventory methodology for piston engine aircraft activities at GA airports. Three one-month field campaigns were conducted at GA airports in Tulsa, OK, Denver, CO and Santa Monica, CA to collect airborne Pb data for model-to-monitor reconciliation. Measured Pb concentrations were compared to modeled airport impacts by performing dispersion modeling with the refined emissions inventory. This presentation focuses on analysis of the ambient particulate Pb measurements. $PM_{2.5}$ and total suspended particulate (TSP) samples were collected at multiple locations at each airport and analyzed for lead content by both inductively coupled plasma – mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). Contributions from the combustion of Pb-bearing aviation gasoline (avgas) were assessed using Pb/Bromine (Br) ratios and Pb isotopic composition. Pb and Br were highly correlated in samples predicted to have high impacts from avgas combustion. However, the Pb/Br ratios were lower than expected from either lead bromide or lead bromochloride. Soil and avgas samples were also analyzed for isotopic composition. Ambient samples collected at high impact sites had isotope ratios consistent with avgas while samples collected at low impact sites had ratios similar to soil or trending toward avgas. Isotope analysis of TSP samples from high impact sites were more similar to avgas than soil and did not trend towards the soil ratios with increasing coarse fraction Pb.

1UA.7

Highly-resolved Modeling of Emissions and Concentrations of Carbon Monoxide, Carbon Dioxide, Nitrogen Oxides, and Fine Particulate Matter in Salt Lake City, Utah. DANIEL MENDOZA, John Lin, Logan Mitchell, James Ehleringer, *University of Utah*

Accurate, high-resolution data on air pollutant emissions and concentrations are needed to understand human exposures and for policy purposes to manage pollutant sources. Quantification of uncertainties is also needed.

The work presented discusses an emissions inventory and concentration estimates for carbon monoxide (CO), carbon dioxide (CO2), nitrogen oxides (NOx) and fine particle (PM2.5) for the city of Salt Lake City, Utah. A comparison between measurement data and simulated concentrations from an atmospheric model (using inventory emissions), is also presented.

The emissions inventory for the criteria pollutants was constructed using the 2011 National Emissions Inventory (NEI). The spatial and temporal allocation methods from the Emission Modeling Clearinghouse data set are used to downscale the NEI data from annual and county-level resolution to hourly and 500m x 500m. Onroad mobile source emissions were estimated by combining a bottom-up emissions calculation approach for large roadway links within Salt Lake City with a top-down spatial allocation approach for other roadways. Vehicle activity data for road links were obtained from automatic traffic responder data and local sources. The emissions inventory for CO2 was obtained from the Hestia emissions data product at an hourly, building and road link resolution.

The AERMOD Gaussian plume dispersion model and the CALPUFF puff dispersion models were used to transport the resulting emissions and estimate air pollutant concentrations at an hourly 500m x 500m resolution. Modeled results were compared against measurements from a mobile lab traveling on pre-determined routes in the Salt Lake City area. The comparison between both approaches to concentration estimation highlights spatial locations and hours of high variability/uncertainty.

Results presented here will inform understanding of variability and uncertainty in emissions and concentrations in order to better inform future policy. This work will also facilitate the development of a systematic approach to incorporate measurement data and models to better inform estimates of pollutant concentrations.

2AC.1

Resolving Complex Hydrocarbon Mixtures Using Gas Chromatography Mass Spectrometry with Soft Ionization.

ARTHUR CHAN, Farhana Hoque, Aviv Amirav, *University of Toronto*

Emissions from petrogenic sources often contain many hydrocarbon isomers that are difficult to resolve, but understanding their molecular structure is crucial for predicting the atmospheric reactivities and aerosol formation from these sources. Recent developments in soft ionization mass spectrometry has allowed for classifying linear and branched alkanes, cycloalkanes, alkenes and aromatics, but the technique requires use of synchrotron radiation. In this work, we describe a new approach using a laboratory-based soft ionization technique to achieve the speciation. Using supersonic molecular beam for the coupling of GC and MS, electron impact ionization is carried out at low sample compounds internal temperatures, thereby enhancing their molecular ion signals and structurally informative high mass fragments. The molecular ion signal is shown to be constant at ~30% of the total ion count for n-alkanes ranging from C8 to C40, making it straightforward to quantify a wide range of volatilities. Using authentic standards, we are able to achieve more detailed understanding of molecular structures for more accurate atmospheric modeling. We are also able to lower the elution temperature of the GC column while maintaining isomer resolution. This allows us to study the composition of thermally labile compounds and high molecular weight compounds. Both of these types of compounds are prevalent in organic aerosols, but current techniques are unable to comprehensively speciate these compounds. This new approach is demonstrated on complex organic mixtures, such as diesel fuel and ambient organic aerosol samples.

2AC.2

Effects of Meteorological Conditions on the Formation of Secondary Organic Aerosol from Amine Precursors.

DEREK PRICE, Mary Kacarab, David R. Cocker III, Kathleen Purvis-Roberts, Philip Silva, *University of California, Riverside*

Ambient aerosol formation is influenced by meteorological properties such as temperature and relative humidity. Temperature, for example, has an effect on the gas to particle partitioning of amine salts. These salts are formed in areas with high agricultural and transportation emissions (e.g., San Joaquin Valley in central California). Daily temperatures in the San Joaquin Valley may fluctuate from 5^{o}C to 20^{o}C in winter and 20^{o}C to 40^{o}C in summer. The dual 90 m^3 indoor environmental chambers at UC-Riverside’s College of Engineering – Center for Environmental Research and Technology (UCR/CE-CERT) were designed to measure atmospheric processes at various ambient conditions. A set of well characterized environmental chamber experiments were conducted on three aliphatic amines. These amines consisted of trimethylamine, diethylamine, and butylamine. In these experiments, an amine was injected into the environmental chamber followed by an oxidant such as hydroxyl radical (OH) or nitrate radical (NO_3). The experiments were repeated at various static temperatures and temperature ramps ranging from 5^{o}C to 40^{o}C. The relative humidity was also varied from 0.5% to 40%. The chemical composition of the gas phase species was measured with a selected ion flow tube – mass spectrometer (SIFT-MS). A scanning mobility particle sizer (SMPS) was employed to measure the concentration and size distribution of the secondary organic aerosol produced. The chemical composition of the particle phase was measured with a high resolution – time of flight – aerosol mass spectrometer (HR-ToF-AMS).

2AC.3

Geraniol-trans (3,7-dimethylocta-2,6-dien-1-ol) Ozonolysis: Kinetics and Mechanism. TADEU LEONARDO SOARES E SILVA, *State University of Rio de Janeiro*

Emission of hydrocarbons in the atmosphere is largely dominated by biogenic sources, with methane, isoprene and terpenes having the highest source strengths. Biogenic emissions of volatile organic compounds (VOCs) play a major role in the atmospheric chemistry of rural and remote areas, exceeding by orders of magnitude those of the anthropogenic origin, with vegetation as the most important natural source of these compounds. Terpenoids represent the most abundant VOCs emitted by plants.

In this work, reactions from 3,7-dimethylocta-2,6-dien-1-ol (geraniol-trans) ozonolysis, are studied. The geraniol-trans is found in the essential oils of plants in Brazil, as oil-of-rose, palma rosa and citronella oil (Java type), and is probably present in the air, through emissions from these plants. It is, therefore, important for the understanding of the chemical phenomena occurring in atmospheres over rural regions of Brazil where the presence of this type of vegetation occurs. This compound is also a significant component of indoor cleaner emissions. The 6-methyl-5-hepten-2-one and 6-hydroxy-4-methyl-4-hexenal are atmospheric reaction products of the biogenic emitted geraniol-trans and linalool. Geraniol is a terpene emitted from orange blossoms and from certain pine trees in southern Europe.

A Density Functional Theory (DFT) study of the mechanisms from geraniol-trans ozonolysis, are presented. The geometries, energies, and harmonic vibrational frequencies of each stationary point were determined by B3LYP/6-31(d,p) and BH&HLYP/cc-pVDZ methods. According to the calculations, the ozonolysis reactions are initiated by the formation of Van der Waals (VDW) complexes to yield primary ozonides, which rapidly open to carbonyl oxide compounds. These carbonyl oxide compounds react to form dioxanes and hydroperoxides. The hydroperoxides reacts by isomerization to form stable products. Glyoxal and methyl-glyoxal have been identified as the final product from geraniol-trans ozonolysis. Our results are in good agreement with the experimental studies.

2AC.4

Photooxidation of Isoprene Epoxydiol (IEPOX)-Derived Secondary Organic Aerosol. KELVIN BATES, Tran Nguyen, Rebecca Schwantes, Xuan Zhang, Matthew Coggon, Richard Flagan, Brian Stoltz, Paul Wennberg, John Seinfeld, *Caltech*

Isoprene epoxydiol (IEPOX), a second-generation oxidation product of isoprene, has recently been identified as a key intermediate in the formation of secondary organic aerosol (SOA) from isoprene under low-NO conditions. Following its reactive uptake onto particles, IEPOX is typically converted to 2-methyltetrols or organosulfates by acid- or ammonium-catalyzed mechanisms. These low-volatility products are generally expected to remain in the particle phase, though their subsequent chemistry has not yet been explored. Using synthetic IEPOX and various inorganic seed particles, we have performed environmental chamber experiments to investigate the fate of IEPOX-derived SOA under exposure to photooxidation by OH radicals. Particle mass concentration and chemical composition were monitored by aerosol mass spectrometry, scanning mobility particle sizing, and liquid chromatography-mass spectrometry of filter samples, while concentrations of gas phase compounds were measured by CF_3O^- chemical ionization mass spectrometry. We will present results showing changes in both gas and particle phase composition during photooxidation, including their dependence on both seed particle composition and OH concentration. Preliminary data show that the photochemical loss of IEPOX-derived SOA mass may be an important consideration for predicting aerosol loading and gas phase oxidative chemistry in isoprene-rich environments.

2AC.5

SOA Formation from Photooxidation of Individual PAHs and Mixtures. 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 from spark and compression ignition engines, wood-burning, and cooking, and may be a major “missing” source of SOA. Individual PAHs SOA experiments such as naphthalene and methylnaphthalene were conducted at the UCR CE-CERT environmental chamber and compared to previous researchers. Measurements were made with a suite of instrumentation that includes a HR-ToF-AMS, VTDMA, and APM-SMPS to comprehensively understand the chemical composition characteristics, volatility and density of particles. Our results show that the SOA yield from PAHs is large and that the f44 and O/C increases with irradiation time. However, in the ambient atmosphere, there are numerous chemical compounds simultaneously reacting. Therefore, the sensitivity of SOA formation to varying HC mixtures is further explored. Serial mixtures of PAHs photooxidation experiments were conducted. Mixtures include naphthalene, 1-methylnapthalene, 2-methylnaphtalene with m-xylene, alpha-pinene, and/or the surrogate mixture used for the Carter O_3 reactivity scales. The mixture SOA yield was evaluated by combining the SOA yield of PAHs and the SOA yield of m-xylene or other select compounds. Preliminary results show that the SOA formation from m-xylene and naphthalene mixture photooxidation was found to be suppressed by m-xylene, and the volatility measured as volume remaining fraction (VRF) of the m-xylene and naphthalene mixture increases from 0.2 to 0.4, which indicates the volatility of mixture SOA is dominated by m-xylene SOA. We expect that adding gas-phase and SOA formation from PAHs into the PM-SAPRC will allow for more accurate prediction of SOA formation from the aromatic-PAH mixtures by accounting for changes in the gas-phase chemical reactivity created by mixing the precursors together.

2AC.6

Mass Spectral Observations of Submicron Aerosol Particles and Production of Secondary Organic Aerosol at an Anthropogenically Influenced Site during the Wet Season of GoAmazon2014. SUZANE SIMOES DE SA, Brett Palm, Pedro Campuzano-Jost, Douglas Day, Weiwei Hu, Matt Newburn, Joel Brito, Paulo Artaxo, Rodrigo A. F. Souza, Antonio O. Manzi, Jose-Luis Jimenez, Lizabeth Alexander, Scot Martin, *Harvard University*

As part of GoAmazon2014, a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) was deployed to characterize the composition, size, and spectral markers present in submicron atmospheric aerosol particles at a site downwind of Manaus, Brazil, in the central Amazon basin. The focus was on the influence of biogenic-anthropogenic interactions on the measured aerosol particles, especially as related to the formation of secondary organic aerosol (SOA). Through a combination of meteorology, emissions, and chemistry, the research site was affected by biogenic emissions from the tropical rainforest that were periodically mixed with urban outflow from the Manaus metropolitan area. Preliminary results from 1 February to 31 March 2014 show that for the wet season, the PM_1 mass concentration varied from 0.4 to 3.0 micro-g/m^3 (5 to 95 percentile). The composition was dominated by organic species (80%), and sulfate (13%). Most of the nitrate is estimated to be organic nitrates. The mass-diameter distribution of the particle population had a dominant mode between 300 and 400 nm (vacuum aerodynamic diameter, d_{va}). At times, a smaller mode at d_{va} between 100 and 150 nm was also present. Highly oxidized organic material was frequently observed, characterized by a dominant peak at m/z 44 that was on average 18% of the total organic mass spectrum. There was a diel trend in the elemental oxygen-to-carbon (O:C) ratio, starting from a typical value of 0.6 in the morning, peaking at 0.7 in the afternoon, and returning to 0.6 at night. The analysis of the results aims at delineating the anthropogenic impact on the measurements. Multivariate statistical analysis by positive-matrix factorization (PMF) is applied to the time series of high-resolution organic particle mass spectra. The factors and their loadings provide information on the relative and time-varying contributions of different sources and processes affecting the organic component of the aerosol particle phase.

2AC.7

Oxidation of Biodiesel Exhaust Particulate Matter with Ozone. JOHN KASUMBA, Britt Holmén, *University of Vermont*

Many recent studies have examined the oxidation of organic compounds in diesel exhaust particulate matter (PM) by ozone, particularly PAHs. However, very limited studies have investigated the ozone oxidation of biodiesel exhaust PM. Fatty acid methyl esters (FAMEs) are found in high abundance in biodiesel exhaust PM. The presence of these FAMEs in biodiesel exhaust PM can potentially alter the kinetics of the reactions between ozone and particle-phase PAHs. Here, we test the hypothesis that unsaturated FAMEs in biodiesel exhaust PM will be preferentially oxidized by ozone, an outcome that can consequently lead to longer atmospheric residence times for the PAHs, which are carcinogenic. In the present study, the kinetics of the reactions between ozone and PAHs in biodiesel exhaust PM (B20) were investigated.

An Armfield CM-12 automotive light duty diesel engine operated in a semi-transient drive cycle was used to generate particulate matter from B20 waste vegetable oil biodiesel. Teflon-coated fiber filters (FF) were used to sample the exhaust PM for gravimetric mass determination. Quarter inch punches were cut out from the filters and exposed to ozone (0.4 ppm) for 0, 1, 2, 4, 8, and 24 hours at room temperature and 50% relative humidity. Additionally, laboratory standards of FAMEs (commonly found in biodiesel) and PAHs were spiked on bare 1/4 inch FF punches and exposed to ozone for the same time periods and conditions. The PAHs and FAMEs in the biodiesel exhaust PM and spiked punches before and after exposure to ozone were analyzed using gas chromatography/mass spectrometry.

The reaction rates of the PAHs in the clean spiked filters, filters spiked with FAMES, and in the biodiesel exhaust PM filters will be discussed.

2AC.8

Brown Carbon Formation in Secondary Organic Aerosol from Heterogeneous Reactive Uptake of Isoprene Epoxydiols. Ying-Hsuan Lin, Sri Hapsari Budisulistiorini, Kevin Chu, RICHARD SIEJACK, Haofei Zhang, Zhenfa Zhang, Avram Gold, Jason Surratt, Kathryn Kautzman, *Towson University*

Isoprene is the most abundant non-methane hydrocarbon emitted into Earth's atmosphere and has been estimated to be a significant contributor to the global secondary organic aerosol (SOA) burden. Under low NOx conditions, isoprene is oxidized by hydroxyl radicals to predominantly yield gaseous isoprene epoxydiols (~70%) that reactively uptake onto preexisting sulfate aerosol to form SOA. We report on the formation of light-absorbing SOA (or brown carbon) from the dark, heterogeneous reactive uptake of trans-β isoprene epoxydiol (β-IEPOX) in the absence of oxidizers and nitrogen-containing compounds. Under dry and acidified sulfate seed aerosol conditions, SOA compounds are found to absorb in the visible and UV regions with average mass absorption coefficients of ~350 cm^2 g^{-1}. The formation of light-absorbing SOA is significantly reduced at greater relative humidities (~50%) and is absent under all neutral seed aerosol conditions. We chemically characterize the brown carbon using mass spectrometric techniques and FTIR. Data show the formation of light-absorbing SOA from isoprene epoxydiols is correlated with the formation of cis- and trans-3-methyltetrahydrofuran-3,4-diols, indicating their formation pathway is likely tied to the formation of brown carbon. Further chemical analysis suggests the presence of oligomeric unsaturated species act as chromophores.

2AC.9

Determining Extraction Efficiencies for the Trace Analysis of Organics in Airborne Particulate Matter. MORGAN DUNDON, Richard Siejack, Robert Ishakis, Kathryn Kautzman, *Towson University*

Chemical speciation of atmospheric aerosols is often accomplished through high-volume filter sampling whereby airborne particles are deposited on quartz or Teflon filters. The filters are extracted and subsequently analyzed by a variety of analytical techniques. The use of high-volume filtering sampling techniques thus provides a facile and common method for characterizing local atmospheric chemistries. There are two common strategies for extracting and analyzing high-volume filters, the first uses Soxhlet extraction and the second uses sonication. No work has been done to examine the relative efficiencies of the two extraction techniques. Our work to validate extraction methods examines extraction efficiencies for a range of organic and inorganic target compounds of both anthropogenic and biogenic origin. We have investigated extraction efficiencies over a range of solvents and with a variety of experimental parameters. Extraction efficiencies for aerosol tracer species extracted in methanol, dichloromethane, and 50-50 methanol-dichloromethane are determined by analysis of derivatized samples using Gas Chromatography-Mass Spectrometry (GC-MS). Extraction efficiencies for inorganic salts using Ion Chromatography (IC) have also been quantified.

2AC.10

Kinetics Modeling of the Functionalization and Fragmentation Mechanisms of Aerosol Oxidation. AARON WIEGEL, Kevin Wilson, William Hinsberg, Frances Houle, *Lawrence Berkeley National Laboratory*

While the heterogeneous oxidation of atmospheric organic aerosols influences their effects on climate, air quality, and visibility, a more detailed understanding of the chemical mechanisms in heterogeneous oxidation is crucial for improving models of their chemical evolution in the atmosphere. Previous experimental work in our lab has shown two general reaction pathways for organic aerosol upon oxidation: functionalization, which adds additional oxygen functional groups to the carbon skeleton, and fragmentation, which leads to C-C bond scission and lower molecular weight oxidized products. Furthermore, these pathways were also found to be dependent on molecular structure, with more branched or oxidized hydrocarbons undergoing more fragmentation than less branched or oxidized hydrocarbons. However, while the mechanisms of hydrocarbon oxidation have been studied extensively in the gas phase, to what extent the gas phase mechanisms of hydrocarbon oxidation can be reliably applied to heterogeneous or bulk oxidation in aerosol remains unclear.

To investigate the role of the condensed phase and molecular structure in the mechanism of heterogeneous organic aerosol oxidation, stochastic kinetics models are developed and compared to measurements of the products in the oxidation of hydrocarbons. Within the aerosol bulk, condensed phase rate coefficients and product branching ratios for peroxy reactions lead to different product distributions than those expected from gas phase peroxy reactions due to the presence of the liquid radical cage at the reaction site. As a result, tertiary alcohols and ketones were found to be the predominate products in the oxidation of squalane as observed in experiments. As the aerosol becomes further oxidized, beta-scission of alkoxy radicals with neighboring functional groups is the primary fragmentation pathway leading to lower volatility products. In conjunction with this fragmentation mechanism, elimination of CO2 from acyloxy radicals was also found to be an important reaction leading to further fragmentation.

2AC.11

Chemical Mechanisms of Atmospheric Aging of Secondary Organic Aerosol. PEIJUN TU, Murray Johnston, *University of Delaware*

Secondary organic aerosol (SOA) is produced by the oxidation of volatile organic compounds (VOC) in the atmosphere. The initial or “fresh” SOA produced from this reaction can undergo further oxidation over time. This “aged” SOA can have very different chemical and physical properties, which may influence its environmental impact. This work seeks to provide a molecular level understanding of SOA aging and its end products.

In this work, fresh SOA was generated in a flow tube reactor (FTR) by the reaction of ozone with biogenic VOC precursors (alpha-pinene, beta-pinene and limonene). The fresh SOA flowed into a photochemical reactor (PC) where it reacted with OH to simulate atmospheric aging. The hydroxyl radicals were created by ultraviolet irradiation of an ozone-water mixture. The mass concentration of aerosol exiting the PC was monitored with a Scanning Mobility Particle Sizer (SMPS). Chemical analysis of the aged SOA was performed by filter collection and analysis by Orbitrap MS.

Measurements of the mass concentration and chemical composition of SOA as it ages suggested that two types of processes occur: fragmentation (loss of SOA mass due to the production of small molecules such as CO2, H2CO, etc.) and functionalization (addition of functional groups such as carbonyls and acids). Fragmentation was indicated by both the loss of aerosol mass determined by SMPS and also the shift from higher m/z oligomers to lower m/z oligomers in the mass spectra upon aging. Functionalization was indicated by the appearance of new m/z ions in the aged SOA spectra that contained additional oxygen molecules. Based on high resolution mass spectra, hundreds of peaks were assigned molecular formulas. Current work involves the use of ESI-MS/MS to infer structural assignments and formation mechanisms.

2AC.12

Evaporation of and Water Uptake by Sub-10 Nano-meter Dimethylamine-Sulfuric Acid Nanoparticles. HUI OUYANG, Siqin He, Christopher Hogan Jr., *University of Minnesota*

The physical and chemical properties of dimethylamine-sulfuric acid (DMAS) nanoparticles are needed to better understand whether such particles would remain stable, dissociate, or grow under atmospherically relevant conditions. Particularly important are the properties of sub 10 nano-meter particles, as newly formed particles in many environments may be composed primarily of sulfuric acid and amines. In this study, the densities, vapor pressure, and extent of water uptake by DMAS nanoparticles were studied using combinations of differential mobility analysis, mass spectrometry, and atmospheric pressure drift tube mobility spectrometry. Specifically we used a parallel plate differential mobility analyzer coupled to a time flight mass spectrometer (DMA-MS) to determine the collision cross section for mass identified, sub 4 nm clusters, generated via an electrospray. The mass-collision cross section relationship was used to infer the density of DMAS nanoparticles with variable percent dimethylamine and variable percent sulfuric acid. The average density of DMAS is found to be ~1574kg/m^3 and roughly independent of nanoparticle size. Subsequently, tandem differential mobility analysis (with two modest to high resolution half-mini DMAs) with a furnace between the DMAs was used to monitor the size change of nanoparticles due to evaporation at four different temperatures. Size-dependent partial pressure-temperature values were then inverted from results. At room temperature, the partial pressure differs from the vapor pressure reported normally for bulk DMAS, and is of the order 10^{-5} Pa near room temperature, indicative that the Kelvin effect enhances DMAS nanoparticle vapor pressure. Finally, a new developed drift-tube mobility analyzer coupled with a half-mini DMA upstream was used to examine water absorption by DMAS in size range of 2.8~7.5nm. Cases with different relative humidity up to 50% were examined. Significant growth due to water uptake is observed for RH > 20%, though less growth for smaller sized particles.

2AC.13

OH- Initiated Heterogeneous Oxidation of Saturated Organic Aerosols in the Presence of SO2: Uptake Kinetics and Product Identification. NICOLE K. RICHARDS-HENDERSON, Michael Ward, Allen H. Goldstein, Kevin Wilson, *Lawrence Berkeley National Laboratory*

Gas-phase oxidation mechanisms for organic gases are often used as a starting point to understand heterogeneous oxidation. The reaction of a simple alkane hydrocarbon by OH proceeds through hydrogen abstraction and under ambient conditions leads to peroxy radical (RO2) formation. RO2 can further react to form: (1) smaller molecular weight products (i.e. fragmentation) via alkoxy radical formation and dissociation and/or (2) higher molecular weight products with oxygenated functional groups (i.e. functionalization). The ability to perturb these two pathways (functionalization vs. fragmentation) is critical for understanding the detailed reaction mechanism that control atmospheric aging chemistry of particles. At high temperatures the presence of sulfur dioxide (SO2) during organic-OH gas-phase oxidation enhances the fragmentation pathway leading to increased alkoxy formation. It is unknown if a comparative affect occurs at room temperature during a heterogeneous reaction. We used the heterogeneous reaction of OH radicals with sub-micron squalane particles in the presence and absence of SO2 as a model system to explore changes in individual mechanistic pathways. Detailed kinetic measurements were made in a flow tube reactor using a vacuum ultraviolet (VUV) photoionization aerosol mass spectrometer and oxidation products are identified from samples collected on quartz filters using thermal desorption two-dimensional chromatographic separation and ionization by either VUV (10.5 eV) or electron impact (70 eV), with detection by high resolution time of flight mass spectrometry (GCxGC-VUV/EI-HRTOFMS). In the presence of SO2 the yields of alcohols were enhanced compared to without SO2, suggesting that the alkoxy formation pathway was dominant. The results from this work will provide an experimentally-confirmed kinetic framework that could be used to model atmospheric aging mechanisms.

2AC.14

Secondary Organic Aerosol from Aqueous Reactions of Green Leaf Volatiles with Organic Triplet Excited States and Singlet Molecular Oxygen. NICOLE K. RICHARDS-HENDERSON, Andrew Pham, Kalliat Valsaraj, Cort Anastasio, *University of California, Davis*

Vegetation emits volatile oxygenated hydrocarbons - the green leaf volatiles (GLVs) – which are formed from the biochemical conversion of linoleic and linolenic acids within plant cells. Stress or damage to vegetation can significantly elevate emission fluxes of these compounds, some of which are fairly water soluble. Aqueous-phase reactions of the GLVs with photochemically generated oxidants – such as hydroxyl radical (OH), singlet oxygen (1O2) and excited triplet states of organic compounds (3C*) – might then form low-volatility products that can act as secondary organic aerosol (SOA). In order to determine if GLVs can be a significant source of secondary organic carbon in fogwater, studies of GLVs in laboratory solutions are needed to elucidate the oxidation kinetics and the corresponding SOA mass yields.

In this study we are determining the second-order rate constants, and SOA mass yields, for five GLVs (cis-3-hexen-1-ol, cis-3-hexenylacetate, methyl salicylate, methyl jasmonate, and 2-methyl-3-butene-2-ol) reacting with 1O2 and 3C*. Experiments are performed at relevant fog water pHs, temperatures, and oxidant concentrations. Rate constants are determined using a relative rate approach in which the decay of GLVs and reference compounds are monitored as function of time by HPLC. SOA mass yields are measured gravimetrically from laboratory solutions containing atmospherically relevant concentrations of photooxidants and GLVs, and irradiated with simulated sunlight. We will use our results to assess the potential contribution of aqueous GLV reactions as a source of SOA in cloudy or foggy atmospheres.

2AE.1

Characterization of Aerosols Generated from Stainless Steel Plasma Cutting.

JUN WANG, *University of Oklahoma Health Sciences Center*

Plasma cutting is a common metal machining process using an electric arc to cut metals. Metal is melted in the process by the plasma generated from inert gas/air out of the nozzle. Due to the extremely high temperature, components in the metal being cut may vaporize and transform to aerosols. Stainless steel is an alloy contains toxic metal such as chromium, nickel, and manganese. The health effects of inhaling stainless steel plasma cutting fume may include inflammatory, carcinogenesis, and neurological disorder. The objective of this study is to investigate the physical and chemical characteristics of aerosols emitted from stainless steel plasma cutting process. A 30-inch conical chamber was built to confine the metal fume generated by plasma cutting. A high capacity plasma cutter was used to cut 3/16 inch grade 316 stainless steel plates inside the chamber. The metal fume was collected on glass fibers filters using a high flow pump mounted on top of the chamber. Fume generation rate (milligram fume per seconds of arc time) was gravimetrically measured using a microbalance. The filters were cut to halves. Hexavalent chromium content in the fume was extracted from one half filter and analyzed by an ion chromatograph following NIOSH method 7605. The other half will be acid digested and the total metal concentration in the fume will be measured using an inductively coupled plasma atomic emission spectroscopy following NIOSH method 7300. Particle size distribution of the aerosols inside the chamber was measured by a scanning mobility particle sizer and an aerodynamic particle sizer over the range of nanometer to micron. Particle morphology will be examined by a scanning electron microscope. The full results will be reported at the conference. The study will help better understand the workers' occupational exposure in metal industry.

2AE.2

Nanoparticle Measurements for the Breathing Zone Model.

JEROME GILBERRY, Meaghan McGrath, Jonathan Thornburg, *RTI International*

Human inhalation exposure to nanoparticles may occur in occupational environments during raw nanomaterial production or during product manufacturing. The consumer may be exposed to the nanomaterial in its original nanosize during the use of the product. Exposure assessment strategies, including surveys or direct measurements, are necessary but can quickly become complex and expensive. Exposure modeling that predicts the dispersion and transformation of nanoparticles produced in occupational or consumer environments is a middle tier solution to exposure assessment. A model can bracket the range of potential exposures to inform the user if exposure measurements are necessary to adequately assess risk. RTI developed the Breathing Zone (BZ) model to predict aerosol inhalation exposure to contaminants; however it does not include equations to account for diffusion and coagulation, phenomena specifically applicable to nanoparticles.

The goal of this project was to experimentally validate equations for input to the BZ model for inhalation exposure. SiO_2 aerosol nanoparticles were generated in a controlled environmental chamber. The particle concentration and size distribution was measured at various distances from the aerosol source and under quiescent, convective, and thermal conditions. Under quiescent conditions, the distribution was bimodal near the nanoparticle generation source, an indication of coagulation. The concentration decreased and coagulation was not observed with increasing distance. Under convection conditions, the concentration was steadier with increased distance from the generation source and there was no evidence of coagulation. With a thermal body in the generation and sampling area, coagulation was substantial close to the source and remained observable at longer distances. It is apparent that nanoparticle coagulation occurred rapidly after generation as it was not possible to measure particles in a pre-coagulation state with the instrumentation used.

2AE.3

Release of Airborne Particles from Nanotechnology-enabled Clothing. LEONARDO CALDERÓN, Letao Yang, Kibum Lee, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

The use of nanotechnology in consumer products is increasing, but there are concerns regarding inhalation exposure and environmental release of the incorporated nanoparticles during product use. As part of our continuing investigation of risks associated with nanotechnology-enabled consumer products, we analyzed potential release of particles from nanotechnology-enabled clothing, with particular focus on clothing with silver nanoparticles.

The TEM as well as various analytical methods were used to determine the presence and quantity of silver. The potential release of particles into the air during clothing wear was simulated by rubbing a clothing item onto itself in a specially-designed glove-box and measuring the released particle number and concentration. The effect of friction forces on the particle release was examined by using a rotary abraser (Taber Industries Inc.) with abrading wheels of different coarseness. These measurements were performed with brand new items as well as items that have been washed multiple times to simulate their natural wear and tear. The released particles were measured using a Scanning Mobility Particle Sizer (TSI Inc.) and an Aerodynamic Particle Sizer (TSI Inc.).

TEM analysis showed the presence of nanoparticles in most items labeled as having silver nanoparticles, but their size and abundance depended on a particular product. Mechanical friction of the clothing particles (both by hand and by an abraser) resulted in the release of nano-sized particles as well as submicron and super-micron agglomerates. The mode of the released particles by number was in the 1-2 micron range. The release of particles intensified, in some case by a factor of ~10, once the clothing items were washed due to the loss of integrity in product matrix.

This ongoing study is showing that the use of investigated nanotechnology-enabled clothing could result in the release of nanoparticles into the air, potentially leading to particle inhalation exposure.

2AP.2

Evolution of Capacitance for Agglomerated Nanoparticles during Sintering. LEO N.Y. CAO, Jing Wang, Heinz Fissan, Sotiris E. Pratsinis, Max L. Eggersdorfer, David Y. H. Pui, *University of Minnesota*

Electrical capacitance of aerosol particles is an important property for classification of particles by electrical mobility, precipitation of particles in electrical fields, measurements of morphological parameters of particles by their charging properties, etc. Usually, a minimum potential energy method developed by Brown & Hemingway (1995) is used to calculate the electrical capacitance developed for agglomerates composed of spherical PPs (primary particles). By discretizing a particle, representing it by finite spherical elements in different sizes only on its surface, we extended this method to particles of arbitrary shapes in this work. We applied the method to compute the capacitance of diffusion limited cluster-cluster agglomerates (DLCA) and their spatial charge distribution and found that the capacitance of DLCA is a function of mobility diameter which is measurable and nearly independent of PP diameter. Based on the obtained capacitance, the modeled particle charge for DLCA in continuum regime of charging agrees well with experimental results. We also simulated DLCA's sintering processes from fractal-like expressed by equivalent PP-diameter and number of PPs to compact structure and investigated the change in their capacitance. The results demonstrated strong effect of particle morphology on the capacitance, with the capacitance decreasing as the structure became more compact and reaching about 40% of the loose agglomerate value when an agglomerate of 128 PPs was coalesced to a sphere.

2AP.3

Gravity-induced Trapping and Aerogelation of Nanoparticles in Flame Reactors. RAJAN K. CHAKRABARTY, Igor Novosselov, Nicholas Beres, Hans Moosmuller, Chris Sorensen, Christopher Stipe, *Desert Research Institute*

Aerogels are volume spanning, semirigid networks of solid nanoparticles (NPs). Owing to their unique material properties such as ultralow density and high surface area, these mesoporous materials have found extensive applications ranging from catching space dusts to purifying air and water supplies. However, aerogel synthesis via the sol-gel process is non-continuous and requires supercritical point drying, hence is time-consuming and expensive. This has prevented their mass production and widespread application. Cost-effective and continuous synthesis routes using gas-phase flame aerosol reactors (FARs), which have been widely adopted by industries for production of nanostructured materials, are yet to be demonstrated as viable options for producing gels. The buoyancy-assisted convection of upward rising (+g) flames in these reactors has prevented achieving sustained high, cluster-dense NP volume fractions fv and greater than millisecond residence time tres as needed for gel synthesis. Here, we report the first experimental realization of continuous aerogel production using a FAR by operating it in negative gravity (-g; up-side-down configuration). Buoyancy opposes the fuel and air flow forces in –g, which eliminates convectional outflow of NPs from the flame and traps them in a distinctive non-tipping, flicker-free, cylindrical flame body, where they grow to millimeter-size aerogel particles and gravitationally fall out. Computational fluid dynamics simulations show that a closed-loop recirculation zone–a deeply metastable state–is set up in the flame wherein NPs experience cluster-dense fv and very long tres. These conditions reduce the time to gel by ≈106 s, compared to +g flames, and facilitate continuous gelation on a millisecond time scale. Our results open up opportunities for continuous and catalyst-free synthesis of a wide variety of aerogels on an industrial scale.

2AP.4

The Crossover from Spherical Particle Scattering to Circular Aperture Diffraction in the Limit of Vary Large Spheres. WILLIAM HEINSON, Chris Sorensen, Amit Chakrabarti, *Kansas State University*

Using the Mie solutions to light scattering for a sphere and applying Q-space analysis, we look at how the scattered intensity evolves from being the square of the Fourier transform of a sphere at phase shift parameter of zero (small, low refractive particles) to the square of the Fourier transform of a circular aperture as the phase shift parameter approaches infinity. We find that as the phase shift parameter, rho, increases, different power law regimes develop. At qR<< rho a power law regime with exponent of -3 is present due to circular aperture diffraction. Then the intensity flattens out until qR=rho, after which a power law regime with exponent of -4 at qR>rho follows.

2AP.5

Q-space Analysis of Light Scattering by Gaussian Random Spheres. JUSTIN MAUGHAN, William Heinson, Amit Chakrabarti, Chris Sorensen, *Kansas State University*

The majority of previous work done with light scattering has been analyzed by plotting the scattered intensity vs. the scattering angle. Q-space analysis, however, examines the scattered intensity as a function of q, the scattering wave vector, or the dimensionless quantity qR, where R is the equivalent radius of the scatterer. When analyzed in Q-space, power law functionalities are found that can be used to describe quantitatively a wide variety of particle shapes. Here we study Q-space analysis applied to scattering from Gaussian Random Spheres (GRS). GRS are described by three parameters, a, the mean radius, nu, the power law exponential, and sigma, the standard deviation of the radii. A dipole dipole approximation (DDA) was used to calculate the scattered light from GRS over a range of size parameters, relative indices of refraction, and sigma. When analyzed in Q-space, the light scattering from GRS exhibit power laws similar to those that have been found from a variety of other shapes. The power law exponents are a function of the phase shift parameter rho.

2AP.6

Characterization of Particle Resuspension from Surfaces. BABAK NASR, Suresh Dhaniyala, Andrea R. Ferro, Goodarz Ahmadi, Sari Paikoff, *Clarkson University*

An emergent threat to human health is the airborne particulate release of chemical/biological agents. The initial direct exposure to these airborne particles is limited to the short time duration right after the agent is released and until it is sedimented out. A longer-term, indirect exposure is, however, possible when these particles get resuspended due to natural or anthropogenic activities. The resuspension rate of particles from surfaces depends on the properties of the particles and the surface and the operating conditions. There are a number of experimental studies on particle resuspension but analysis and comparison of their results are complicated by inconsistency in the use of test particles, surface properties, and operating conditions. In addition, researchers use a range of different measures to characterize resuspension, further complicating inter-comparison efforts. In this study, we assimilated data from a wide range of fundamental particle resuspension studies and conducted a parametric analysis to establish the dependence of particle resuspension rate on different test conditions. To further address the challenge of understanding the dependence of particle resuspension on different parameters, we developed a dynamical graphical-user-interface (GUI) system for users to visualize and analyze the data. In our presentation, we will provide details of GUI system and its capabilities and describe the results obtained from our parametric analysis of published data.

2AP.8

Growth of Small Molecular Clusters: Comparison of Growth Rates Determined from Cluster Appearance Times and Collision–Evaporation Fluxes. Tinja Olenius, Ilona Riipinen, Katrianne Lehtipalo, HANNA VEHKAMÄKI, *University of Helsinki*

Particle growth rate is a well-established quantity used to characterize new particle formation events in the atmosphere, and to assess the probability that freshly formed particles survive to larger sizes before being scavenged. At present, instrumental development enables the detection of molecular clusters down to a mobility diameter of approximately 1 nm. Consequently, measured cluster concentrations have been recently utilized to extract cluster growth rates based on the appearance times of different cluster sizes. The appearance time is defined as the time at which the concentration of a certain size reaches 50% of its maximum value. On the other hand, it is not clear if the apparent growth rates determined from the appearance times coincide with the effective growth rates corresponding to the molecular fluxes between the clusters. In this work, we simulate the time evolution of a population of sub-3 nm molecular clusters and determine cluster growth rates (1) with the appearance time method, and (2) from the collision–evaporation fluxes between subsequent sizes. For simplicity, we consider a model substance with an evaporation profile corresponding to classical liquid droplet model and a situation where the growth occurs solely via monomer additions. We find that there may be significant differences between the growth rates determined with the two approaches, especially for the smallest clusters that have the highest evaporation rates. The appearance time –based growth rates are found to be generally higher than the flux-equivalent growth rates. Both quantities also depend qualitatively on ambient conditions, such as the magnitude of an external sink and the time evolution of the vapor monomer concentration. These aspects should be considered when analysing growth rates deduced from cluster measurements.

2AP.9

Alignment of Aerosolized Glass Fibers by an Applied Electric Field. Bon Ki Ku, C.S. Lauber, G. J. DEYE, Leonid Turkevich, *NIOSH*

Dielectrophoretic alignment is the presumed physical basis for length separation of fibers as effected in the Baron Fiber Classifier. In this study, we have investigated directly the alignment of glass fibers in an electric field. Glass fibers are aerosolized by vortex shaking; the aerosol passes through a cylindrical (asbestos sampling) cassette and is collected on an MCE filter. The cassette is outfitted with a parallel plate capacitor, so that the aerosol flows in the gap between and parallel to the plates (i.e. perpendicular to the electric field). The collected fibers are strongly oriented parallel to the imposed electric field. The angular orientation distribution is measured as a function of aerosol humidity and charge state of the fibers: i) as aerosolized, ii) Boltzmann distribution of neutralized fibers, iii) ESP neutralized fibers. The changes in the angular distribution with aerosol conditions suggest possible microscopic mechanisms responsible for the fiber alignment.

2AQ.1

Long-Range Transport of Agricultural Smoke to Houston, TX during September 2013: Effects on Aerosol Optical Depths. ANDREAS BEYERSDORF, Sharon P. Burton, Gao Chen, Jack Lin, Robert Martin, Richard Moore, Athanasios Nenes, Kenneth Thornhill, Edward Winstead, Luke Ziemba, Bruce Anderson, *NASA Langley Research Center*

The ability to predict ground-level aerosol loadings from satellite measurements is essential to guiding future air quality policy. This relationship is hindered by the presence of lofted layers detached from surface conditions. During the DISCOVER-AQ project in Houston, Texas (September 2013), lofted aerosol layers originating from agricultural fires in the Mississippi River Valley were measured by both in situ instrumentation and airborne High Spectral-Resolution LIDAR (HSRL). These elevated aerosols contributed up to 80% of the aerosol optical depths (AODs) and thus estimation of ground-level PM2.5 from AOD was not possible. These aerosol were considerably aged with higher single scattering albedos and water-uptake potential (f(RH)) than fresh agricultural fires measured during both the DISCOVER-AQ and SEAC4RS projects due to the formation of secondary aerosols. In addition to measurements during DISCOVER-AQ, historic long-term measurements of AOD (from AERONET) and PM2.5 (from ground-based monitoring sites) will be examined to determine the frequency of these long-range transport events.

2AQ.2

The Impact of Emissions from Mobile Sources and Biomass Burning on Ambient PM2.5 EC and OC in the SEARCH Network, 1999 - 2013. CHARLES BLANCHARD, George Hidy, *Envair*

Haze in the southeastern US is widely identified with anthropogenic pollution aerosol superimposed on a background of secondary organic aerosol (SOA) from oxidation of isoprene and other biogenic volatile organic compounds. Long-term measurements obtained from the Southeastern Aerosol Research and Characterization (SEARCH) network of urban and rural sites between 1999 and 2013 offer additional information on the contributions of anthropogenic emissions to observed organic aerosol concentrations and trends. The SEARCH measurements of trace gases and aerosols document important changes in air chemistry resulting from reductions of air pollutant emissions in the region. Anthropogenic emissions of sulfur dioxide (SO2), nitrogen oxides (NOx = NO + NO2), volatile organic compounds (VOC), carbon monoxide (CO), and motor-vehicle PM2.5 each decreased by approximately a factor of two in the southeastern U.S. between 1999 and 2013. During the same period, all eight sites (four urban, four non-urban) of the SEARCH network exhibited declining ambient concentrations of primary and secondary air pollutants. SEARCH ambient trends in SO2, NOy, CO, NMOC, EC, OC, SO4, and particulate NO3 tracked same-pollutant or precursor emission trends. The SEARCH data show that OC and EC emissions from biomass burning and mobile-source exhaust are major (>50% combined) contributors to particle carbon both locally and regionally in the Southeast. This result derives from different analyses that include (a) chemical mass balance receptor modeling, accounting for transportation emissions and open burning, (b) statistical investigation of combined EC-OC trends and emissions, (c) integration of thermal-desorption measurements of non-polar OC compounds with EC and OC observations, (d) application of non-soil potassium as a tracer of biomass burning, and (e) evaluation of modern vs. fossil carbon concentrations and source emissions. The findings provide an important perspective on the role of primary particle emissions compared with SOA production processes.

2AQ.3

The Southeastern Center for Air Pollution and Epidemiology: Results from the Measurement Campaign. LAURA KING, Hongyu Guo, Ting Fang, Vishal Verma, Eric Edgerton, Armistead Russell, Rodney Weber, *Georgia Institute of Technology*

The Southeastern Center for Air Pollution and Epidemiology (SCAPE) is an EPA-funded Clean Air Research Center between the Rollins School of Public Health at Emory University and the schools of Civil and Environmental Engineering and Earth and Atmospheric Sciences at the Georgia Institute of Technology. SCAPE examines air quality and its health effects through a measurement campaign spanning urban and near-road sites in Atlanta, GA, Birmingham, Al and East St. Louis, IL, as well as rural background sites in Yorkville, GA and Centreville, AL.

Measurements were made on a continuous or semi-continuous basis of particle phase water soluble organic carbon (WSOC), brown carbon (BrnC), black carbon (BC), elemental carbon (EC), organic carbon (OC), ozone, NO, NO2, and PM2.5 mass. Measurements also included 23 hour filter based samples of soluble anions and cations, water soluble metals, elemental carbon, organic carbon, water and methanol soluble brown carbon, and oxidative potential. These measurements were made with pairs of instruments, in which one set of instruments was permanently located at a fixed urban background site in Atlanta, GA while the other set was installed in a trailer which was moved monthly between the other sites.

Measurements were made from May 2011 to September 2013 at seven different sites, rotating on a monthly basis. Results from the measurement phase of this study show regional, seasonal and diurnal trends in measured species as well as direct comparisons between the base site in Atlanta, Georgia and the other locations. These measurements will be used in epidemiological modeling as part of SCAPE to assess the health risks presented by exposure to air pollution mixtures.

This research was made possible by USEPA STAR grant RD83479901.

2AQ.4

Single Particle Diversity and Its Impact on Heterogeneous Reactivity during the SOAS Field Campaign. ANDREW AULT, Amy Bondy, Rebecca Craig, Rachel O'Brien, Ryan Moffet, Bingbing Wang, Alexander Laskin, Mary Gilles, Kerri Pratt, Victor Nhliziyo, Steve Bertman, Paul Shepson, *University of Michigan*

Atmospheric aerosols have contributed to a cooling trend in the southeast United States over the last century, but a great deal of uncertainty remains regarding how individual particle composition and reactivity impact direct scattering and absorption of solar radiation. Samples were collected at the Centreville, Alabama site during the Southern Oxidant and Aerosol Study (SOAS) from June-July 2013. Single particle measurements using an array of microscopy and spectroscopy techniques were used to identify sources and monitor how particles were modified by condensation, coagulation, and heterogeneous reactions. These analyses provide detailed information on particle size, morphology, internal structure, elemental composition, and the functional groups present. A high degree of variability was observed between and within populations of particles from different sources (secondary organic aerosol (SOA), soot, sea spray, mineral dust, etc.). Particles with a thick SOA coating had unique features related to phase and secondary uptake that led to a complex internal structure. Sea spray particles were identified via ratios of inorganic ions and were present at greater concentrations than expected for the inland Centreville site, with interesting secondary chemistry involving nitrate and sulfate formation. The secondary reactions and internal structure of particles in the Southeast U.S. have the potential to play an important role in water uptake, scattering, absorption, and cloud nucleation properties of the particles, which significant impact climate.

2AQ.5

Radiocarbon Measurements of PM2.5 Total Carbon and Elemental Carbon from Centreville, AL during the SOAS Field Study. ERIC EDGERTON, Yanlin Zhang, Soenke Szidat, Andre Prévôt, Stephanie Shaw, John Jansen, Karsten Baumann, Charles Blanchard, *Atmospheric Research & Analysis*

Radiocarbon (14C) analysis is a widely accepted technique for elucidating sources of carbon in aerosols. Recent advances have made it possible to analyze the 14C content of both total carbon (TC) and elemental carbon (EC) in aerosol samples, and, hence, calculate 14C for organic carbon (OC) by difference. Since EC is invariably produced by incomplete combustion processes, 14C data for EC permits new insights into relative contributions of mobile sources and biomass burning. This presentation will address 14C measurements on 23-hour duration PM2.5 samples collected during the SOAS campaign in Centreville, AL.

Samples for off-line chemical analysis were collected at Centreville, AL from June 1 to July 16, 2013. Twenty-three hour air samples (starting at 0800 each day) were collected on 8”x 10” pre-fired quartz (QMA) filters using a Tisch Environmental 6070 high-volume sampler equipped with a PM2.5 inlet. Samples were analyzed for 14C in TC and EC fractions following the procedure of Zhang et al., 2012. 14C(TC) is measured on carbon from an intact filter, while 14C(EC) is measured after aqueous extraction and thermal combustion in several steps for removal of OC.

Preliminary analysis of two 3-day composite samples collected early and late in the SOAS campaign show intriguingly high Fmodern for EC (i.e., 0.74 and 0.69). These values imply that roughly two-thirds of EC comes from biomass burning (BB). Given that BB produces much more OC than EC, these results also suggest non-negligible BB contributions to OC concentrations. Results from samples covering the entire campaign will be presented and BB contributions to TC, EC and OC will be discussed.

2AQ.6

Chemical Characterization of Atmospheric Fine Aerosol at the Jefferson Street, Atlanta, GA Using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM): Results from Winter, Spring and Summer 2014. WERUKA RATTANAVARAHA, Sri Hapsari Budisulistiorini, Philip Croteau, Karsten Baumann, Eric Edgerton, Manjula Canagaratna, John Jayne, Douglas Worsnop, Stephanie Shaw, Jason Surratt, *University of North Carolina at Chapel Hill*

Atmospheric fine aerosol (particulate matter, PM2.5) is associated with adverse effects on human health was well as on air quality and climate change. In order to understand the formation, sources and behavior of ambient PM2.5, long-term continuous chemical characterization is essential, especially to aid in the development of effective control strategies. In this study, the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) was redeployed at the Jefferson Street (JST) site in Atlanta, GA on February 08th, 2014 after sampling at the Look Rock Mountain site in TN during 2013 in order to continuous chemically characterize non-refractory PM with aerodynamic diameter less than or equal to 1 micro-meter (NR-PM1). The JST site is one of the research sites of the Southeastern Aerosol Research and Characterization (SEARCH) network that is equipped with a suite of collocated gas, particle, and meteorological measurements. In addition to the collocated SEARCH measurements, high-volume filter samplers were periodically operated to collect PM2.5 for subsequent off-line chemical analyses of organic aerosol constituents in order to compare with the ACSM data. The dataset was analyzed separately by season: winter, spring and summer. Positive matrix factorization (PMF) was applied to the organic mass spectra measured by the ACSM in order to resolve potential sources. The preliminary results showed that organic aerosol dominated the major portion of atmospheric aerosol in winter (58%) and spring (62%). By applying PMF to characterize organic aerosols, three potential factors were identified in both winter and spring: hydrocarbon-like organic aerosol (HOA), low-volatility oxygenated organic aerosol (LV-OOA) and semi-volatile oxygenated organic aerosol (SV-OOA). These preliminary PMF results will be placed into context against JST collocated measurements and OA tracers measured from filters using off-line gas and liquid chromatographic methods both interfaced to mass spectrometry.

2BB.2

Quantifying Personal Exposures to Biomass Cookstove Emissions using RTI International's MicroPEM™ Technology. RYAN CHARTIER, Charles Rodes, J. Randall Newsome, James Carlson, Samual DeFilipp, Seung-Hyun Cho, Jonathan Thornburg, *RTI International*

The RTI MicroPEM personal exposure monitor (v3.2) was used to assess personal and indoor exposures to cookstove particulate matter (PM2.5) during biomass cookstove studies in Sri Lanka and Kenya in 2012. The MicroPEM measures real-time mass concentrations while simultaneously collecting an integrated PM sample on an internal referee filter. The on-board triaxial accelerometer provides real-time wearing compliance validation and participant activity levels that can be used to estimate ventilation rates and inhaled PM dose. The robustness of the device, low participant burden (< 240g), and customizable settings make the MicroPEM suitable for deployment across studies with a wide range of participant ages and PM source strengths. MicroPEMs were deployed in 53 Sri Lankan and 12 Kenyan households for 48-hour personal and indoor sampling periods. The Sri Lanka field study focused on quantifying personal exposures in homes different stove (3-stone or Anagi) and chimney combinations (chimney or no chimney), while deployment in Kenya was for a subset of homes participating in a stove intervention study. In both study settings local field staff were successfully trained and relied upon to setup, deploy, collect, and service the MicroPEMs, leading to impressive data capture rates of >97.5% in Sri Lanka and >92% in Kenya. Precision data for collocated MicroPEMs were collected at both field locations and accuracy against an integrated filter sampler was assessed in Kenya. Additional real-time and integrated MicroPEM data quality indicators have been collected during laboratory testing and domestic U.S. field study deployments and these data will also be presented here. RTI has been working to develop an Enhanced Children's MicroPEM (ECM) suitable for personal sampling using small children (< 5yrs). This device is 50% smaller by volume and 45% lighter than the current v3.2 MicroPEM. Initial laboratory and field validation data for this very low burden monitor will be addressed.

2BB.3

How Fuel and Household Characteristics May Explain Variability in Biomass-burning Cookstove Emissions in Rural Rajasthan, India. ANNA LEAVEY, Jessica Londeree, Ravi Shrimali, Gautam Yadama, Pratim Biswas, *Washington University in St Louis*

Approximately two million tons of biomass are burned daily around the globe, in traditional three-stone cookstoves and open fires, enabling almost 3 billion people to warm and feed themselves. Recent estimates by the World Health Organization and other leading experts put the 2010 mortality rate from household air pollution from solid fuel combustion at around 3.5 million, nearly doubling previous estimates[1]. Ninety-nine percent of these deaths occur in developing countries, especially among women and children. One of the most affected countries is India, where almost 85% of rural households depend on firewood, crop residue and cowdung cakes[2]. Quantifying the emissions from these cookstoves, and understanding the factors that influence their variability, may help to identify and improve the lives of millions of the world's most vulnerable people.

Gas and particulate measurements were collected between June-August, 2012, for 51 households using traditional cookstoves, in rural villages in and around Udaipur, India. A questionnaire was also administered during each visit, to obtain data on fuel and household characteristics, and cooking practices, and simple and multivariate regression analysis was conducted. Many of the predictor variables demonstrated complex associations. For lung-deposited surface area ($\mu m^2 cm^{-3}$) the strongest predictors were fuel diameter ($R^2 = 0.14$) and fuel amount ($R^2 = 0.13$). For $PM_{2.5}$ ($\mu g m^{-3}$), the presence of other ventilation and the type of kindling used explained 18% and 17% of the variability, respectively. Carbon monoxide (ppm) emissions were more difficult to explain using the collected variables, but other ventilation, roof type and the presence of smoking were all statistically significant ($p < 0.05$). Some of these variables may be indicative of socio-economic status and could be used as a proxy of exposure. These associations should be further explored.

2BB.4

Transmission Electron Microscopy Analysis of Biomass-Burning Aerosol Particles during BBOP Campaign 2013.

KOUJI ADACHI, Arthur J. Sedlacek, Lawrence Kleinman, Duli Chand, Peter Buseck, *Meteorological Research Institute*

From July to October 2013, the Department of Energy's Atmospheric Radiation Monitoring (ARM) program sponsored an aircraft-based field campaign (Biomass Burning Observation Project (BBOP)) to study the near-field evolution of particulate emissions from biomass burning. Aerosol particles from wildfires in the Western US (Idaho, Oregon, and Washington) and from agricultural burns in the Mississippi Embayment (Arkansas) were sampled. Transmission electron microscopy (TEM) was used to analyze the mixing states, shapes, and compositions of aerosol particles within the smoke at differing plume ages. Here, we focus on tar ball particles, which are a subset of organic aerosol that is characterized by a spherical shape and amorphous composition. Tar balls are presumed to be brown-carbon (BrC) particles that can contribute to light absorption in the atmosphere. Since tar balls can be identified from their spherical shape using electron microscopy, an investigation of their detailed compositions, formation processes, and occurrence in the atmosphere, all of which are largely unknown, can be conducted. In this campaign, we found that tar balls primarily originated from wildfires. They are most abundant in relatively aged plumes (>several hours from emission). On the flight conducted on July 30, organic aerosol particles formed tar balls as the smoke plume aged. Their shapes, sizes, and compositions were similar to those from Mexico measured during the MILAGRO campaign (2006), but their number fractions were more abundant in the current study. In this presentation, we will discuss their occurrence, formation, and implications of their climate effects from the results of TEM and other on-line instruments.

2BB.5

Impact of Biomass Combustion Activities from Olive Oil Industry on Air Quality in South European Regions.

BEGONA ARTINANO, Ana Sanchez de la Campa, Esther Coz, Rocio Fernandez Camacho, Marta Becerril, Pedro Salvador, Rosa Perez Pastor, Susana Garcia Alonso, Jesus de la Rosa, *CIEMAT*

Olive oil production in Southern Europe represents roughly the 70% of the global production. Nevertheless olive waste entails an important environmental problem that has been recently addressed through different technological solutions. Biomass combustion seems to be an efficient and economical way out for olive wastes. Additionally, the economic crisis has favored the use of olive wood waste as alternative fuel for domestic heating in any type of combustion facility. The impact on air quality of all these activities is still unknown and subject to debate, in part due to a lack of a regulatory framework.

To characterize this impact, an experimental study aimed at assessing the contribution of the different sources to measured atmospheric particle matter (PM10) concentrations has been started in a relevant olive oil producing region of Spain. These concentrations have exceeded in occasions the European air quality normative.

Chemical composition of PM10 was obtained from collected filters. Ctotal concentration represents 30-50% of PM10, being OC the dominant specie (85% of Ctotal). Maximum concentrations were observed in OC and K.

Ultrafine particles (UFP) and Black carbon (BC) were monitored with CPC and MAAP instruments. Peaks of UFP levels and OC-EC concentrations during the late afternoon have been related with local domestic combustion sources. The response of a 7 wavelength Aethalometer AE33 suggested a strong influence of a biomass combustion source during the daytime with UVPM(lambda@370nm)/nIR-BC(lambda@880nm) ratios of 2. Specific wood burning tracers (levoglucosan, mannosan and galactosan) have been analyzed by GC/MS for source apportionment analysis.

This project has been funded by Consejeria de Medio Ambiente (10/2013/PC/00 Project) and Consejeria de Economia (2011 RNM 7800 Project) of Junta de Andalucia (10/2013/PC/00 Project), Fundacion Ramon Areces (AEROCLIMA), MINECO (MICROSOL CGL2011-27020) and Fundacion Biodiversidad (PARTICULAS). The Air Quality Office of Junta de Andalucia and AMAyA are also acknowledged for their support.

2BB.6

An Integrated Particulate and Gaseous Emissions Model to Investigate the Effects of Cookstove Design and Operating Conditions. SAMEER PATEL, Chang Ki Kang, Ahmed Amin Abokifa, Pratim Biswas, *Washington University in St Louis*

Almost half of the world's population depends on biomass for cooking; and inefficient biomass combustion has serious repercussions on both public health and climate. At the same time, biomass is a potentially sustainable and carbon-neutral energy resource; and therefore receiving attention as a serious contender to help us meet our energy demands. In recent years, a large variety of improved cookstoves have been introduced to the market which have been disseminated by organizations such as the United Nations and the World Health Organization.

Improved cookstoves have demonstrated lower emissions compared to traditional cookstoves but still emit unsafe levels of pollutants. While gaseous emissions, and to a lesser extent, particulate matter emissions from different types of cookstoves have been characterized in both laboratory and field settings [1,2], there is a lack of understanding regarding the variations in emission characteristics with cookstove design and operating conditions which limit further improvement in the design of cookstoves.

In this study, a combustion model was integrated with a particle growth dynamics model to predict size distributions of PM and gaseous emissions (CO, CO_2 and CH_4). The cookstove was modeled as a packed bed of biomass under steady-state combustion. Both traditional and improved (gasification-based) cookstoves were modeled. Sensitivity analysis was performed for airflow rate, both primary and secondary in case of gasification-based cookstoves, and bed temperature. Model results confirmed lower emissions ($PM_{2.5}$ and CO) from improved cookstoves. An optimum airflow rate associated with minimum emission levels was also determined. Lower air flow resulted in incomplete oxidation of VOC's due to oxygen deficiency while higher airflow rate lowered the temperature thus decelerating the oxidation rate of VOC's.

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

2CC.2

Effect of Raindrop Size Distribution on Scavenging of Aerosol Particles from Gaussian Air Pollution Plumes Emitted from Point and Line Sources. BORIS KRASOVITOV, Tov Elperin, Andrew Fominykh, *Ben-Gurion University of the Negev*

We suggest analytical model of scavenging of aerosol particles by rain in Gaussian air pollution plumes emitted from point and line industrial sources. The effect of raindrops size distribution was taken into account by using Monte Carlo simulations whereby we assumed 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 and inside raindrops. We derived explicit analytical expression which allows analyzing the dependence of the rate of the aerosols scavenging from air pollution plumes emitted from point and line sources on different parameters, e.g. rain intensity, pollutant emission rate, droplet size distribution. Aerosol concentration distributions were calculated for different scenarios of atmospheric stability. It is found that maximum ground level concentration of aerosols depends on rainfall intensity, and the location of the maximum approaches the emission source when rainfall intensity increases. 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 for the assessment of human exposure to various chemical, biological and radiological contaminants.

2CC.3

An Overview of the NASA ACCESS Flight Experiment. BRUCE ANDERSON, Richard Moore, Andreas Beyersdorf, Charles Hudgins, Robert Martin, Michael Shook, Kenneth Thornhill, Edward Winstead, Luke Ziemba, Aaron Swanson, *NASA*

Although the emission performance of gas-turbine engines burning alternative aviation fuels have been thoroughly documented in recent ground-based studies, there is still great uncertainty regarding how the fuels effect aircraft exhaust composition and contrail formation at cruise altitudes. To fill this information gap, NASA conducted a series of flight experiments using the instrumented LaRC HU-25 sampling aircraft to make detailed measurements of aerosols and ice particles in the near-field behind the NASA DC-8 aircraft as it burned either standard petroleum-based fuel or a 50:50 blend of standard fuel and a hydro-treated esters and fatty acid (HEFA) fuel produced from renewable carbon feed stocks. The first phase of this “Alternative-Fuel Effects on Contrails and Cruise EmiSSions”, or ACCESS, project was successfully conducted spring 2013 during which extensive exhaust and contrail measurements were acquired on five separate missions conducted over the Edwards Air Force Base complex in California. Additional flights (ACCESS-2) were performed during spring 2014 to further examine the effects of fuel composition on engine emissions and investigate the linkages between exhaust soot and contrail ice characteristics. This presentation describes the ACCESS flight experiments, compares cruise-altitude emission measurements with similar data from ground tests, and examines contrail microphysical properties as a function of fuel properties and plume age.

2CC.5

Simulation of Particle Number and Cloud Droplet Concentrations in the Midwestern United States Using WRF-Chem. CAN DONG, Charles Stanier, Robert Bullard, Ashish Singh, *University of Iowa*

New particle formation (NPF) and growth can influence the concentration of aerosols and cloud droplets, which have been acknowledged to play an important role in both global climate and human health. Several mechanisms have been proposed to explain secondary particle formation and growth. In this study, the NPF explicit version (Matsui et al, Journal of Geophysical Research, 116(D19208), 2011) of the Weather Research and Forecasting Chemistry (WRF-chem) model was used to simulate the particle number concentration in the Midwest.

The three-dimensional chemical transport model has a total of 20 size bins ranging 1-10000 nm in diameter. Particle number concentration, aerosol size distribution, and cloud droplet concentration were simulated in summer 2008 and evaluated versus aircraft and surface measurements in Bondville, Illinois. Bondville is characterized by frequent NPF and growth, and particle concentrations greater than 14 nm of 2,500 – 12,000 #/cm3 depending on season and time of day. Sensitivity of these model outputs to changes in SO2 and NH3 consistent with recent trends in these precursors will be evaluated and compared to measurements. Sensitivity of model prediction to selection of empirical nucleation schemes (activation and kinetic) and the binary homogeneous nucleation will be investigated in the boundary layer and the free troposphere, respectively.

Aspects to be discussed include the selection of activation and kinetic coefficients, and contribution of NPF to aerosol particle concentration estimated from differences between nucleation-on and nucleation-off simulations. Sensitivity analysis will also be performed to investigate aerosol number vertical profiles versus model parameter selection with comparison to observed profiles.

2CC.7

Atmospheric Impacts of Black Carbon Emissions Reductions through the Strategic Use of Biodiesel.

HONGLIANG ZHANG, Kento Magara-Gomez, Michael Olson, Tomoaki Okuda, Keeneth Walz, Michael Kleeman, James Schauer, *University of California, Davis*

The use of biodiesel as a replacement for petroleum based diesel fuel has gained considerable interest in the past decade as a strategy for greenhouse gas emissions reductions, energy security, and economics. The use of biodiesel fuel also has the potential to reduce elemental carbon (EC) concentrations in the atmosphere due to the reduced emissions from conventional diesel engines that are not equipped with after-treatment devices. This study examines the impact of biodiesel blends on EC emissions from a commercial off-road diesel engine and simulates its atmospheric impacts. The reduction in black carbon emissions utilizing pure biodiesel, as compared to ultra-low sulfur commercial diesel (ULSD) fuel, was found to be 76% for the engines examined in this study. Reduced emissions for primary pollutants translate directly into reduced concentrations of these components in the atmosphere, but the effects on secondary particulate matter are more complex. Redistribution of secondary particulate matter to particles emitted from other sources can change the size distribution and therefore potential health effects of those components. Modification of meteorological variables can influence secondary particulate matter formation through non-linear processes. In the present study, simulations that adopted 75% biodiesel blended with ULSD by all non-road diesel engines produced a up to 50% reduction in predicted concentrations of EC, less than ±5% changes in nitrate and total PM2.5 mass concentrations in California. These changes in ground level concentrations did not lead to significant effects on radiative forcing at the top of the atmosphere since the adoption of biodiesel produced larger coatings of secondary particulate matter on atmospheric particles containing residual EC leading to enhanced absorption associated with those particles. The net effect was a minor change in atmospheric optical properties despite a large change in atmospheric EC concentrations. These results emphasize the importance of considering EC mixing state in climate research.

2CC.8

Future Projections of Aerosol Optical Depth, Radiative Forcing, and Climate Response due to Diminishing Aerosol Emissions.

DANIEL WESTERVELT, Larry Horowitz, Vaishali Naik, Denise Mauzerall, *Princeton University*

It is widely expected that global emissions of atmospheric aerosols and their precursors will decrease strongly throughout the remainder of the 21st century, due to emission reduction policies enacted based on human health concerns. However, the resulting decrease in atmospheric aerosol burden will have unintended climate consequences. Since aerosols generally exert a net cooling influence on the climate, their removal will lead to an unmasking of global warming as well as other changes to the climate system. Aerosol and precursor global emissions decrease by as much as 80% by the year 2100, according to projections in four Representative Concentration Pathway (RCP) scenarios. We use the Geophysical Fluid Dynamics Laboratory Climate Model version 3 (GFDL CM3) to simulate future climate over the 21st century with and without aerosol emission changes projected by the RCPs in order to isolate the radiative forcing and climate response due to the aerosol reductions. We find that up to 1 $W\ m^{-2}$ of radiative forcing may be unmasked globally by 2100 due to reductions in aerosol and precursor emissions, leading to average global temperature increases up to 1 K and global precipitation rate increases up to 0.09 $mm\ d^{-1}$ (3%). Regionally and locally, climate impacts are much larger, as RCP8.5 projects a 2.1 K warming over China, Japan, and Korea due to reduced aerosol emissions. Our results highlight the importance of crafting emissions control policies with both climate and air pollution benefits in mind. The expected unmasking of additional global warming from aerosol reductions highlights the importance of robust greenhouse gas mitigation policies and may require more aggressive policies than anticipated.

2CC.9

Microscopic Studies of Ice Nucleation. BINGBING WANG, Daniel Knopf, Mary Gilles, Gourihar Kulkarni, Shawn Kathmann, Libor Kovarik, Alexander Laskin, *Pacific Northwest National Laboratory*

Formation of atmospheric ice in clouds can proceed by homogeneous and heterogeneous nucleation. Better understanding of ice nucleation is of critical importance to elucidate fundamental processes of aerosol-ice cloud interactions – one of the most challenging problems for predictive understanding of Earth's climate change. We develop and apply microscopy approaches for fundamental studies of heterogeneous ice nucleation on atmospheric particles. Hosted by environmental scanning electron microscope, we expand experimental observations of individual ice nucleation events at conditions approaching the upper troposphere/lower stratosphere. Applying multi-modal micro-spectroscopy methods the physicochemical properties of the identified ice nuclei can be characterized. Combined with theoretical chemistry calculations, the experimental data will be analyzed to gain better understanding of ice nucleation and parameterizations for cloud models.

2CH.1

Filtration of Combustion Aerosols by Facepiece Respirators and Stationary IAQ Filters. SHUANG GAO, Jin Yong Kim, Michael Yermakov, Xinjian He, Yousef Elmashae, Tiina Reponen, Sergey A. Grinshpun, *University of Cincinnati*

Filters used in filtering facepiece respirators (FFR) and in indoor air quality (IAQ) control devices are usually tested with aerosol simulants such as NaCl, KCl, or dioctyl phthalate. It is assumed that these tests produce filter efficiency levels representative of real aerosol hazards, e.g., particulate combustion products. However, little data are available to justify the above assumption. In this study, we tested the samples of two types of filters: one was an N95 FFR filter widely deployed in occupational environments, and the other was a MERV 14 stationary indoor filter used in heating, ventilation and air conditioning (HVAC) systems. Both were challenged with three combustion aerosols (produced by burning wood, paper and plastic) and with a NaCl aerosol. Each tested filter sample was mounted on a specially designed holder. The particle concentrations and size distributions upstream and downstream of the filters were determined by a Nanocheck (Grimm Technologies, Ainring, Germany) in a size range of 15 to 900 nm. Different air flow rates were applied to the filter samples representing typical inhalation conditions for respirators and conventional air exchange rates for IAQ control devices. For both filter types, we observed significant difference ($p<0.05$) between the total particle penetrations of the tested combustion materials and NaCl particles. The plastic combustion aerosol showed the lowest filtration efficiency, followed by paper, wood, and NaCl. The size-selective analysis indicates that the greatest difference between penetrations of combustion and NaCl particles occurred within a size range of 20–80 nm, and the difference was found dependent on the challenge aerosol, flow rate, and type of the filter. It was concluded that the filter efficiency obtained with a well-established simulant such as NaCl may overestimate the protection level offered by the same filters against combustion aerosols.

This work was supported by NIOSH Contract 200-2013-M-56581.

2CH.2

The Effect of Air Dilution on WOx Nanoparticle Generation and Thermal Rebound in Filtration. RAHELEH GIVEHCHI, Zhongchao Tan, *University of Waterloo*

Despite a large and growing body of literature in the field of nanoparticle filtration efficiency and thermal rebound theory, great uncertainty still remains regarding the critical diameter for nanoparticles, below which, thermal rebound occurs. According to thermal rebound theory, the removal efficiency of small nanoparticles decreases if their size is reduced. The objective of this research is to investigate the effect of dilution flow on glass-fiber fibrous filter efficiency and the thermal rebound of nanoparticles. A tungsten aerosol generator was employed to generate tungsten oxide (WOx) nanoparticles in the range of 1.2 to 20 nm. The nanoparticle concentration is controlled by changing the carrier flow and dilution flow. A scanning mobility particle sizer was used to measure the WOx nanoparticle size distribution of a sample through an isokinetic sampling probe. The penetration of particles through the filter is calculated as the ratio of the downstream particle concentration and upstream particle concentration. Results showed that increasing the dilution flow generates smaller nanoparticles in higher concentration. And, the fluctuation of measured efficiency curve dropped as the dilution ratio increased. Furthermore, thermal rebound was detected in experiments for sub-3 nm particles. The results of this study suggest that under a lower diluted flow, the coagulation of nanoparticles enlarges the size of particles and decreases their concentration; however, the coagulation of larger particles does not affect the thermal rebound of smaller particles.

2CH.3

Filtration Characteristics of Granular Ceramic Filter. MYONG-HWA LEE, Hyun-Jin Choi, Jeong-Uk Kim, *Korea institute of Industrial Technology*

Ceramic filter is generally used to remove particulate matters in hot flue gas. The granule typed ceramic filters made of SiC powders were prepared and their filtration characteristics were investigated with a single collector efficiency model in this study. We found that diffusion was a dominant collection mechanism for particles smaller than 0.7 µm, and direct interception and inertia were dominant collection mechanisms for particles lager than 0.7 µm in a granular ceramic filter based on the model. In addition, filter performance factor, qFM considering physical strength, collection efficiency and pressure drop was introduced to evaluate the ceramic filter properties, and SiC50 filter was the best in ceramic filters fabricated in this study.

* This research was financially supported by the Eco-Innovation Project(2012-00011-0002) through the Ministry of Environment, South Korea.

2CH.4

The Effect of Simulated Air Conditions on N95 Respirator Performance. JOEL RAMIREZ, Patrick O'Shaughnessy, *University of Iowa*

Despite previous research in the field of respirators efficiency and resistance to flow, uncertainty still remains regarding the effect of moisture in a respirator. The objective of this study was to determine the effect of different simulated air conditions on the resistance to flow, as a measure of comfort, and the efficiency of N95 Filtering Face-piece Respirators. A penetration curve and resistance to flow (Rf) of two models of N95 filtering face-piece respirator (FFR) were evaluated in a test system developed to mimic inhalation and exhalation, and provide changes to relative humidity (RH) and temperature (T). Penetration was tested before and after a 2-hr Rf test using a sodium chloride aerosol measured with a scanning mobility particle sizer. The Rf test was performed under four T and RH conditions. A second round of tests included the addition of an inorganic dust to determine the effect of dust loading on Rf. Results showed that the critical condition was simulated condition 3. For simulated condition 3, model A inhalation Rf increased on average 2.43 mm H_2O; model B inhalation Rf increased on average 9.34 mm H_2O; model A had, on average, a penetration difference between the before Rf test and after Rf test of 0.91%; Model B had, on average, a penetration difference of 0.75% between the before Rf test and after Rf test; most penetrating particle size (MPPS) for Model A was 40.6 nm before Rf test and 46.3 nm after Rf test; and MPPS for Model B was 48.4 nm before Rf test and 55.1 nm after Rf test. When the FFRs were challenged with an inorganic dust, Rf for Model B increased faster than for Model A. Results of this study shows that air conditions that involve high RH (i.e. simulated condition 3), increase FFR Rf.

2CH.5

Effects of Particle and Spray Droplet Charge on Respirable Dust Capture by Surfactant Sprays. MEI WANG, Peter Raynor, *University of Minnesota*

Objective
To measure the effects of particle and surfactant-containing spray droplets on the capture of respirable particles.

Methods
Monodisperse polystyrene latex aerosols (with diameters of 0.6, 1.0, or 2.1 micro-meters) and polydisperse coal dust aerosols were generated in a nebulizer and fluidized bed aerosol generator respectively. The aerosols then either remained unneutralized or were given a neutralized, net positive, or net negative charge using a neutralizer and a diffusion charger before entering a wind tunnel.

Some of the particles were removed as they passed through sprays with 0 or 1×10-4 M concentrations of anionic, cationic, or nonionic surfactant. The remaining particles were sampled and charge-separated at different voltage levels using an electrostatic classifier, then counted and sized in an aerodynamic particle sizer. Measurements with the spray on and off allowed the calculation of spray collection efficiency. Overall collection efficiencies and efficiencies against particles with specific charge levels were measured. Spray droplets of plain water or different surfactant solutions were also sampled and charge-separated at different voltage levels using an electrostatic mobility analyzer, and then counted and sized in an image-based droplet sizer.

Results
Dust collection significantly increased with increasing particle diameter ($p<0.001$) for both PSL and coal dust aerosols. Both droplet and particle charge significantly affect spray efficiency. Negatively and positively charged particles were captured most efficiently when highly charged particles interacted with highly charged droplets with opposite charge. Strongly-charged particles tend to be collected more efficiently than weakly-charged particles. Charged particle capture was associated more strongly with surfactant-containing spray droplet charge level rather than with surfactant type.

Conclusions
The charge level of both particles and spray droplets critically influences the capture of both PSL and coal dust particles, especially for higher charge levels and smaller particle sizes.

2CH.8

Evaluation of Sampling Media for Use in a Nanoparticle Respiratory Deposition Sampler. LEVI MINES, Jae Hong Park, Imali Mudunkotuwa, Vicki Grassian, T. Renee Anthony, Thomas Peters, *University of Iowa*

The objective of this work was to broaden the applicability of an innovative nanoparticle respiratory deposition (NRD) sampler by identifying alternate sampling media to collect and quantify multiple metals. Sampling media were identified and classified into several groups: membranes, foams, mesh screens, and granular beds. The collection efficiency by size of the sampling media was measured in triplicate for metal particles generated from a spark discharge system, using a fast mobility particle sizer (FMPS; 3091, TSI, US). Collection efficiencies were compared to the nanoparticulate matter (NPM) sampling criterion, which approximates deposition in the human respiratory system for particles smaller than 300 nm with a 50 percent collection efficiency cut-point at 40 nm and is a proposed collection criteria curve for exposure monitoring of nanoparticles. Several classes of sampling media showed promise for matching the NPM sampling criterion in both theoretical and experimental situations. Nylon, polycarbonate, and PTFE membranes did not match the NPM sampling criterion curve with constant collection efficiencies by size at 77 percent (SD 1.1), 17 percent (SD 5.3), and 78 percent (SD 4.5) respectively. Several foam sampling media exhibited the correct shape of the collection efficiency curve, and one 25-mm diameter foam stopper approximated the NPM sampling criterion with a 50 percent (SD 0.1) collection cut-point at 28 nm. Widely different sampling media (foams, mesh screens, and granular beds) can be designed to collect particles with efficiencies by size matching deposition in the human respiratory system for particles smaller than 300 nm. Investigation will continue to further evaluate sampling media at varying solidities, identify new sampling media, and evaluate the collection efficiency of layers of different classes of sampling media. Final selection of sampling media will be based on collection efficiency by size, compatibility with analytical methods, minimized metals interference, commercially availability, and cost.

2HA.1

Modeling Deposition of Cigarette Puff Mixture in Human Lungs. BAHMAN ASGHARIAN, Owen Price, Caner Yurteri, John McAughey, *Applied Research Associates, Inc.*

Biological response from smoking is directly related to the dose of inhaled cigarette puff. Thus, to study the health impact of smoking, the inhalation of cigarette puff must be studied to determine the site and amount of deposition on lung airway surfaces. Deposition and uptake of components of cigarette smoke in the lung, which may be present in both droplet and vapor forms, are directly related to their thermodynamic states in the smoked air. Uptake of a vapor component depends on partition coefficient while droplet deposition depends on physical size. The smoke mixture undergoes a continuous phase change, which affects both vapor uptake and droplet deposition. To study the fate of inhaled smoke puff, a unified model of vapor uptake and droplet deposition for cigarette smoke was developed in which a two-way coupling was assumed between the vapor and droplet phases. Droplet evaporation reduced its size while increasing the concentration of its components in the vapor phase of the smoke. In addition, droplets underwent coagulation and hygroscopic growth while their movement and deposition were affected by their colligative behavior (particle-particle interaction or cloud effect). The cigarette puff was assumed to be made up of nicotine, water, soluble and insoluble components of tar. The presence of vapor nicotine reduced the evaporation rate compared with the case of no vapor nicotine present in the air. However, cigarette droplets were void of nicotine when reaching the alveolar region. Hence, lung dose of nicotine was mainly due to vapor uptake. Model predictions were in agreement with reported measurements. This study was funded by British American Tobacco Investments Ltd.

2HA.2

What is Effect of Water Pipe Height on Particulate Formation in Mainstream Waterpipe Smoke? CINDY DEFOREST HAUSER, Jessica Annonio, *Davidson College*

Hookah (also known as narghile, shisha, and hubble-bubble) is a form of tobacco use which began in India in the 15th century and has since spread to various parts of the Middle East, Mediterranean, and western countries including the United States. Tobacco is flavored with ma’ssel, a sweet tasting paste, placed in the head of the waterpipe, and heated with charcoal. As the user inhales, the air that is heated as it is pulled over the charcoal vaporizes volatile and semivolatile constituents in the tobacco. These compounds condense as they enter the cooler region of the pipe and form smoke. The smoke is pulled into the body of the waterpipe, bubbled through liquid contained in the bowl and inhaled. In this study, a standard smoking protocol of 63 puffs for 3 seconds each spaced at 30-second intervals was used. Particulate matter (PM) from mainstream waterpipe smoke is characterized by size (TSI OPS 3330), mass (TSI DustTrak 8533) and number concentration (TSI CPC 3007) for waterpipes with 22cm, 36cm, and 55cm pipe heights. The total mass of particulates per session generally increases with waterpipe height and an increase in flow rate. The fraction of the mass per session that is PM1 or smaller increases with the height of the pipe. As waterpipe height is increased, there is a decrease in the total number of particulates between 0.3um and 10um. The particle size distribution shifts towards decreasing particle diameter in general, and more heavily favors smaller particles with a taller waterpipe height. Initial results with the condensation particle counter suggest additional particulates below 0.3um.

2HA.3

Estimation of Electron Microscopy Image-based Aerodynamic and Diffusion Diameters for Carbon Nanotube Aerosols. BON KI KU, Pramod Kulkarni, *Centers for Disease Control and Prevention, NIOSH*

Knowing transport characteristics of aerosol particles is important in assessing their fate in the respiratory system. Diffusion and aerodynamic diameters typically capture key deposition mechanisms in the submicrometer size range. However, for nonspherical particles with high aspect ratios, such as aerosolized carbon nanotubes, these diameters can vary widely, requiring their independent measurement. The objective of this study was to estimate aerodynamic and diffusion-equivalent diameters of airborne carbon nanotubes (CNTs) and compare these estimates with those directly measured using real-time instruments. The as-received nanomaterials were aerosolized using different techniques including dry dispersion and nebulization. The airborne properties of the particles were measured using real-time instruments by tandem mobility-mass approach. Particles with single electrical mobility were collected on a grid and analyzed by Transmission Electron Microscopy (TEM) to obtain an aerodynamic diameter of the particles. From the TEM image analysis, projected area, maximum length, and 2-D radius of gyration were measured. An approach was developed to estimate the aerodynamic diameter by estimating radius of gyration and projected area equivalent diameter from the particle image, and the material density known from the manufacturer. Without accounting for particle shape correction, the aerodynamic diameters calculated from microscopy were overestimated compared to direct measurements. After accounting for the dynamic shape factor correction, most of the estimated data agree with the direct measurements within 30%. The uncertainty of these estimates depends on degree of overlapping features in the particle structure, and nonuniformity in tube diameter and material density. The approach could be useful in calculating approximate airborne properties from microscopy images of carbon nanotube agglomerates with relatively open structures, when other methods are not readily available.

2HA.4

Formation of Hydroxyl Radical from Cooking and Vehicle Exhaust Particles Extracted in a Cell-free Surrogate Lung Fluid.

SHEXIA MA, Ke Ren, Laiguo Chen, Zhencheng Xu, *South China Institute of Environmental Sciences*

Epidemiological and toxicological studies have shown a relation between the inhalation of atmospheric particles and adverse cardiopulmonary health effects. Previous studies have suggested that the adverse health effects from ambient particulate matter (PM) are linked to the formation of reactive oxygen species (ROS) by PM. The generation of reactive oxygen species (ROS) by particles is one current hypothesis for their toxic effects. Thus a quantitative measurement of ROS is important since that will be an index to assess the oxidative stress that particles may cause in the lung. Here we report on •OH formation from PM collected from cooking and vehicle exhaust particles as well as urban particles in Guangzhou buffered extract solution as a surrogate lung fluid (SLF). We quantified •OH in PM extracts using a cell-free, phosphate buffered saline (PBS) solution with four antioxidants: ascorbate, citrate, glutathione, and uric acid. The results show that generally the vehicle exhaust PM generates much more •OH than the cooking PM. Mass-normalized •OH generation by ambient PM2.5 was a little larger than that of cooking PM but lower than that of vehicle exhaust PM. By measuring calibration curves of •OH generation from copper and iron, and quantifying copper and iron concentrations in our particle extracts, we find that PBS-soluble iron is primarily responsible for •OH production by the cooking and vehicle exhaust PM. Our results suggest that the in vivo generation of free radicals, specifically •OH, by inhalation of PM2.5 is partially due to transition metals.

2HA.5

Airway-by-Airway Imaging of Particles Deposited in Animal Lungs.

CHRISTOPHER WALLIS, DongYoub Lee, Annalisa Smullin, Anthony Wexler, *University of California Davis*

Laboratory animals are widely used as models for exploring both adverse and beneficial health effects caused by inhalation of suspended particles. Administering therapeutic drugs by inhalation offers advantages such as avoidance of first pass metabolism, faster absorption, low cost, and patient convenience. Knowledge of where particles have deposited is an important factor in understanding the effects of this type of administration. Similarly, such knowledge also aids studies of harmful effects from exposure to suspended particles through occupational exposure, air pollution, or smoke. Mapping deposition throughout the airways of laboratory animals is crucial since the location often determines subsequent transport and the health effects elicited. There are few methods for identifying the exact pattern of deposition once the drug or particle enters the airways.

Here we present a newly developed method for simultaneously imaging airways and deposited particles in three dimensions with high resolution. Inhalation exposure to fluorescent particles is performed and the lungs are then inflated and flash frozen. Silicone casting material mixed with fluorescent dye of a different color is injected into the frozen lung to support and color the lumen. The lung is then embedded in ice and mounted in an Imaging Cryomicrotome. This instrument is used to serially section the sample while capturing fluorescent images of the block face at each slice. Optical excitation and emission bands are chosen to separately image the deposited particles and fill material. Slicing unfixed lung tissue presents a challenge, even when frozen. A fine water mist is employed intermittently throughout the slicing process to further support the tissue. We present our preliminary results, including three dimensional reconstruction of both the conducting airways and deposited particles, as well as numerical analysis of deposition in individual airway segments.

2HA.6

Generating a Pharmaceutical Aerosol with High Charge and Low Device Losses.

LANDON HOLBROOK, Worth Longest, *Virginia Commonwealth University*

Three systems are developed and evaluated with the goal of producing highly charged pharmaceutical aerosols with low device losses for improving respiratory drug delivery to the lungs of ventilated infants. These systems are evaluated based on aerosolization rate, particle loss, particle size distribution and charge per particle of an albuterol sulfate solution by filtration or impaction using a validated High Performance Liquid Chromatography (HPLC) technique. The new aerosolization systems evaluated are a Wick Electrospray (WES) device, a Condensational Vaporization (CV) device, and a Modified Vibrating Mesh (MVM) device connected to a streamlined induction charger. The WES device is composed of a streamlined airspace that connects a counter electrode and a liquid reservoir containing a shaped wick submerged in a solution at a high voltage. The CV device uses a heated capillary to vaporize a solution that is held at a high voltage. The MVM system is a commercially available AeroNeb Lab nebulizer with a modified driving signal to produce one tenth of the normal aerosol by mass. A charged electrode in the shape of a ring below the vibrating mesh creates a charged aerosol through induction. Each system is tested using a filter to determine the emitted dose and aerosolization rate. Next, the particle size distribution is evaluated using the Mini-Moudi impactor at 2 L/min. Finally, a modified Electrical Low-Pressure Impactor (ELPI) is used to simultaneously determine the particle size distribution and charge on each impactor stage at a flow rate of 30 L/min. In contrast with the other two systems, the MVM device was found to produce a highly charged aerosol with low device loss that is viewed as ideal for targeted aerosol drug delivery to ventilated infants.

2HA.7

Source, Size and Seasonal Differences in the Biological Potency of Ambient Particulate Matter Collected at Three Different Locations across Canada.

SUBRAMANIAN KARTHIKEYAN, Dalibor Breznan, Errol Thomson, Yunus Siddiqui, P. Goegan, Michael Denison, P. Kumarathasan, Jeff Brook, Renaud Vincent, *Hazard Identification Division, HECSB, Health Canada*

Population studies have shown that the health effects of particulate air pollution vary depending on location, season, and particle size. The objectives of this work are to better understand the impact of particle characteristics on cytotoxicity and inflammatory potential in vitro, to summarize dose-responses observed in a panel of endpoints into biological potency estimates, and to assess the value of potency estimates as predictors of population health risk. Concurrent PM10 and PM2.5 samples were collected at Downsview (Ontario), Saint John (New Brunswick), and Pitt Meadows (British Columbia) in summer and winter. Particles were extracted from filters and analyzed for cytotoxicity and inflammatory potential in epithelial-like A549 cells, and macrophage-like J774A.1 cells. The potency of particles was determined according to Fold effect = $(\text{Dose} + 1)^{b}$eta, where beta is the slope of the dose-response relationship. It was also tested if factoring particle potency estimates would improve the correlation between exposure (ambient particle concentration used as a surrogate) and rates of adverse health outcomes. Cytotoxicity was significantly impacted by location ($p<0.05$), with particles from Pitt Meadows being the most potent. Secretion of inflammatory cytokines was impacted by both location and season. PAH ratios pointed to domestic fuel combustion in Pitt Meadows, and automotive combustion in Downsview and Saint John, as dominant sources. The elements Ag, Bi, Cu, Ti, and Zn emerged as drivers of cytotoxicity. Overall, the biological potency of ambient particles was impacted by the location and season of sampling, and was related to the physicochemical characteristics of particles. Nevertheless, the correlation between particle concentration and health outcomes was not improved by the incorporation of potency estimates into the calculation of risk. Potency data from a larger number of ambient PM samples may be required to fully validate the application of potency measurements in the refinement of population health risk estimates.

2HA.8

Evaluation Criteria for Bioaerosol Samplers. JANA KESAVAN, Jose-Luis Sagripanti, *US ARMY ECBC*

Humans contract a variety of serious diseases through inhalation of infectious aerosols. Thus, the importance of monitoring air for microbial or toxic content is recognized in clinical, occupational, and biodefense arena. However, accurate monitoring of potentially contaminated environments can be hampered by selection of aerosol samplers with inadequate performance for the intended task. In this study, 29 aerosol samplers were evaluated based on their respective air flow, size, weight, power consumption, and efficiency in sampling particles with size ranges within the respirable range. The resulting data demonstrates that sampling air flow and efficiency vary widely, and cannot be predicted from the physical characteristics of air samplers, and hence, that proper selection of air samplers should be more involved than shopping for a device based on the limited characteristics that are published. The findings are summarized in an approach to rationally select bioaerosol samplers for use in the monitoring of infection control and environmental biomonitoring. For example, in the case of bioaerosol sampling, the sampled organism ratio of 1:24 between the Midget Impinger and the BioSampler respectively shows that one of the samplers is significantly more (24-fold) efficient in collecting organisms compared to the other comparable device, highlighting the need for careful selection of aerosol samplers in most applications. In conclusion, the presented data demonstrates that improper selection of air samplers could result in a failure to collect germs or toxins in the respirable range and thus under estimete the true risk, creating a false sense of security under circumstances that could result in unnecessary loss of life as in contaminated health care settings, or in other environments that are accidentally or purposely contaminated with infectious or toxic aerosols.

2HA.9

Evaporation Kinetics of Secndary Organic Aerosols Derived from Engine Exhaust Precursors. Mohammad Baasiri, ALAN SHIHADEH, *American University of Beirut*

Organic aerosols constitute a major fraction of particle pollutants in the atmosphere, and they exert important influences on human health and global climate. When predicting concentrations of organic aerosols in the atmosphere, regional air quality models commonly assume that gas-particle partitioning is rapid, and that therefore semi-volatile species closely follow thermodynamic equilibrium partitioning between the condensed and vapor phases. Based on recent evidence from single-particle studies that secondary organic aerosols (SOA) exist in a glassy, amorphous state for which mass transfer is intrinsically slow compared to atmospheric time scales, the assumption that SOA is well-described by equilibrium thermodynamics has been called into question. In this study, the evaporation kinetics of an ensemble of SOA nanoparticles are observed when they are heated to 40 ˚C in a constant temperature, atmospheric pressure flow tube. In particular, particle volume changes were tracked in time, and the observations fitted to a theoretical model of particle evaporation in order to obtain the effective evaporation coefficient. SOA was generated by photo-oxidizing diluted (5000:1) exhaust from a single-cylinder gasoline engine. Investigated particle mass loadings spanned a range from 18 micrograms/m^3 to 40 micrograms/m^3. It was found that particle evaporation was well described by Maxwell's equation, modified for non-continuum effects, with effective evaporation coefficients of order 0.1. These results indicate that at least for engine exhaust SOA, mass transfer rate is not constrained by intra-particle diffusion processes. More importantly, these results suggest that atmosphere anthropogenic SOA attain phase equilibrium on time scales approaching minutes or tens of minutes in extreme cases, and that contrary to recent literature, treatment of SOA partitioning using thermodynamic equilibrium indeed may be valid.

2HA.10

Effects of User Puff Topography, Device Power, and Liquid Nicotine Concentration on Electronic Cigarette Nicotine Yield: Measurements and Model Predictions. Soha Talih, Zainab Balhas, Thomas Eissenberg, Rola Salman, Nareg Karaoghlanian, Ahmad El Hellani, Rima Baalbaki, Najat A. Saliba, ALAN SHIHADEH, *American University of Beirut*

Electronic cigarettes (ECIGs) are a product category that encompasses a wide range of technologies and use methods. They are marketed as non-combusting nicotine delivery devices that use an electrically-powered element to heat a liquid to form an inhalable aerosol. While controversy over their potential public health consequences rages, there is little available empirical data on the factors that influence ECIG aerosol emissions and delivery as regulatory agencies consider questions of product labeling and abuse liability. In this study we examined how user puffing behavior, ECIG liquid composition, and ECIG design features influence nicotine emissions. ECIG aerosols were generated using 5 distinct puffing profiles that represented a range of plausible ECIG use behaviors. In addition, electrical power (3.0–7.5W) and e-liquid nicotine concentration (18-36 mg/mL) were varied. A theoretical model based on mass and energy conservation principles and boundary layer theory was also developed to simulate the ECIG aerosol production process and to provide insight into the empirical observations. The model inputs include product design features and operating conditions, as well as puff behavior and thermophysical properties of the ECIG solution. We found that nicotine emissions varied by more than 50-fold across conditions, and that under some conditions a few ECIG puffs can produce as much nicotine as an entire conventional tobacco cigarette. Puffing profiles with longer puff durations resulted in disproportionately higher nicotine emissions, while puff flow rate had no effect on nicotine emissions. Higher nicotine concentration and higher voltages resulted in higher nicotine emissions. Measured nicotine emissions were highly correlated to the theoretical predictions (R2=0.99), indicating that ECIG emissions can be predicted using physical principles, with knowledge of puff topography and a few ECIG device design parameters.

2HA.12

Respiratory Dose Assessment 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 known to be different for different size particles, specific dose of size-fractionated PM under realistic exposure conditions would be of interest in health risk assessment. We investigated deposition characteristics of typical bi-modal ambient aerosols under three different inhalation exposure conditions: resting, mild exercise and moderate exercise (tidal volume (ml)/ frequency (min-1) = 750/12, 1250/20, 1500/25). Oro-nasal breathing was considered during exercise. Test aerosols were composed with two uni-modal aerosols having the mass median diameter of 0.3 um and 5 um with GSD of 1.8 and 2.0, respectively. Mass ratios (MR = 1st mode distribution/total) were varied from 0-1 with an increment of 0.1. A validated mathematical model was used to calculate total and regional lung deposition (tracheobronchial, TB and alveolar, AL) for three size fractions, Ultrafine (PM0.1), Fine (PM0.1-2.5) and Coarse (PM2.5-10). Results show that for mass deposition both F and C contribute to TB and AL with their respective contribution approximately following MR. During exercise, C increases in TB but decreases in AL while F decreases in both TB and AL. UF is negligible regardless of MR. For surface area, F and UF contribute to both TB and AL more with F. C increases in TB during exercise at MR< 0.5. For number deposition, both UF and F deposit in TB and AL with a respective contribution of approximately 6:4 regardless of exposure conditions. Contribution of C was negligible. In conclusion, for typical bimodal ambient aerosols UF, F and C deposit at the same site of the lung with varying proportions. PM size of dominant deposition varies with deposition site and dose metric.

2IA.1

High Face Velocity (0.5-1.0 m/s) Penetration of sub-50 nm Nanoparticles through HVAC Filter Media Used in Residence. DEQIANG CHANG, Sheng-Chieh Chen, David Y. H. Pui, *China Northeastern University, University of Minnesota*

In HVAC system used in residence, the medium efficiency filter media are usually used for purification and run at high face velocity, about 0.5 m/s to 1.0 m/s. In this operating condition, these filter media can provide satisfactory removal efficiency to fine particles and remain a lower pressure drop. The efficiency of this type of filter media to nanoparticle at such high face velocity is the research content of this paper.

In this study, the penetrations of sub-50 nm nanoparticles through filter media used in HAVC were tested at different face velocity with Ag particles as challenging aerosols. Five types of filter media which were made of different size fibers and have different thickness and charge density were tested. The pressure drops at different face velocity were also recorded. The results show that the penetrations at high filtration velocity is larger than that at low velocity and the Most Penetratiable Particulate Size(MPPS) moves to the smaller particle size range with the face velocity increase.

2IA.3

Comparison of Indoor and Outdoor Air Quality in Latino Communities in Peru, Chile, and USA. Wyatt Champion, Francisco Barraza, Hector Jorquera, LUPITA MONTOYA, *University of Colorado Boulder*

The contribution of human activities to indoor air pollution is a major concern in developing areas. The use of solid fuels for heating and cooking results in high levels of fine particulate matter (PM2.5) indoors, while practices unique to a culture (like raising animals indoors) may further exacerbate poor indoor air quality. Products of combustion and the biological components of particulate matter (PM) have also been shown to have compounding negative health effects in humans. To better understand exposures of Latino populations to indoor air pollution, air quality monitoring studies were conducted in three different Latino communities: a rural Andean community in Cusco, Peru, a suburban Latino community in North Boulder, Colorado, and an urban area in Santiago, Chile. Indoor and ambient samples were collected for either 24 or 48 hours onto Teflo and Tissuquartz filters and analyzed for biological components of PM, while the Tissuquartz filters were analyzed for elemental and organic carbon content (EC/OC). Differences in PM mass and associated components were observed among these three communities. The rural Peruvian homes exhibited the highest concentrations of pollutants indoors due to solid fuel use. Compared to Boulder households, Santiago homes were found to have lower concentrations of OC indoors and outdoors, but higher EC concentrations (both indoors and outdoors), likely due to its urbanized environment and motor vehicle emissions.

2IA.4

Size-Segregated Mass Concentrations and Elemental Compositions of Particulate Matter (PM) Emitted during Toasting and Cooking.

Soudabeh Gorjinezhad, MEHDI AMOUEI TORKMAHALLEH, Melek Keles, Fatma Öztürk, Cansu Azgin, Hediye Sumru Unlüevcek, Berfin Tanis, Elif Cihan, Nergis Ozaslan, Nurseli Soy, *Middle East Technical University Northern Cyprus Campus*

Particles from cooking sources can cause high pollutant exposures with likely adverse health effects. Understanding the health effects of indoor cooking sources and how to reduce them will require the knowledge of the concentration and the composition of the pollutants. Little is known about the elemental compositions of particles emitted during cooking activities. Preliminary results obtained by Amouei Torkmahalleh et al. (2013), and presented to “Conference Environment and Health –Basel, Switzerland (2013)” found the presence of Fe, Zn, Mn in total particle mass during heating of cooking oils. The aim of this study is to perform controlled measurements of the particle size-segregated mass and elemental concentrations as well as OC/EC concentration to understand the contribution of each cooking components to overall PM exposure. The cooking components include electric stove, cooking pan, cooking oil, additives, and meats. Source apportionment analysis is also performed using EPA-PMF to investigate the contribution of cooking components. Additionally, particle mass and elemental concentrations from cooking different Mediterranean food as well as toasting are investigated. The experiments are conducted using an electric stove in an on campus house at Middle East Technical University Northern Cyprus Campus in Güzelyurt, Northern Cyprus. Filter based mass measurements using an Eight Stage Non-Viable Impactor are performed to collect the generated particles from the range of PM0.4 to PM3.3. The sampling is done in the kitchen, and close to the breathing level of the cook. The collected filters are analyzed using an inductively coupled plasma mass spectrometer (ICPMS) to measure the elemental concentrations. An OC/EC analyzer is utilized to determine the elemental and organic carbon concentrations. All experiments are replicated four times. This study provides new information on the composition and size fractions of different metals during cooking and toasting in particular, some potentially toxic metals such as chromium.

2IA.5

Preliminary Evidence for Aqueous Oxidation of Organic Compounds in Indoor Air.

SARA DUNCAN, Yong Lim, Jeffrey R. Kirkland, Barbara Turpin, *Rutgers University*

Aqueous processing of organic compounds alters the composition of ambient outdoor organic aerosols and could affect budgets of some gases. Since 20-50% of homes in the United States are considered “damp,” with relative humidities over 80%, it is likely that aqueous chemistry also plays a role in indoor air chemistry. This aqueous chemistry may occur in water films (e.g., on walls and skin) and in wet particles. Gas phase concentrations of organic compounds are frequently higher indoors than outdoors, and oxidants such as hydroxyl radical and nitrate radical are also found in indoor environments. Thus, aqueous chemistry indoors may alter human exposure to indoor pollutants.

Samples were collected and composited inside a living room in a local home using a mist-chamber apparatus (collection volume of 25 milli-liters and flow rate of 30 liters per minute) that scrubs water-soluble compounds out of the air and into the aqueous phase. Oxidation experiments were then conducted with these aqueous samples to identify reactive species for further study. The first experiment was conducted with a mist-chamber sample containing 780 micro-molar dissolved organic carbon. Hydroxyl radicals were generated in 11 cuvettes (3 milli-liter) held equidistance from a 254 nm ultraviolet lamp by photolyzing 1 milli-molar hydrogen peroxide. Cuvettes were removed from the reactor at 0 - 150 minutes and analyzed by electrospray ionization mass spectrometry (ESI-MS) and ion chromatography (IC). Oxalate was produced (approximately 50 micro-molar). ESI+ revealed the masses of fifteen reactants with unit mass resolution. Additional experiments, control experiments and MS-MS will be used to further characterize these precursor compounds.

2IA.6

Heating and Indoor Air Quality on the Navajo Nation.

JOANNA GORDON, John Ortega, Mike Russel, Evan Coffey, Josh Bowen, Ashley Collier, Ricardo Piedrahita, Nick Masson, Margaret Mayer, Barbara Klein, Perry Charley, Michael Hannigan, *University of Colorado at Boulder*

On the Navajo Nation, a diverse set of fuels are used to heat homes during winter months. The most common fuels used for home heating are wood, coal, propane, natural gas, and pellets. The type of fuel used for heating is thought to be an important parameter in consideration of indoor air quality during periods of cold weather in this region. Previous studies have revealed some homes on the Navajo Nation that burn coal for heat can contain relatively high concentrations of fine particulate matter. To better understand the extent to which the type of heating fuel chosen can impact indoor air quality, gas phase pollutants and fine particulate matter are monitored inside and outside homes in two communities on the Navajo Nation: Shiprock, New Mexico and Tsaile, Arizona.

The filter samples collected enable characterization of the fine particulate matter in homes via gravimetric and ECOC (Elemental Carbon-Organic Carbon) analysis. These measurements give insight toward the chemistry of combustion byproducts from different fuels and how they may respectively affect indoor air quality. The monitored gas phase species include carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen dioxide and ozone. The gas phase measurements are gained through the employ of Pods, recently developed air monitors from the Hannigan Research Group at the University of Colorado. They serve as a low cost and portable alternative to other available technologies, enabling concurrent measurements in multiple homes, and a basis for comparison of homes using different fuels under very similar meteorological conditions.

2IA.7

Emission Patterns of PM and UFP from 3D Printers. Scott Steady, Bill Hoffman, ELLIOTT HORNER, *UL Environment*

The recognition that hardcopy devices (printers, copiers) are a source of fine and ultrafine particulate (UFP) matter (PM) led to testing standards which are now in wide use. PM emission levels are measured under standard conditions along with gaseous emissions, including ozone, VOCs and aldehydes. Emission levels must not exceed allowable limits in order to meet the testing standards, which are required in some jurisdictions or by some purchasers. The advent of 3D printing technology has introduced a new potential source of exposure in the indoor environment. The materials used (plastics) in 3D printers are also chemically different than the toners used in hardcopy devices and 3D print jobs will typically run much longer than hardcopy devices do. Further, 3D printers are being developed for consumer as well as commercial use and substantial markets are anticipated for these devices. Although these new products use different materials over longer times, yet in occupied spaces suggests that characterization of the PM emission patterns is needed. We have measured substantial amounts of UFP under some conditions but much lower emission patterns in some conditions. The effects of printing material and operating temperature on the emission pattern of the aerosol can be characterized with the environmental testing chamber technology that is used for standard testing of hardcopy devices. In addition to the emission patterns, the particle sizing spectrometer provides the ability to describe the aging pattern of the aerosol. This characterization of an emerging potential exposure will address the effects of printing material, operating temperature and duration of print job as well as describe basic aerosol aging patterns.

2IA.8

Effects of Walking Factors on Particle Resuspension via Human Walking. Kyung Sul, Yilin Tian, ANDREA R. FERRO, *Clarkson University*

Resuspension from human walking is known to be a significant source of particles in indoor air. Previous studies have found that there is large person-to-person variability in resuspension rate estimates determined from human participants. However, it is not fully understood how various factors affect particle resuspension. In this study, three walking factors are tested and their effects on resuspension fraction are analyzed. The factors tested are rotational speed of a foot of the device (zero (stomping), slow, medium, and fast rotational walking), pressure beneath the foot on the flooring (low and high), and type of flooring (vinyl and carpet). A mechanical foot apparatus is used as a standardized resuspension mechanism. The apparatus mimics human walking and repeats the same gait cycle with controlling electric actuators. The flooring is seeded with the ultrafine Arizona Test Dust (ATD) and stored in a chamber with controlled temperature and relative humidity for one day. The apparatus resuspends settled particle on the flooring. Size-resolved indoor particle concentrations in the chamber housing the apparatus are measured by an optical particle counter semi-continuously. A mass balance approach is used to calculate resuspension fractions for each condition using a full factorial experimental design. The effects of each factor and two factor interactions are analyzed. The tested factors contribute to the observed person-to-person variability and the strength of the effects depends on the flooring type.

2IA.9

Variability of Aerosols and Chemical Composition of PM10, PM2.5 and PM1 in the Prague Underground Metro. MICHAEL CUSACK, Jakub Ondrecek, Nicholas Talbot, Jaroslav Schwarz, Vladimir Zdimal, *Institute of Chemical Process Fundamentals of the ASCR, v. v*

One of the principal measures employed by developed countries to combat traffic congestion and emissions in urbanised areas is through the promotion of public transport. Of the various modes of public transport available in many urban areas, underground trains are considered one of the cleanest from an environmental perspective. However, the air quality in underground train networks has been shown to be especially poor, and not clearly understood. This work is a result of a 24 hour measurement campaign performed on a platform of the Prague metro. Real time measurements of PM concentrations, particle number concentrations and particle number size distribution were performed, of which the latter two were measured for the first time in the Prague metro. Furthermore, few publications exist on particle number size distribution for metro microenvironments. Gravimetric sampling of PM was also performed, providing vital information on the chemical composition of PM10, PM2.5 and PM1.

The variation of PM was found to be directly affected by the movement of incoming and outgoing trains into the tunnel, from turbulence and resuspension, with highest concentrations occurring during morning rush hour. Concentrations subsequently decreased when trains were less frequent. Particle number concentrations did not vary substantially during the day, increasing only gradually. Concentrations were at their highest when trains were less frequent. PM was found to be characterised mostly by Fe species (66% of PM10) as a result of wheel-rail mechanical abrasion. The next most abundant species were total carbon and secondary inorganic aerosols, most likely from surface air entrainment. Finally, certain trace elements such as Ba, CuO, MnO, ZnO, Cr_2O_3, Mo, Sb, Sn, Ni, Co, Li and Cd are all enriched during hours when trains are passing the platform, relative to out-of-operation hours, the probable sources being wheel-rail abrasion, sparking from electrical cables and brake pads.

2IA.10

An Experimental Assessment of the Dissociation of Ammonium Nitrate Aerosol.

NICHOLAS TALBOT, Vladimir Zdimal, Jakub Ondrecek, Jaroslav Schwarz, *PhD candidate*

The dissociation kinetics of ammonium nitrate was investigated experimentally utilizing a tandem differential mobility analyzer/scanning mobility particle sizer system (Dassios and Pandis, 1998). Monodisperse aerosol of ammonium nitrate has been produced by nebulizing ammonium nitrate solution, drying the polydisperse particles, bringing them to Boltzmann charge equilibrium using a Kr85 aerosol neutralizer, and selecting one mobility fraction in the Vienna type DMA. The aerosol generation system was located in a thermally insulated box kept at controlled temperature below 10 degrees C. The monodisperse aerosol was then diluted by mixing it with a dry, particle-free air and fed into a laminar flow reactor in which temperature, relative humidity and flow rate were controlled. Particle size distributions both upstream and downstream of the reactor were determined by an SMPS, consisting of a TSI EC 3080 provided with a long DMA, and a TSI CPC 3775. The stability of the aerosol generating system was further checked by the UCPC 3025A monitoring continuously the total particle concentrations.

In the series of dissociation experiments, we studied the size changes of the ammonium nitrate aerosol for three selected particle sizes (50, 100 and 200 nanometres), at four reactor temperatures (15, 20, 25, and 30 degrees C), and several flow rates (between 0.6 to 1.6 litres per minute).

The observed changes of particle size were compared to the predictions of a mathematical model taking into account the ammonium nitrate dissociation kinetics, Kelvin effect and diffusion of ammonia and nitric acid from the particle to the bulk phase taking into account the measured concentration of ammonia gas in the bulk phase. The model assumed evaporation in the continuum regime using the Fuchs-Sutugin correction term (Wexler and Seinfeld, 1990). Two cases are considered in relation to the evaporation process, evaporation from an ammonium nitrate solution and evaporation from a dry ammonium nitrate particle.

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2IA.11

Wintertime Indoor and Outdoor PM2.5 Northern Utah's Cache Valley.

Randy Martin, KORI MOORE, *Utah State University*

The Cache Valley in northern Utah, with a resident population of around 125,000 and no significant air pollutant point sources, has been well documented as having some of the nation's highest PM2.5 levels during wintertime inversion events. Since 2000, the air shed has exceeded the current EPA 24-hr standard (35 micrograms per cubic meter) an average of 19 times per year (range: 2 – 40). The area was officially promulgated as non-attainment in December 2009. Past research has shown that during elevated PM2.5 episodes, the bulk of the PM2.5 consists of ammonium nitrate. It is well established that the thermal equilibrium drives the particle back into the gaseous precursors at warmer temperatures and drier humidities and, as such, one of the protective measures recommended by state and local agencies has been for the susceptible populations to remain inside during poor air quality days. As a measure of the efficacy of this recommendation, indoor PM2.5 concentrations were measured at numerous residential and public buildings across several winter episodes and compared to local outdoor concentrations. Indoor PM2.5 concentrations were determined using AirMetrics MiniVol portable, filter-based samplers. While the ambient concentrations were found to vary from <5 to >80 micrograms per cubic meter, the indoor concentrations never exceeded 30 micrograms per cubic meter. Although there was some variability, the filter-based data produced a rough linear PM2.5 relationship of INDOOR = (0.19 * OUTDOOR) + 1.64, with an overall correlation coefficient of 0.49. Additionally, a subset of studies was conducted using MetOne Aerosol Profilers, a type of optical particle counter, which showed indoor particle counts for diameters $\leq$ 2.5 micrometers were $\leq$ 15% of outdoor particle counts. These data indicate that, in reference to the PM2.5 experienced in the Cache Valley, remaining indoors does serve as an effective protective measure.

2IA.12

Using Direct Feedback from IAQ Monitors to Change Human Behavior and Reduce Exposure to PM.

SANGEETHA KUMAR, Haley Grassi, Jing Qian, Julia Jacobs, Angela Benedict, Andrea R. Ferro, *Clarkson University*

Clarkson University (CU) and the St. Regis Mohawk Tribe are piloting a program using direct feedback from indoor air quality (IAQ) monitors as an intervention strategy to reduce exposures to indoor particulate matter (PM) sources. IAQ monitors were placed in the homes of forty residents of the St. Regis Mohawk Tribe in Akwesasne, NY for two weeks to measure baseline concentrations of PM and 5 other IAQ markers. An intervention was then conducted, which included a home audit and tailored mitigation strategies based on the audit and baseline IAQ data. The monitoring continued for another two weeks. Participants kept activity diaries for the duration of the study to correlate levels of PM with specific activities. Data analysis includes a comparison of pre- and post-intervention levels of IAQ marker concentrations as well as characterization of the IAQ associated with specific sources. The study also found several homes with critical IAQ problems (e.g., leaking stoves) that were corrected. Based on the results of the exit survey instrument, participants valued highly the direct feedback from the monitors as well as the tailored mitigation strategies provided in person by the technician. Significant improvements in IAQ were observed using this intervention strategy.

2IA.13

Overview of Air Quality Regulations in South America.

ANDRÉ HENRIQUE PEREIRA DE FREITAS LEAL, Lupita Montoya, *University of Colorado Boulder*

In the US, the Environmental Protection Agency (EPA) established the National Ambient Air Quality Standards (NAAQS) selecting six pollutants as indicators: particulate matter, carbon monoxide, nitrogen dioxide, sulfur dioxide, ozone and lead. The transportation growth and accelerated urban development in developing countries are a threat to air quality worldwide. In Latin America, most of the air quality regulations established are based on EPA regulations. Previous efforts to determine the state of ambient air quality regulations in Latin America have been performed but that information is limited and hard to access. Indoor air quality regulations are even more scant. The main objectives of this project are to:

1) Determine and compare outdoor air quality regulations existing in South America countries with those of the US EPA and WHO guidelines.
2) Identify indoor air quality studies and regulations from countries in South America and assess that information.
3) Discuss the quality of the information available and prepare recommendations.

2IM.2

Atmospheric Aerosol Measurement Using Tethered Balloon Package System and Equipment Development. Kang-Ho Ahn, HEE-RAM EUN, Hong-Ku Lee, Lee Gun Ho, Yong-Hee Park, Chi-Young Choi, In-Kyu Hwang, *Hanyang University, R. of Korea*

It is important to understand the atmospheric aerosols compositions and size distributions since they greatly affect the environment and human health. Particles in the convection layer have been a great concern in global climate changes. To understand these characteristics satellite, aircraft, and radio sonde measurement methods have usually been used. An aircraft aerosol sampling using a filter and/or impactor was the method commonly used. However, the flight speed particle sampling had some technical limitations. Moreover, the flight legal limit, altitude, prohibited airspace, flight time, and cost was another demerit. To overcome some of these restrictions, Tethered Balloon Package System (T.B.P.S.) controlled by electrical winch was developed with a very light optical particle counter (OPC), impactor, and condensation particle counter (CPC). Not only does it collect and measure atmospheric aerosols depending on altitudes, but it also monitors the atmospheric conditions, temperature, humidity, wind velocity, pressure, GPS data, during the measurement.

2IM.3

MWCNTs Dispersion and Aerosolization Using EAAA (Electro-static Assist Axial Atomizer). GUN-HO LEE, Hong-Ku Lee, Hee-Ram Eun, Yong-Hee Park, In-Kyu Hwang, Chi-Young Choi, Jin-Kwon Kim, Ellen Kim, Il Je Yu, Kang-Ho Ahn, *Hanyang University, R. of Korea*

Carbon nanotubes (CNTs) are one of the nanomaterials that were discovered by Iijima in 1991 for the first time. They have long cylindrical and axi-symmetric structures and are made by rolling graphene sheets. Due to their large length-to-diameter ratio, they are called nanotubes. CNTs are categorized as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) based on the shell structures. CNTs are broadly used in various fields, such as scanning probe microscopy, ultra fine nano balance and medicine, due to their extraordinary thermal conductivity, electrical and mechanical properties. Because long, straight CNTs have the same shape as asbestos, which cause cancer in cells lining the lung, there have been many studies on the effects of MWCNTs on human health that have been conducted. Stable atomization of CNTs is very important for the estimation of inhalation toxicity. In the present study, electro-static assisted axial atomizer (EAAA), which is the instrument that uses MWCNTs and aerosolizes them by transforming the single fiber shape using ultrasonic dispersion and electric field, was invented. EAAA consists of a ultrasonic bath for dispersion of MWCNTs and a particle generator for atomizing single fibers. The performance evaluation was conducted in order to assess the possibilities of a 6-hour straight atomization with stability, which is the suggested exposure time in a day for the estimation of inhalation toxicity.

2IM.4

Chemical Analysis of Microliter-sized Liquid Samples Using Ultrasonic Nebulization and Aerosol Mass Spectrometry. KELSEY BOULANGER, Eben Cross, James Hunter, Anthony Carrasquillo, Manjula Canagaratna, John Jayne, Philip Croteau, Jesse Kroll, *MIT*

Aerosol mass spectrometry allows for detailed characterization of the chemical composition of organic species dissolved in liquid samples. However, traditional aerosol atomization typically requires liquid volumes of tens to hundreds of milliliters, which excludes many environmental samples. Here we demonstrate a nebulization technique whereby small volumes, on the order of ten microliters, are aerosolized and sent into an Aerodyne Aerosol Mass Spectrometer (AMS) for highly time- and mass-resolved chemical analysis. This technique passes ultrasonic vibrations through a thin film on top of a liquid reservoir, leading to the nebulization of liquid droplets placed on the film and significantly reducing the liquid volume traditionally necessary for AMS analysis. We present results from a variety of standards, including solutions of ammonium nitrate, ammonium sulfate, and various organic compounds, and compare aerosol species ratios, elemental ratios, and mass spectra to those obtained through conventional atomization. We examine the effects of sample concentration, volume, and airflow on the mass spectra as well as the total mass spectrometric signal and linearity. We also demonstrate the applicability to environmental samples using filter extracts from chamber secondary organic aerosol (SOA) experiments and comparing to online direct AMS measurements of aerosol composition. This is a promising technique for obtaining mass spectra of samples previously considered too small for AMS analysis, making it a viable option for the chemical characterization of environmental samples and other small-volume analytes.

2IM.5

Shear Induced Mixing of Laminar Flows: Implications for Aerosol Measurements. MATTHEW BROWN, Suresh Dhaniyala, *Clarkson University*

Most widely used aerosol instruments rely on a common flow design to achieve highly sensitive measurements. The flow arrangement typically is composed of two concentric laminar flows that merge together in a measurement region, as in a Differential Mobility Analyzer (DMA) or an optical particle counter. When the flows merge, it is assumed there is no particle mixing or dispersion, resulting in diluted flow. For accurate aerosol measurements under a range of operating conditions, it is important to verify this assumption. In this study, we designed an experimental setup to obtain near axi-symmetric concentric flows and determined the extent of particle mixing under various shearing velocity conditions. The mixing characteristics were then obtained as a function of the relative velocity ratios of the two flow streams upon introduction. The experimental results suggest that there is a strong correlation between the extent of particle mixing and the velocity ratio of the flows. The results of this study are used in conjunction with aerosol transport modeling to relate measurement accuracy (sizing with a DMA or an optical particle counter) to its operating conditions. The experimental results of flow mixing and the implications for particle measurements will be presented.

2IM.7

A New Personal Sampler for Measuring Inorganic Acid Mist and Gases: The Validation Test. CHIH-HSIANG CHIEN, Lin Shou, Alex Theodore, Chang-Yu Wu, Yu-Mei Hsu, Brian Birky, *University of Florida*

A novel personal sampler has been designed to overcome the inaccurate measurement of inorganic acid mist and gases in NIOSH Method 7903: a parallel impactor for classifying acid mist following ACGIH/ISO/CEN defined human respirable fraction, a porous membrane denuder for adsorbing acidic gases, and a filter pack to collect small particles penetrating the impactor and the denuder. The personal sampler was demonstrated to maintain particle collection efficiency greater than 99% for 4-hour sampling time as well as 4-hour gas collection efficiency over 95% for sulfur dioxide, hydrochloric acid, and nitric acid with a feed concentration of 10, 10, and 4 ppm, respectively. Additionally, the sampler successfully separated the collection of sulfur dioxide from that of sulfuric acid, thus eliminating the interference when the sulfur dioxide and sulfuric acid coexist.

To further validate the sampler’s performance, testing was carried out according to OSHA’s Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis. Under both low (22%) and high (64%) relative humidities, the sampler’s analyte recovery was above 99%. While particle growth due to the hygroscopicity of sulfuric acid shifts particle collection toward the impactor at high RH, the mass concentration of sulfuric acid was conserved for the combined impactor and filter collection. The storage stability of the sulfuric acid samples taken every 5 days showed that, for ambient storage, the overall standard error of the samples collected in 25 days was 5.76% with 95% confidence limit of 11.28%, while for refrigerated samples, the standard error was 4.96% and 95% confidence limit was 9.65%, indicating both storage methods impose no significant effect on the samples.

For aerosol collection, the parallel impactor has been further developed for the thoracic fraction. Further experiments will be carried out to verify whether the personal sampler’s particle collection efficiency follows the thoracic convention.

2IM.8

Development of Sheathless Particle Classifier with Electrometer. HIROYUKI YAMADA, Hiroshi Okuda, *National Traffic Safety and Environment Laboratory*

A nano-aerosol monitor (NAM) which is a combination of a classifier based on new concept and electrometer has been developed. The classifier of NAM does not require the sheath flow which may decrease a sensitivity. Since the electrometer is in favor of using under the vibrating conditions, the NAM can be applicable to PN-portable emission measurement system (PEMS). It was confirmed that the NAM can classify particles as expected with sodium chlorite particles with 23 nm. The equality of data by the NAM and PMP methodology was confirmed with exhausts from recent automobiles with chassis dynamometer and constant volume sampler (CVS). As for tested vehicles, a gasoline direct injection passenger car and two diesel heavy duty trucks with DPF were selected. In all cases, the profiles by the NAM were similar to those by PMP methodology and exhibited linear correlation to the PMP methodology even in various test modes. The NAM does not have a volatile particle remover (VPR) which is equipped with the PMP methodology to remove the volatile particle. Therefore, in the exhausts from recent vehicles, ratios of volatile particles seem to be a constant in various conditions, and it is possible to obtain similar data with the PMP methodology by the particle measurement system which does not have the VPR.

2IM.9

Standard Test Method for the Measurement of Filtration Efficiency of Electret Facepiece Respirators Challenged with Diesel Exhaust. SWATHI SATISH, Jacob Swanson, David Kittelson, David Y. H. Pui, *University of Minnesota*

Electret respirators are widely used by workers in underground mines as respiratory protection against exhaust from heavy duty diesel engines. The current NIOSH standard testing procedure for evaluating the filtration efficiency of air-purifying respirators requires using sodium chloride (NaCl) or dioctyl phthalate (DOP) as the test aerosol. This method is not easily adaptable for diesel exhaust as preliminary results show that unlike NaCl and DOP, diesel particulate matter (DPM) has characteristics that depend very nonlinearly on operating and sampling conditions. This poster presents a methodology that enables us to achieve a high degree of control over those properties of DPM that have the potential to significantly impact the measurement of filtration efficiency. By fixing the ratio of elemental carbon (EC) to organic carbon (OC) in the exhaust, the dilution ratio and the residence time, DPM with reasonably well-defined characteristics will be obtained regardless of the diesel engine used to generate exhaust.

Exhaust from a diesel engine is first treated with an over-sized diesel oxidation catalyst (DOC), which oxidizes all of the organic compounds to produce dry black carbon aerosol. Organic carbon in the form of motor oil vapor is injected into the high temperature flow stream. The resulting mixture is diluted with clean dry air to facilitate adsorption and condensation of oil vapors onto the soot particles, forming the required standard test aerosol. The respirator is tested with this aerosol at 85 L/min and its filtration efficiency is determined using mass concentration measurements obtained from laser photometers placed upstream and downstream of the respirator. The significance of the proposed method lies in the concept of creating DPM with a unique set of properties according to the requirements of its application.

2IM.10

NIOSH Center for Direct Reading and Sensor Technologies. D. Gayle DeBord, MARK D HOOVER, *National Institute for Occupational Safety and Health*

To further increase its capabilities and partnerships to develop, validate and apply new technologies to address relevant occupational and environmental exposures, the National Institute for Occupational Safety and Health has established a virtual NIOSH Center for Direct Reading and Sensor Technologies. The new center will serve as a home for NIOSH's longstanding work in the area of exposure assessment devices—work that is done across the Institute. The Center has identified key strategic goals to better understand and control occupationally relevant hazards, exposures to those hazards, and potential resulting health effects. Initial activities are being directed to 1) coordinating a national research agenda for direct reading and sensor technologies, 2) developing guidance documents pertinent to direct reading methods and sensors such as validation and performance characteristics, 3) development of training protocols and 4) establishing partnerships to collaborate in the Center's activities. These activities recognize and will capitalize on the fact that sensors are being used more frequently in many different settings from research to clinical practice. These activities also align with conclusions of the recent National Research Council report on Exposure Sciences for the 21st Century which identified direct reading methods and monitors as being an important driver for the future of exposure sciences. Major questions include: Do these methods accurately measure what they are supposed to be measuring? How can they be adequately calibrated and validated? When are they limited to use for screening and when can they provide an accurate characterization of specific hazards? And, finally, given the large amounts of data that may be collected from such technologies, how can those data be feasibly analyzed and interpreted? NIOSH welcomes partnerships and collaboration to ensure that sensors will be one of the technologies that can move exposure sciences forward at a rapid pace.

2IM.11

Detection of Light vs. Heavy Atoms with a Laser Induced Plasma Ionization Source for Single Particle Analysis. ANDREW J. HORAN, Justin Krasnomowitz, Murray Johnston, *University of Delaware*

On-line determination of the chemical composition of nanoparticles (<100nm dia.) in the atmosphere represents a significant analytical challenge. Laser induced plasma ionization in the Nano Aerosol Mass Spectrometer (NAMS) has proven effective for determining quantitative elemental composition of these particles containing low atomic number non-metals (C, O, N, S, Si). The ability to detect and quantify larger elements, both metals and non-metals, is desirable, but not fully tested. Here, the properties of this ionization are explored for a selection of elements which span the Periodic Table. Solutions of group I and VII salts, $Cr(NO_3)_3$, $Fe(NO_3)_3$, $AgNO_3$, $Al(NO_3)_3$ TiO_2, ZnO, poly(dimethylsiloxane), $Pb(NO_3)_2$ and silver nanoparticles are aerosolized (TOPAS ATM226 generator) to produce a flow of 80-100nm diameter particles. Additionally, mixtures of these solutions with organic molecules such as HEPES and sucrose are examined.

Particles are sampled through a flow limiting orifice and focused in an aerodynamic lens assembly for transmission into the ion source region. Positive ions produced by laser irradiation are analyzed with a reflecting time-of-flight mass spectrometer (R.M. Jordan Company). Charge states of atomic ions are used to assign the dominant type of ionization. Particles containing low atomic number nonmetals give multiply charged atomic ions indicative of plasma ionization. Few singly charged ions are observed (other than H+). In general, we have found that the relative mole fractions of C, O, N, S, Si are quantifiable to within +/- 10% of expected values. For elements in groups I, II, and VII, the mass spectra consist of both singly and multiply charged ions. Elemental compositions are generally quantifiable to within 20% of expected values. Metals toward the center of the Periodic Table give primarily singly charged ions indicative of desorption ionization. The metal ion signal is not quantitative, but the non-metal anion components are generally quantitative to each other.

2IM.12

Reduced Graphene Oxide: Towards an Absorbing Aerosol Standard. JAMES RADNEY, Christopher Zangmeister, *National Institute of Standards and Technology*

Gas-phase absorption measurements have made steady technical advancement due to the utilization of calibration standards that allow for instrument calibration and intercomparison. To date, no such material exists for aerosol optical measurements. Here, we demonstrate the feasibility of thermally reduced graphene oxide (rGO) aerosol as a candidate for an absorbing aerosol standard. Graphene oxide solutions were prepared by horn sonication of multi-sheet assemblies in DI H2O to produce a solution that is shelf-stable for long periods of time. The solution was aerosolized forming aerosol particles with a morphology resembling crumpled paper and reduced at 220 degrees Celcius to produce particles that behave as mass absorbers for sizes below $\approx$ 400 nm. Using pre-measured mass specific cross-sections, we observe agreement between the solution concentration and spectra of the polydisperse aerosol, measured using a photoacoustic spectrometer. Further, we show that rGO makes a good candidate for comparison between in situ spectra and filter based measurements.

2IM.13

Electrospray Aerosol Generator with Integrated Soft X-Ray Neutralizer and Usability Enhancements. SHERRIE ELZEY, Jacob Scheckman, Aaron Avenido, Tim Johnson, *TSI Incorporated*

Electrospray is a common and useful technique for aerosolization of suspended particles and generation of small particles from solutions of dissolved solutes. Electrospray offers significant advantages as a particle generator for aerosol measurements, such as Scanning Mobility Particle Sizer (SMPS) particle size analysis, because it produces stable and small liquid droplets (~150 nm). This method is regularly used to generate particles as small as 2 nm to greater than 200 nm. These particles can then be analyzed in applications including basic aerosol research, protein sizing, manufactured nanoparticle sizing, and others.

The droplets formed by electrospray are highly charged and decrease in size as they dry. The surface charge on the droplet increases and the repulsive force can cause the droplets to fragment. The remaining small particles are highly mobile and strongly repel each other. To combat droplet disintegration and particle losses, electrosprayed droplets can be neutralized using radioactive sources such as Po-210 (Kaufman et al., 1993).

Low-energy soft X-ray neutralizers have been used as an alternative to radioactive sources (Shimada et al., 2002; Lee et al., 2005). Like radioactive neutralizers, soft X-ray neutralizers are able to bring particles to a stable bipolar charge distribution. This has recently been characterized for use in SMPS analysis (Knobel et al., 2013).

Here, we present a new Electrospray Aerosol Generator (EAG) with an integrated soft X-ray neutralizer. During verification of this new device, the size of the generated droplets was characterized and the stability of particle output was evaluated. The EAG was then used to aerosolize PSL of various sizes, as well as metal oxide nanoparticles, for further size distribution analysis with an SMPS. The EAG presented here has also been enhanced to improve usability. A primary mode of status feedback in an electrospray is visualization of the Taylor cone generated by balancing flows and voltages. In most cases, a small viewing window is used to magnify the capillary tip. Instead of a viewing window, a digital camera is used to produce the image of the electrospray at the capillary tip, and the live video image is displayed on the instrument's touch panel.

Additionally, a particularly short capillary is used, minimizing surface area for particle adhesion and reducing the occurrence of capillary clogging. Further, the capillary mount is designed for easy replacement and also allows for easy connection to an autosampler for automated sample analysis.

2NP.1

Particle Formation in Vehicle Exhaust: Modelling the Nucleation and Growth. MIIKKA DAL MASO, Miska Olin, Topi Ronkko, Jorma Keskinen, *Tampere University of Technology, Tampere, Finland*

Automobile emissions contain significant amounts of particles, some of which are formed during the combustion process (soot particles). Exhaust after-treatment systems (ATS) can lead to gas-phase formation of low-volatility vapours which can act as nucleation precursors, such as sulphuric acid or organic diacids. These vapours also condense in diluting exhaust, growing the fresh particles to larger sizes. Obtaining an accurate description of the nucleation and growth processes in the cooling exhaust is challenging from both modelling and experimental viewpoints. Few observations exist of the aerosol size distribution in the size range of a few nanometers, especially coupled with observations of gas-phase nucleating species such as sulphuric acid.

In this study, we have simulated the dilution process after emission, and the later development of the emitted size distribution as a function of the variation of the raw emission as well as the environmental conditions. We present three different modeling approaches: a) molecular-resolution process modeling of the dynamics of the freshly-formed size distribution, b) 0-D process modeling of aerosol dynamics and secondary aerosol formation after initial dilution, and c) detailed computational fluid dynamics (CFD) studies of experimental situations with either natural or laboratory dilution conditions.

With comparisons to experimental data, we discuss the sensitivity of sulphuric acid-driven particle formation in vehicle exhaust to environmental conditions such as relative humidity and temperature; in addition, we show the sensitivity of the formation of nanoparticles to the pre-existing particle concentration, and different ATS. According to our results, classical nucleation theory is unlikely to be an adequate description of particle formation in this case; in addition, we show that emulating real-world dilution conditions in laboratory dilution systems is subject to constraints related to turbulent mixing that may affect the observed size distribution and therefore, also the obtained emission factors significantly.

2NP.2

Chemical Mechanisms of Nanoparticle Growth Studied through a Combination of Ambient and Laboratory Measurements. MURRAY JOHNSTON, Bryan R. Bzdek, Joseph DePalma, Andrew J. Horan, *University of Delaware*

Improved predictions of the frequency, growth rates, and climatic impacts of new particle formation (NPF) require knowledge of the chemical mechanisms by which nucleated nanoparticles grow. Our group has performed a combination of ambient measurements, laboratory experiments and computational work to study growth mechanisms of nanoparticles. The two main contributors to growth during NPF are sulfate and organics. Quantitative elemental composition measurements with the nano aerosol mass spectrometer allow the relative amounts of each to be quantified. Both laboratory and field measurements show that particle phase sulfate is adequately described by condensation of gas phase sulfuric acid. Neutralization of sulfate by either ammonia or amines is somewhat less understood, and recent work suggests that it is dependent on particle water content. Carbonaceous matter is poorly understood at a molecular level, although elemental and molecular composition measurements of ambient particles show that it is highly oxidized. Recent ambient measurements show that this carbonaceous matter often contains a substantial amount of nitrogen. This important discovery is the subject of current laboratory experiments of nanoparticle growth under controlled conditions where nitrogen incorporation might be expected to occur. This work is aided by the use of a new method for nanoparticle collection that allows molecular analysis of size-selected particles down to 10-nm in diameter.

2NP.3

Aerosol Formation Initiated by Nucleation of Radical-Water Complexes. SAMBHAV KUMBHANI, Emily Burrell, Shirts Randall, Jaron Hansen, *Brigham Young University*

Aerosols affect climate and human health both directly and indirectly. Atmospheric aerosols are either primary or secondary. Primary aerosol particles enter the atmosphere directly and include sources such as soot, mineral dust, sea salt and pollen. Secondary aerosols form in the atmosphere by the condensation of gases. The formation and growth of secondary particles is typically modeled using nucleation theory. However, the number aerosol particles in the atmosphere predicted by models is smaller than what is actually measured. Radical-molecule complexes may act as an initial nucleating site for particle formation. HO_2 radical is the most abundant peroxy radical in the atmosphere and forms a strong hydrogen-bonded complex with water. We studied aerosol nucleation through HO_2-H_2O complex formation using a flow reaction coupled to a scanning mobility particle sizer (SMPS). We measured the size distribution (between 0.8 and 1000 nm) and concentration of aerosol particles with respect to reaction time, initial concentration of HO_2 radical, and concentration of water vapor. The experimental work was complimented with high level ab initio studies of the HO_2-$(H_2O)_n$ (n = 1–5) complexes. The computational work provids insight into the Gibb’s free energy, enthalpy, and entropy of complex formation. Both experimental and computational results indicate that HO_2-H_2O complex can act as a nucleating agent for new particle formation. Future work will investigate the ability of other radicals to initiate particle formation.

2NP.4

Observation of Sub-3 nm Particles and New Particle Formation Events in Urban Shanghai, China. Shan Xiao, MingYi Wang, JianMin Chen, Xin Yang, QingYan Fu, LIN WANG, *Fudan University*

Measurements of nucleation mode particles, especially sub-3 nm particles, are crucial in investigating atmospheric New Particle Formation (NPF) processes. In this study, particle size distribution in the range of 1.34 nm~615.3 nm was recorded from 25th Nov. 2013 to 25th Jan. 2014 in urban Shanghai, using the combination of one Particle Size Magnifier (PSM), one nano-Scanning Mobility Particle Sizer (SMPS), and one long-SMPS. During the 62-day campaign, 12 NPF events were identified with strong burst of sub-3 nm particles up to 2×105 particles cm-3 and subsequent fast growth to nanoparticles. The observed nucleation rate J1.34, formation rate J3, and growth rates GR1.34~2.39nm, GR2.39~7nm, and GR7~20nm were calculated to be 113.1~272.4 cm-3 s-1, 2.7~10.6 cm cm-3 s-1, 0.49~8.1 nm h-1, 3.1~35.67 nm h-1, 4.46~38.34 nm h-1, respectively. The Condensational Sink (CS) was in the range of 0.030~0.10 s-1. The observed CS, GR7~20nm, and J3 are similar to those from other urban cities in China (Wu Z. J. et al. (2007)). Nucleation rate J1.34 and GR1.34~2.39nm, as the first one measured in China, are much larger than those in Europe (Kulmala M. et al. (2012)) and North America (Yu H. et al. (2014)).

H2SO4 proxy calculated from the concentration of sulfur dioxide (SO2) and solar radiation intensity was in the range of 2.3~6.4×107 molecules cm-3, which contributed to 30% of GR2.39~7nm, and 18% of GR7~20nm in average, respectively. Hence, volatile organic compounds (VOCs) likely played an important role in these NPF events.

Based on comparison of diurnal profiles of sub-3nm particles, H2SO4 proxy, and PM2.5, NPF processes in urban Shanghai are likely to occur with high concentrations of H2SO4 proxy and low PM2.5.

2NP.5

Shrinkage of New Atmospheric Particles in an Urban Area of Southern Europe. Elisabeth Alonso-Blanco, F. Javier Gomez-Moreno, Lourdes Nunez, Manuel Pujadas, BEGONA ARTINANO, *CIEMAT*

New Particles Formation (NPF) processes involve a first formation phase of particles from precursors (gases, ions…) and a second phase of growth. Some authors as (1) (2) (3) and (4) have observed during the latter a sudden decreasing trend in the particle size, a.k.a. shrinkage.

Changes in meteorological conditions during the NPF process, especially, a wind speed and temperature increase can determine the occurrence of shrinkage processes (1;2). These changes facilitate the evaporation of semi-volatile species condensed in the recently formed aerosol. Shrinkage processes have been analyzed in an urban background site in Madrid (Spain) through the following measurements and instruments:

1) Scanning Mobility Particle Sizer (TSI-SMPS: DMA3081 with CPC 3775) providing aerosol size distribution (14-660 nm).
2) Differential Optical Absorption Spectrometer (DOAS: OPSIS AR-500) for ambient concentrations of NO, NO2 and O3.
3) Meteorological tower providing data on precipitation, pressure, temperature, relative humidity (RH) and wind speed and direction at the site.

A number of shrinkage processes have been characterized during NPF events linked to an increase of wind speed during the growth phase of the newly formed particles. Mostly, these occur during spring and summer, when nucleation takes place at this site.

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2NP.6

Insight into Particle Growth Rates and Controls from Two Years of SMPS and HTDMA Data. MANASI MAHISH, Don Collins, *Texas A&M University*

Data from a scanning mobility particle sizer (SMPS) and a humidified tandem differential mobility analyzer (HTDMA) have been used to study the controls on growth of recently formed particles at the DOE Southern Great Plains site in Oklahoma. New particle growth events during 2009 and 2011 that spanned at least several hours were identified and both the particle size distributions and size-resolved hygroscopicity distributions from each episode were fitted with lognormals. Time series profiles of the resulting growing mode median particle diameters and hygroscopic growth factors were then fitted using appropriate mathematical forms and their time-dependent slopes used to quantify the rates of change of particle size and hygroscopicity, reflecting the overall addition of mass and the net properties of that mass, respectively. These changes were also translated into those of the hygroscopicity parameter, kappa, to better link with other datasets and to more easily partition the contributions of generic aerosol components to the observed growth. After subtracting the change attributable to coagulation, the remaining growth was assumed to result from condensation of a more hygroscopic inorganic component and a less hygroscopic organic component having a kappa estimated from available aerosol chemical speciation monitor (ACSM) data describing the PM1 aerosol organics. The rates of addition of those two condensable components were related to requisite gas phase concentrations to better separate the hourly, daily, and seasonal variations in responsible atmospheric chemistry of interest from interference from the quantifiable size-dependence of the growth rate. Both the frequency of the observed growth events and the particle growth rates during them have summer maxima and winter minima. Partitioning of the more and less hygroscopic condensing species often varies during an event, with the more hygroscopic component contributing relatively more during the daytime. Both representative case studies and averaged profiles will be presented.

2NP.7

Particle Nucleation and Vertical Profiles of 8-15 nm Particles at the DOE Southern Great Plains Facility from 300m to 1000m Above Sea Level. JOHN ORTEGA, James N. Smith, James Greenberg, *National Center for Atmospheric Research*

New particle formation events have been witnessed globally in widely varying environments. It is generally assumed that particle formation events require a low background aerosol population so that condensable oxidized organic gases and sulfuric acid clusters will form stable clusters rather than condense onto existing particles. There have been numerous campaigns and long-term monitoring stations based on ground-level measurements that have observed the formation of nucleation-mode particles. However, simultaneous measurements that show the horizontal and vertical extent of these new particles and associated concentration of condensable gas-phase species is difficult. The technology for remote sensing (satellite-based) techniques is not available. Measurements of new particle formation from airplanes is not practical because of expense, the unpredictable nature of the events, and the limited amount of time and space over which sampling can occur. During the 2013 Southern Great Plains-New Particle Formation Study in Oklahoma, vertical profiles (from 0 – 1000 m above ground level) of aerosol number concentration were made using two condensation particle counters (CPC) on a tethered balloon. The CPCs were configured to detect particles with diameters larger than 8 and 15 nm respectively. The particle concentration profiles between these two diameters were then calculated by taking the difference of the two measurements. A small meteorological package was used to obtain pressure (altitude), temperature, wind speed and wind direction. On several occasions, small particle concentrations were dramatically higher between 300 and 500 m above the ground than at the surface, indicating that nucleation occurred aloft. On other occasions, particle concentrations were generally homogeneous. Concentrations above the mixed layer (~600-800 m above ground) were generally much lower. This presentation will summarize the vertical measurements, instrument performance, meteorological conditions, and comparisons with concurrent ground-based particle size distributions (both at the launch site and 100km to the south).

2PH.2

An Automated Microenvironmental Aerosol Sampler (AMAS) for Location/Activity Exposure Assessment.

CASEY QUINN, David Cate, Dan Miller-Lionberg, Charles Henry, John Volckens, *Colorado State University*

This work describes the development and evaluation of an automated microenvironmental aerosol sampler (AMAS). Existing personal exposure assessment devices and methods are expensive and cumbersome which hinders exposure assessment for larger-scale epidemiology studies. The AMAS is a low-cost, wearable device containing four filter-pump assemblies designed to measure personal exposure to air pollution for both panel-based epidemiological studies as well as 'citizen science' applications. A novel aspect of this device is that it collects particulate matter from within distinct personal microenvironments (such as at home, at work, and in transit). The device operates autonomously, using data from on-board sensors (GPS, light intensity, temperature, pressure, acceleration) to determine when an individual enters a given microenvironment and then initiates sampling through one of three micropump-filter assemblies. The AMAS is about the size of a cell phone, weighs less than 250 g, and consumes about 900 mW of power, which allows for up to a forty-eight-hour run time. Anodic stripping voltammetry, colorimetric microfluidic paper-based analytical devices (mPADs), and image processing were used to quantify the trace metals (lead, cadmium, and zinc), reactive oxygen species, and black carbon collected on the filters. These analytic techniques provide rapid but accurate sample analysis which also reduce analytic costs by a factor of 10 overall (total analysis cost under $2 per sample). Filter analysis results for reactive oxygen species (5-20 pmol min-1 µg-1), lead (3-6 ng), cadmium (1.0-2.5 ng), zinc (1.5-4 ng), and black carbon (0.2-4 µg (m3)-1) were determined for the 48-hour personal samples. These detection sensitivities translate to air concentrations of nanograms per cubic meter (or lower, depending on sampling duration in each microenvironment). The sampler collection efficiency and evaluation methods were verified using traditional analytical techniques and personal samplers. The results indicate that the AMAS is a feasible approach for low-cost analyses of exposures in common microenvironments.

2PH.3

Impact of Urban Growth Form and Fleet Electrification on Emissions, Concentrations, and Exposures for Nitrogen Oxides and Select Toxic Volatile Organic Compounds.

HAOFEI YU, Amy L. Stuart, *University of South Florida*

Oxides of nitrogen (NOx) and select volatile organic compounds (VOCs) are important pre-cursor gases for secondary aerosols and also pose a threat to public health themselves. Worldwide, urbanization and increased vehicle traffic have substantially impacted their emissions and ambient concentrations in urban areas. Previous studies suggest that urban planning and "cleaner" vehicles could help decrease emissions and improve air quality. However, differences in impacts on distinct pollutants, and on human exposures, are still poorly characterized. In this study, the impact of alternative urban growth forms and fleet electrification on emissions, ambient concentrations, and exposures for five pollutants (NOx, 1,3-butadiene, benzene, formaldehyde, and acetaldehyde) were investigated. Three potential future scenarios for the Tampa area in the year 2050 were developed, representing sprawl growth, compact growth, and compact growth with vehicle fleet electrification. Emissions for each scenario were projected using planning data and ambient concentrations in Hillsborough County were estimated with the CALPUFF dispersion model. Chronic and acute population-weighted exposures were subsequently estimated from annual average and 1-hour maximum concentrations, respectively. Results suggest that the compact scenario would have less total emissions in the Tampa Bay region than sprawl for all pollutants except acetaldehyde. Lower NOx concentrations and exposures were also predicted for Hillsborough County, but the opposite was predicted for the VOCs studied. Fleet electrification was predicted to decrease total emissions, concentrations and exposures of the VOCs, but increase all three for NOx, due to the increased burden on power plants. Differences in the type and location of emission sources were responsible for differences in impacts between pollutants. Results suggest that urban planning policies directed at improving public health must carefully considered impacts of distinct pollutants and time scales of exposure. Without this, improvements for some pollutants may be counteracted by decrements for others.

2PH.5

E-cigarettes: Aerosol Sampling and Droplet Size Measurement. JOHN MCAUGHEY, Ross Cabot, Caner Yurteri, David Lawson, *British American Tobacco*

Electronic Cigarettes (also known as e-cigarettes or Electronic Nicotine Delivery Systems – ENDS), are a new type of product gaining popularity with adult cigarette smokers. They typically produce a condensation aerosol by rapidly evaporating a formulation containing nicotine, water, glycerol and propylene glycol mixtures.

The regulatory landscape around these devices is diverse and they are variously considered as consumer, tobacco or medicine products. Areas of regulatory interest may include the nature and consistency of the device output and how these may influence delivered and retained dose of the formulation components. Thus there is a core need for particle size and concentration data, and the development of robust measurement methods.

This study sought to measure droplet size distributions by real-time analytical methods using commercially available equipment. Measurements were conducted by electrical mobility (EM: Model DMS-500 MkII, Cambustion, UK) and by laser diffraction (LD: Spraytec, Malvern, UK). The Smoking Cycle Simulator (SCS: Cambustion, UK) was used to generate appropriate puff profiles with minimal dilution.

Volume-weighted median droplet diameters (dV50) from a variety of e-cigarette devices were typically less than 500 nm by LD and less than 300 nm for EM, slightly larger than equivalent tobacco smoke measurements of approximately 210 nm. Precision data were dependent on the e-cigarette tested but coefficients of variation of less than 4–5% were observed for the better performing products. This degree of precision meets the acceptance criteria for droplet size distribution (dV50 ± 20% for dV50 < 1000 nm) for laser diffraction measurements defined in the US Pharmacopeia. No equivalent standards are available for electrical mobility measurements. In conclusion, droplet size measurement for e-cigarettes can be readily achieved using commercially available sampling and measurement instrumentation, with suitable precision to meet potential regulatory requirements.

2UA.1

Urban and Suburban Intermodal Fraction of Atmospheric Aerosol in Winter 2014. JANA KOZAKOVA, Jan Hovorka, Jaroslav Schwarz, *Charles University in Prague*

Fine (PM1) and coarse (PM10-2.5) aerosols differ not only in size but in chemical composition, health effects, type of sources and others. A dividing line between fine and coarse aerosol is not clearly defined. These fractions overlap in the aerodynamic particle size range 1-2.5 micrometers, also called the intermodal fraction. Sources of both coarse and fine aerosols contribute to the intermodal fraction to a different extent relating to different meteorological conditions and types of locations. According to several studies, the intermodal fraction highly correlated with coarse aerosol in dry areas during high wind speed episodes. In contrast, other studies have shown higher or comparable correlation with fine aerosol. The aim of this study was to characterize the intermodal fraction in urban and suburban localities and estimate at what extent fine/coarse aerosol sources contribute to this fraction. Measuring campaign took place from 5.2.-7.3.2014 at urban and suburban locality situated up-wind of the Ostrava city. At both sites, five minute integrates of aerosol size distribution from 0.524-20 micrometers were determined and daily samples of size resolved aerosol particles were sampled by Personal Cascade Impactor Sampler (PCIS) and Berner Low Pressure Impactor (BLPI). The results from PCIS showed that the intermodal fraction represented mass range 3-31% of the total PM10 in both locations with higher mass range in the suburban locality. Average concentrations of coarse, intermodal and fine fraction are 5.1, 3.5 and 40.4 micrograms per cubic meter in urban locality and 2.4, 3.8 and 32.0 micrograms per cubic meter in suburban locality. In-depth aerosol source identification to the intermodal fraction will be conducted with the help of ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP-MS) and transmission electron microscopy (TEM) applied to aerosol samples.

The project is supported by the Czech Grant Agency (P503/12/G147) and the Charles University Grant Agency (274213).

2UA.2

European Air Pollution Hot-Spot: Evidence of Industrial Plume over a Residential Area.

CECILIA LEONI, Jan Hovorka, *Charles University in Prague*

The Ostrava Region in the Czech Republic is a heavily polluted industrial area. Industrial sources and local heating are the main causes of air quality degradation. Also, Ostrava's basin geomorphology and frequent temperature inversions in winter contribute to increased pollutants concentration. To characterize dominant air pollutants and to apportion their main sources, a comprehensive study on atmospheric aerosol was conducted at district Ostrava-Radvanice and Bartovice, one the most polluted district of the city.

During a monthly campaign (5.2-6.3 2014) five minute data of aerosol number size distributions (14-736 nm), CO, SO_2, NO, NO_2, O_3, CH_4 concentrations and meteorological parameters were recorded. The sampling station was placed in the district of Ostrava-Radvanice and Bartovice at 1.5 km distance from a large iron and steel-producing complex.

Fine particles number concentration – PNC above 10^4 cm^{-3} accounted for 70% of total measurements. Aerosol particle number distributions were frequently bimodal with count median diameters - CMD of 40 nm and 100 nm. We registered higher peaks of PNC about $1.2x10^5$ cm^{-3}, at CMD 40 nm, along with higher concentrations of CO (4 ppm) and SO_2 (50 ugm^{-3}), whereas background campaign averages were for PNC $1.3x10^4$ particles cm^{-3}, and 0.6 ppm and 7 ugm^{-3} for CO and SO_2 respectively. We also recorded CO peaks (10 ppm) in absence of SO_2, with PNC $2.5x10^4$ cm^{-3} and CMD of 40 nm.

Since we did not register significant local heating sources near the station and the vehicular traffic is rather moderated we may conclude that the higher ultrafine PNC at CMD 40 nm and higher CO and SO_2 concentrations derive from the industrial plume transiting over the station.

The project is supported by the Czech Grant Agency (P503/12/G147).

2UA.4

Relationship between PAHs and Elemental Composition of Size-segregated Aerosol.

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

Elevated concentrations of particle-bond PAHs are frequent urban air quality problem in the Czech Republic. EU limit exceedance for B[a]P is everyday reality during cold period of winter when, as an extreme, we recorded peak value of 300 $ng.m^{-3}$ of B[a]P in 2012 in the Ostrava city during comprehensive characterization of urban aerosol study. The study comprises determination of 24 hours averages of 16 US-EPA PAHs in four size aerosol fractions and hourly values for 17 elements in three size aerosol fractions. Therefore, we may analyze relationship between highly time resolved peaks in elemental composition and PAHs enrichment in size-segregated aerosol. The study consisted of sampling campaigns conducted for 14 or 30 days in four cities in the Czech Republic. First, we analyzed database recorded during 30 days campaign conducted in Ostrava city in winter 2012. Due to very low air temperatures and low wind-speeds heavy smog was formed and persisted for first 20 days of the campaign. According to analysis, no simple relationship between PAHs and aerosol elemental composition was observed probably because of main PAHs-containing emissions were well mixed during the smog episode. In contrast, during the last 10 days of the campaign, when temperature and wind speed have risen and smog was dispersed, we observed enrichment of both heavy metal and B[a]P in fine aerosol fraction. Analysis of wind speed/direction points to plume from heavy industry complex nearby the station. Data analysis from other cities is currently under progress.

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

2UA.7

Microcharacterization and Identification of Non-exhaust Particles from On-road Driving and Laboratory Measurements using SEM-EDX Analysis.

SEOKHWAN LEE, Sunyoup Lee, Hongsuk Kim, *Korea Institute of Machinery and Materials*

In recent years, growing concern about climate change and air pollution has resulted in stringent legislative actions, such as limits for particulate matter (PM). To date, substantial reductions in traffic-related pollution have focused on exhaust emissions, but recent studies have reported that non-exhaust sources such as road dust, re-suspension of materials from the pavement surface, and wear of vehicular parts (tires, brakes, etc.) contribute as much as exhaust emissions to traffic related pollution.

Tire wear particles (TWPs) are a significant pollutant, especially as a source of zinc in the urban environment. Several studies have been conducted to investigate the characteristics of TWPs. They identified rubber particles from tire wear experiments in the laboratory and found Zn using SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy) analysis. They also determined the chemical composition of TWPs and reported that the coarser fractions generated by studded tires were dominated by Si, Ca, K, and Fe.

In addition to investigating tire-related particles, several authors have characterized brake wear particles (BWPs) emitted from the brake lining during vehicle deceleration in the laboratory. They determined mass size distributions and conducted a chemical analysis of BWPs in a closed chamber. They reported that the mode diameters of BWPs were <0.1 μm and >10 μm (bimodal), and Fe, Cu, Sb, and Ba were the most abundant elements.

This study characterizes the morphology and chemical composition of traffic-related non-exhaust particles from on-road driving (roadway particles) and laboratory measurements (TWPs and BWPs) using SEM-EDX analysis. The results show that coarser fractions generated by tires had multi angular morphology, and was dominated by Zn, S, Si, Al, Fe, and Mg. The BWPs consisted mainly particulates Cu, Ba, Sb, Fe, Zr, and mineral elements (Al, Ca, and K), and had round-edged morphology.

2UA.8

Evaluation of Carbonyl Compounds Levels in Residential and Industrial Areas of Tijuana BC, Mexico Air Basin.

Jesus Guerrero-García, GUILLERMO RODRÍGUEZ-VENTURA, Ernesto Velez-Lopez, Lilia Hurtado, Javier Emmanuel Castillo-Quiñones, Penelope Quintana, Miguel Zavala, Luisa Molina, *Universidad Autonoma de Baja California*

Industrial areas in Tijuana B.C., México are spread along the city, in some cases are near to residential areas and most of them are localized in periphery areas, up and down to prevalent wind stream direction.

State Report of Air Emissions 2010, for Tijuana-Playas de Rosarito region, estimate VOC´s emissions are 27,629.7 tone/year, PM10 and PM2.5 are 33,802.8 and 76,873.7 tons/year respectively.

Recent studies in Calmex 2010 shown that black carbon (BC) and carbonyl compounds (CCs) are an important pollutants associated to PM2.5 and CO emission in Tijuana air basin. In particular, formaldehyde and acetaldehyde among many CCs are highly important, as they simultaneously belong to the 15 species of hazardous air pollutants in Mexico and USA. This study aimed to characterize the behavior of CCs in urban air of Tijuana, to investigate the major controlling factors on the distribution of CCs and to provide scientific information needed in mapping out, an appropriate air quality management measure for air quality network.

Measurements were carried out form November 2012 to May 2013, carbonyl samples were done at four sites; SS-LM (residential), SS-ITT (residential), SS-SPA (industrial), SS-Beach (reference). CCs analysis was carried out using SOP MLD 022 (CALEPA, 2001). Meteorological and tracers data were provided from the Monitoring Stations of the Secretary of Environmental Protection of Baja California (SPABC). In general, average concentration of formaldehyde (6.13 µg/m3) appeared to be the most abundant CCs, followed by acetaldehyde (1.89 µg/m3) and acetone (1.36 µg/m3), concentrations of CCs are 1.5 times higher in summer than winter seasons probably due to the enhanced volatilization and photochemical reactivity. Mean concentrations of formaldehyde is twice higher in the industrial site than in residential site. Total CCs concentration was three times higher in urban air related to reference site.

2UA.9

Atmospheric Aerosols in Southeast Asia: Sources and Impacts. RAGHU BETHA, Xian Huang, Rajasekhar Balasubramanian, *National University of Singapore*

Atmospheric Aerosols in Southeast Asia (SEA) contain a complex mixture of organic and inorganic substances, derived from a wide variety of emission sources. These sources include combustion of fossil fuels for power generation, transportation, industrial processes, biomass burning and vegetation. Apart from direct emissions, new particles are also formed in the atmosphere. While the impacts of local urban sources of particulate air pollution have been characterized within SEA, the influence of biomass burning in particular peat fires on regional air quality, visibility degradation, climate change and public health remains incompletely understood because of its sporadic nature. In addition, there is a critical need to identify and quantify the major sources of aerosols in the context of urban air quality improvement. Field studies were conducted in Singapore to gain insights into the transport, source contributions, and the impacts of aerosols from various sources on the environment and public health. It was observed that trans-boundary smoke aerosols derived from peat fires were usually transported from Indonesia to Singapore above the boundary layer and were intermixed with relatively clean air masses of oceanic origin at surface levels by convective winds, resulting in unique physical, chemical and optical characteristics of urban aerosols at downwind sites. During episodic peat fires, the carbon content of atmospheric aerosols increased to 55% (~35% during clear days) of which nearly 70-75% was estimated to be contributed by peat fires. Relatively large fractions (60-75%) of aerosols are found to be in the sub-micron range and were elevated by a factor of 15 during peat fires. Changes in the radiative properties of aerosols were strongly influenced by “aged” carbonaceous aerosols. Secondary or new particle formation was suppressed during hazy days. Health risk estimates revealed that the carcinogenic risk to individuals exposed to biomass burning-impacted aerosols increased significantly by 40% compared to those who are not exposed.

2UA.10

Morphological and Elemental Classification of Long-range Transported Fine and Ultrafine Particles by STEM-EDX Individual Particle Analysis. SHILA MASKEY, Hoseung Chae, Kihong Park, *GIST*

Fine (<2.5 µm) and ultrafine (<100 nm) ambient particles affect radiation balance, cloud formation, visibility impairment, and result possibly an adverse health consequence. The mass concentrations, size, composition and sources of the particles in certain urban areas are strongly affected by long-range transport. During long-range transport, particles could change their properties due to coagulation, cloud processes, condensation or reactions with air pollutants by various heterogeneous pathways. Because of their diverse sources and formation pathways, the particle consists of various chemical constituents with different morphology. In this study, the elemental compositions, morphologies and mixing states of individual aerosol particles in two size fractions were analyzed using scanning transmission electron microscopy coupled with energy dispersive X-ray (STEM-EDX) technique.

The long-range transport particle (LTP) event in Korea was identified by 72-h backward air mass trajectory and PM mass concentration data. Aerosol samples were collected during LTP event (18-19 March, 2014) from the terrace of Gwangju institute of science and technology (GIST) campus (35:13N, 126:50E), Gwangju, which is surrounded by a residential, industrial, and agricultural area. Fine and ultrafine particles were collected on copper TEM grids using $PM_{2.5}$ impactors and nanometer aerosol sampler (TSI, 3089, USA), respectively. Approximately 430 measured particles in the LTP event of samples were mainly classified into carbonaceous, mineral dust, volatile inorganic, heavy metal-containing, and fly ash particles based on their morphology and X-ray spectral data. Among the particle types, carbonaceous particles were categorized into: soot, semi-volatile organic, non-volatile organic, biogenic, and biomass burning particles. Many of the particles in both size fraction samples were internally mixed with S, N and/ or C. For comparison, the analysis of aerosol samples collected during non-event (25 June, 2014) day is being carried out.

3AC.1

Photochemical Aging of Brown Carbon Aerosols. Paige Aiona, Hyun Ji Lee, Alexander Laskin, Julia Laskin, SERGEY NIZKORODOV, *University of California, Irvine*

Atmospheric aerosols directly influence climate because of their ability to scatter and absorb solar and terrestrial radiation. Primary sources such as biomass burning as well as secondary heterogeneous atmospheric reactions have been shown to produce “brown carbon” (BrC) organic aerosols capable of absorbing visible and near-ultraviolet radiation. Nitrogen-containing organic compounds (NOC) appear to be a quintessential element of BrC, and they may be solely responsible for the high absorption coefficients of BrC. The goal of our research is to investigate photochemical stability of different types of BrC and to address the role of NOC in controlling the light-absorption properties of BrC. We are presenting results of smog chamber experiments and bulk aqueous phase experiments that examine the production and photodegradation of BrC in reactions between reduced nitrogen compounds (ammonia and amines) and common organic carbonyls. Specifically, we focus on reactions of 1,4-dicarbonyls, which appear to efficiently produce stable heterocyclic organic compounds in the presence of reduced nitrogen compounds. BrC produced by biomass burning is investigated for comparison. UV-Vis spectroscopy is used to measure the mass absorption coefficients of BrC and high resolution mass spectroscopy is used to investigate its molecular level composition. In addition, photolysis of BrC by actinic radiation is investigated in order to predict its effective lifetime with respect to photodegradation. We observe that BrC resulting from biomass burning is relatively stable with respect to photodegradation, whereas BrC produced in secondary reactions of carbonyls is highly photolabile. This study underscores the highly variable nature of BrC, which complicates representation of BrC in climate and air-pollution models.

3AC.2

Investigation of the Chemical Aging and Absorption of Carbonaceous Aerosol from Wood Fires. ANTONIOS TASOGLOU, Spyros Pandis, *Carnegie Mellon University*

Smog chamber experiments were conducted to investigate the chemical and physical transformations of organic aerosol (OA) of biomass burning emissions exposed to OH radicals. A major focus of the study was the effect that chemical aging has on the absorption by the corresponding particles. The chemical processing of biomass burning OA results in the condensation of additional material on the initial particles and chemical changes of the OA. These changes can enhance the absorption of solar radiation by the biomass burning black carbon (BC). In our experiments we investigated emissions from yellow pine wood burning. The chemical aging of the biomass burning emissions was promoted by the production of hydroxyl radicals by three different sources: (1) HONO photolysis, (2) HOOH photolysis and (3) dark OH formation via ozone-alkene reaction. In the first case the experiments took place under high NOx conditions while in the other two under high NOx. Experiments were also conducted under low and high relative humidity conditions. A Soot Particle Aerosol Mass Spectrometer (SP-AMS) was used for the chemical characterization of the particles. For the study of the absorption of black carbon, we used a suite of instruments including an aethalometer and a green and a blue photoacoustic extinctiometer (PAX). A thermodenuder was used to characterize the changes of the particle volatility with chemical age. The changes in particle mass concentration, chemical composition, volatility, and absorption will be discussed.

3AC.3

Aging of Alpha-pinene First-Generation Ozonolysis Products by Reactions with OH. NINGXIN WANG, Spyros Pandis, Neil Donahue, *Carnegie Mellon University*

Secondary organic aerosol (SOA) formation from volatile organic compounds in the atmosphere can be thought of as a succession of oxidation steps. The production of later-generation SOA via continued oxidation of the first-generation products is defined as chemical aging. Our work investigates aging of the SOA produced during alpha-pinene ozonolysis through smog chamber experiments. SOA is first formed through reaction of alpha-pinene and ozone. During the second step, the first-generation products are allowed to react further with hydroxyl radicals (OH) generated via H_2O_2 or HNO_2 photo-dissociation.

All experiments were conducted in the environmental chamber at Carnegie Mellon University. The SOA was characterized by a High-Resolution Time-of-Flight Aerosol Mass Spectrometer. Vapor loss to the chamber walls represents an experimental challenge for these aging measurements. Introduction of OH at different times after the formation of the first-generation products is used to quantify this effect. The effects of NOx (high and low level) and relative humidity were also investigated. Exposures of the SOA to OH varying from approximately 10^6 to $5x10^7$ hr molecules cm^{-3} were used, covering a significant range of atmospherically relevant aging timescales. A second-generation aerosol mass yield is used to quantify the aging effects with different levels of exposure to OH. Changes in the aerosol chemical composition were also measured.

3AC.4

Molecular Corridors Represent the Multiphase Chemical Evolution of Secondary Organic Aerosol. MANABU SHIRAIWA, Thomas Berkemeier, Katherine Schilling, John Seinfeld, Ulrich Poeschl, *MPIC*

The dominant component of atmospheric organic aerosol is that derived from the oxidation of volatile organic compounds (VOCs), so-called secondary organic aerosol (SOA). SOA consists of a multitude of organic compounds, only a small fraction of which has historically been identified. Formation and evolution of SOA is a complex process involving coupled chemical reaction and mass transport in the gas and particle phases. Current SOA models do not embody the full spectrum of reaction and transport processes nor do they identify the dominant rate-limiting steps in SOA formation. The recent advent of soft ionization mass spectrometry methods now facilitates a more complete molecular identification of SOA than heretofore possible. Based on such novel measurements, we show here that the chemical evolution of SOA from a variety of VOC precursors, including α-pinene, isoprene, limonene, and C12-alkanes, adheres to characteristic “molecular corridors” with a tight inverse correlation between volatility and molar mass. Sequential and parallel reaction oxidation and dimerization pathways progress along these corridors through characteristic regimes of reaction-, diffusion-, or accommodation-limited multiphase chemical kinetics that can be classified according to reaction location, degree of saturation, and extent of heterogeneity of gas and particle phases. These molecular corridors constrain the properties of unidentified products and reaction pathways and rates of SOA evolution, thereby facilitating the further development of aerosol models for air quality and climate.

3AC.5

Formation of Low-Volatility Organics in Organic Acid/Inorganic Salt Mixtures. SILJA HÄKKINEN, Ilona Riipinen, V. Faye McNeill, *University of Helsinki, Columbia University*

Previous studies have shown that particulate-phase processing within organic acid/inorganic salt aerosol mixtures can lead to enhanced partitioning of the organic acid e.g. via organic salt formation. Formation of low-volatility organics will affect the chemical and physical properties of the aerosol and may further alter its ability to act as a cloud condensation nuclei. In this study we investigate the formation of low-volatility organics within mixtures of organic acid with sodium chloride and ammonium sulfate. The main focus is on dicarboxylic acids succinic acid and oxalic acid which are among the most abundant organic acids in the atmospheric aerosol. Quantitative information on the magnitude of low-volatility organic material formation was obtained by combining experimental data with a kinetic model describing aerosol evaporation inside a flow tube. The experiments were performed with a TPD Aerosol-CIMS (Temperature Programmed Desorption Aerosol Chemical Ionization Mass Spectrometer). The aerosol was produced by atomizing a solution and dried prior to entering a vaporization flow tube. The volatilized organic compounds were ionized chemically and detected using a quadrupole mass spectrometer. The obtained results from the model-measurement analysis show that the formation of low-volatility organic material in the studied mixtures depends on the vapor pressure of the organic acid and the acidity of the aerosol mixture. The results can help explaining observed anthropogenic enhancement in the formation of secondary organic aerosol from biogenic origin.

3AC.6

Organosulfates Formation in Secondary Organic Aerosol Produced from Photooxidation of Various VOCs In the Presence of NOx and Sulfuric Acid Aerosol Using Natural Sunlight. Jiaying Li, MYOSEON JANG, *University of Florida*

In this study, we hypothesized that the yields of organosulfates in the sulfuric acid seeded secondary organic aerosol (SOA) increase with the high concentrations of alcohols and aldehyde compounds in the SOA. To prove this hypothesis, organosulfates were produced via reactions of sulfuric acid aerosol with SOAs produced from the photooxidation of various volatile organic compounds (VOCs), such as isoprene, alpha-pinene, and toluene, in the presence of different NO_x levels using an outdoor Teflon film chamber. The dialkylsulfates were quantified by the difference between the total sulfates that were estimated with a particle into liquid sampler ion chromatography (PILS-IC) and the inorganic sulfates estimated using the aerosol acidity data measured by a colorimetry integrated with a reflectance UV-Visible spectrometer (C-RUV). In this study, the yield of dialkylsulfates ($Y_{diOS\text{-}OC\text{-}SO4}$) was described by normalizing the concentration of dialkylsulfate with both the total sulfate concentration and the OC concentration. The highest $Y_{diOS\text{-}OC\text{-}SO4}$ appeared in isoprene SOA and the lowest $Y_{diOS\text{-}OC\text{-}SO4}$ in alpha-pinene SOA. For all SOAs, the higher $Y_{diOS\text{-}OC\text{-}SO4}$ was observed under the higher NO_x conditions, suggesting that carbonyls enhanced via RO_2-NO chemistry under higher NO_x levels react with sulfuric acid and form dialkylsulfates. To investigate the influence of aerosol compositions on $Y_{diOS\text{-}OC\text{-}SO4}$, the concentrations of functional groups in SOA were predicted using an absorptive partitioning of organic products between the gas (g), organic aerosol (or) and inorganic aerosol (in) phases. The concentration of organic products produced through gas phase photochemical reactions of VOCs were predicted using the explicit mechanisms (e.g., Master Chemical Mechanism) integrated with a kinetic solver. The aerosol functional group distributions predicted by the model were also compared to those estimated by the data obtained from a Fourier Transform Infrared (FTIR) spectrometer. Although the model predictions are limited to thermodynamic base SOA compounds, the overall trend in concentration of functional groups reasonably agrees with the FTIR data. The correlation between $Y_{diOS\text{-}OC\text{-}SO4}$ and the concentrations of functional groups in the SOA inorganic aerosol phase were analyzed, and results showed that the concentrations of –C-OH, -ONO2, and –C=O were strongly correlated to the $Y_{diOS\text{-}OC\text{-}SO4}$.

3AE.1

Advances in Nanoparticle Sampling and Analysis Methods.

GARY CASUCCIO, Traci Lersch, Henry Lentz, Dan Miller-Lionberg, John Volckens, *RJ Lee Group, Inc.*

Collection, analysis, and speciation methods for engineered, naturally occurring, and incidental nanoparticles are needed to determine workplace and ambient exposures. Advances in sampling and analysis techniques in this ultra-fine size fraction have evolved for the measurement of nanoparticles. A portable thermophoretic sampler has been developed that deposits ultra-fine particles in the air directly onto an electron microscope (EM) grid. The sampler has high collection efficiencies for ultrafine particles and further, sample integrity is maintained because unlike filter-based sampling techniques, no sample preparation is needed prior to the EM analysis.

The sampled EM grids are inserted directly into a high resolution EM for examination of particle associations, composition, and concentrations. Manual examination using EM techniques can be used to distinguish particle phases and evaluate relationships such as agglomerated state verses unbound particles. Advances in automation of EMs can be applied for direct particle size measurements to obtain quantitative data on particle concentration and size distribution of the collected particles down to 20 nm.

Data from studies using samples collected with the thermophoretic sampler are illustrated and compared to results from both direct-reading instruments and from integrated air samples with a focus on identifying the advantages and limitations of this technology.

3AE.2

Aerosol-to-Liquid Phase Collection: A Method for Making Liquid Suspension Containing Dry-Dispersed Nanomaterials with a Known Mass Concentration.

KENJIRO IIDA, Hiromu Sakurai, Junko Nakanishi, Kensei Ehara, *AIST*

Intratracheal instillation test have been considered as a cost-friendly alternative to exposure studies for evaluating the toxicities of nanomaterials. Intratracheal instillation test requires a liquid suspension of solid nanomaterial with a known mass concentration. In this study, dry-dispersed nanomaterials are directly collected into liquid phase from aerosol phase to make suspensions to be used for intratracheal instillation tests. The mass in the collected liquid can be obtained from the measurements in aerosol phase.

Nanomaterial power is fed intermittently to a cylindrical chamber which both ends are covered with a vibrating latex membrane. The powder is aerosolized, and inhalable fraction of the generated particles penetrate through a cyclone. The aerosol is mixed inside a chamber and sampled by aerosol instruments downstream. A nephelometer monitors the mass concentration of aerosol particles, and the concentration is regulated at a fixed value within 5-25 mg/m^3. The sizes of dry-dispersed powder ranged over submicrometer to micrometer range, and the size distributions remained stable during dispersion experiments which are performed continuously for 6 to 8 hours.

Dry-dispersed nanomaterial were collected from aerosol phase directly into liquid phase using a Growth Tube Collector (GTC). Supersaturated water vapour condense onto incoming aerosol particles, and final droplet sizes at the exit of the GTC were about 3 um. These droplets impact onto the surface of liquid contained in a vial. Two kinds of powder material were used; P25-TiO2, JIS standard powder No.8 (Kanto-loam stratum). Collection efficiencies were reasonably high and reproducible. The results suggests that the mass of aerosol particles collected into liquid can be predicted form a mass concentration of aerosol particles, a sampling flowrate of GTC, and a sampling time.

3AE.3

Characterization of 3-D Printer Aerosol Emissions. MARIT MEYER, Kristin Bunker, Gary Casuccio, *NASA Glenn Research Center*

The emerging market of small, affordable 3-D printers has dramatically increased manufacturing capabilities for individuals, small businesses, and even astronauts on the International Space Station (ISS). These opportunities are accompanied by the risk of aerosol exposure, bringing what are traditionally 'manufacturing aerosols' into office spaces, homes and into the limited air of the ISS. Furthermore, 3-D printers are not always operated with special ventilation or personal protective equipment. Ultrafine particle emissions from acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) thermoplastic extrusion materials have been researched and documented (Stephens et al. 2013), but many additional materials are now available for this additive manufacturing technique. Multi-material or composite material feedstock, powdered metal, and ceramic filament 3-D printing are now possible, but the aerosols generated from these materials in the 3-D printing process have not been characterized. Aerosol emissions from several types of 3-D printers and several different printing materials have been collected directly onto a transmission electron grid using a thermophoretic sampler (TPS). The grids were examined in an ultra-high resolution scanning electron microscope (SEM) and scanning transmission electron microscope (STEM). Electron microscopy images and energy dispersive-spectroscopy spectra will be presented that provide information on the particle size, morphology, and elemental composition of the particles being released during 3-D printing. In addition, particle size distributions obtained from the electron microscopy analysis will be presented and compared to concentration and size distribution data from aerosol reference instruments.

Reference: Stephens, B., Azimi, P., El Orch, Z. and Ramos, T. , 2013. Ultrafine particle emissions from desktop 3D printers. Atmospheric Environment 79 334-339.

3AE.4

Uncontrolled Combustion of Shredded Tires in a Landfill: Emission Characterization, Population Exposure and Public Health Responses. ASHISH SINGH, Scott N. Spak, Elizabeth Stone, Jared Downard, Robert Bullard, Mark Pooley, Pamela Kostle, Matthew W. Mainprize, Thomas Peters, Doug Beardsley, Charles Stanier, *University of Iowa*

Emergency tire fires in the US and elsewhere are not well characterized for emissions of particulate mass, number, composition, and various organic and inorganic gases. Emergency air monitoring and methods of impact assessment during emergency fires are inconsistent and not easily implemented by the response teams.

During a major tire fire in Iowa City in 2012 a variety of ambient measurements were conducted along with dispersion modelling were conducted to fill the gap in tire plume characterization and population impact assessment. We present a list of emission factors for fine particle (PM2.5) mass, total number, 19 PAHs, organic carbon (OC), elemental carbon (EC), and sulfur dioxide (SO2). Results from this study are compared EPA lab simulated open tire fire for particle mass and PAH. The PM2.5 emission factor for burning tires in this study is more than an order of magnitude lower than the PM10 emission factor reported by EPA at 65 -105 g kg-1.

For an appropriate air quality emergency response, this study evaluated a list of priority air pollutants based on hazard ratio and proposed a multi-pollutant air quality index specific to tire fire. Hazard ratios were used to rank acute and chronic relative risks from individual fire pollutants, finding SO2 ~ PM2.5 > CO > benzene ~ acrolein > formaldehyde ~ black carbon. Using a dispersion model in conjunction with the proposed AQI, we estimate that smoke concentrations reached unhealthy outdoor levels out to distances of 2.9 km and 7.2 km, at 24 and 1 hr averaging times, respectively

3AE.5

Measurement of Aerosols Generated by Combustion of Different Materials. SERGEY A. GRINSHPUN, Jin Yong Kim, Michael Yermakov, Shuang Gao, Tiina Reponen, Pramod Kulkarni, *University of Cincinnati*

The real-time measurement of concentration and particle size distribution of combustion aerosols is crucial for assessing the aerosol exposure and developing appropriate control strategies. In this effort, we deployed four aerosol instruments to measure aerosols generated by burning wood, paper and plastic in a 25 cubic meter exposure chamber. The chamber facility was used to simulate an exposure of fire fighters during the fire overhaul operations. One instrument was a non-size-selective condensation particle counter (P-Trak, TSI, Inc., St. Paul, MN, USA); three others were recently developed particle size spectrometers: Nanocheck (Grimm Technologies, Inc., Ainring, Germany), Nano-ID (Particle Measuring Systems, Inc., Boulder, CO, USA), and PAMS (Kanomax-USA, Inc., Andover, NJ, USA). The total aerosol concentration values obtained with the P-Trak were consistently lower than those measured with the three particle size spectrometers, which can be associated with differences in the operational particle size ranges. The size distributions recorded by the particle size spectrometers for the tested combustion materials were primarily single-mode with peaks observed in a range from 30 to 60 nm. The possible reasons behind the similarities and differences between data produced by different instruments have been reviewed. The feasibility of the four tested measurement methods for characterizing combustion aerosols and human exposure in the laboratory and field settings is discussed.

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3AE.6

Indoor Air Quality in Latino Homes in Boulder, Colorado. Luis Escobedo, WYATT CHAMPION, Ning Li, Lupita Montoya, *University of Colorado Boulder*

Americans spend most of their time indoors where exposure to poor indoor air quality (IAQ) can result in diminished health. This study measured the indoor air quality in 30 homes of a low-income Latino community in Boulder, Colorado during the summer of 2012. Participants were administered a survey which pertained to health conditions, previous exposures to smoke, and potential indoor air pollution sources such as cigarette smoke, heating fuel, and building materials. Twenty-four hour samples of fine particulate matter (PM2.5) from both the indoor and ambient air were collected for each home. Concurrent air samples were collected onto 47mm Teflo and Tissuquartz filter at each location. The Teflo filters were analyzed gravimetrically to measure PM2.5 and their extracts were used to determine levels of proteins and endotoxins in the fine fraction of PM. The Tissuquartz filters were analyzed for elemental and organic carbon content (EC/OC). Results indicated that the indoor air contained higher concentrations of PM2.5 than the ambient air, and that the levels of OC were much higher than EC in both indoor and outdoor samples. This community showed practically no smoking in their homes and kept furry pets indoors at very low rates; therefore, cooking is likely the primary source of indoor PM. For responders with significant previous exposure to PM, it appeared to be primarily from occupational environments or childhood exposure abroad. Our findings indicate that for immigrant communities such as this, it is important to consider not only their housing conditions, but also the relevant prior exposures when conducting health assessments.

3CC.1

Measurement of the Optical Properties and Contact Freezing Ability of Supercooled Water Droplets Using Optical Tweezers. Hassan Beydoun, Kyle Gorkowski, Mark Aboff, Jim Walker, Jonathan P. Reid, RYAN SULLIVAN, *Carnegie Mellon University*

Supercooled water is a ubiquitous substance in the atmosphere due to the significant energy barrier to the nucleation of the ice phase. Heterogeneous ice nucleation is a poorly constrained process with the contact freezing mode remaining the most nebulous due to the experimental challenge of colliding a supercooled water droplet and a potential ice nucleus in a controlled and directly observable manner. A refrigerated optical tweezers system capable of trapping individual water droplets at controlled subzero temperatures has been developed to permit the investigation of a range of supercooled water properties. Preliminary findings indicate that this system can detect individual droplet-ice nuclei collisions via the quenching of the surface-sensitive whispering gallery modes that occur at discrete wavelengths of water’s Raman mode. This paves the way for a novel contact freezing measurement system that retrieves contact freezing efficiencies directly without requiring any assumptions regarding the number of collisions prior to freezing. The occurrence of droplet freezing is 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. Novel measurements of the refractive index of supercooled water have also been retrieved using this method. These results indicate that the increase in water’s refractive index with decreasing temperature has been greatly underestimated.

3CC.2

The Role of Aqueous Chemistry in Cloud Formation: Impact of Oligomerization. SHUNSUKE NAKAO, Yong Lim, Barbara Turpin, Alexandra Boris, Jeffrey Collett, Sonia Kreidenweis, *Colorado State University*

Aqueous reactions in clouds or hydrated haze particles are potentially significant pathways for secondary organic aerosol (SOA) formation; SOA formed via aqueous reactions is termed aqSOA. One of the characteristics of aqSOA is that it is generally highly oxidized (high O/C), and hence expected to have high hygroscopicity. Therefore, aqSOA may play a key role in cloud droplet activation (and subsequent evaporation and activation cycles) at low supersaturation conditions. Recent studies have reported oligomer formation through aqueous reactions, possibly via radical-radical combination at the high organic concentrations typically encountered in wet aerosols. The oligomerization process may increase aqSOA mass by producing low vapor pressure products; however, it may also lower particle hygroscopicity by increasing molar volume (based on Raoult’s law).

In this study, we examined pyruvic acid (PA) photolysis as a simplified system of oligomerization with the following aims: 1) evaluating the impact of oligomerization in terms of aqSOA formation and CCN activity, 2) evaluating the relative importance of oligomerization to ammonium salt formation, and 3) evaluating the effectiveness of molar-volume based parameterization of the single hygroscopicity parameter, kappa, over the commonly used O/C parameterization. Oligomerization of the PA photolysis products resulted in an increase of molar volume of reaction products while keeping O/C nearly constant, making this a suitable system for exploring the impact of aqueous oligomerization on CCN activity. The aqueous reaction products were separated by ion chromatography before size-resolved CCN measurements, allowing detailed analysis beyond the conventional bulk O/C parameterization. Prediction of kappa based on reaction products will be discussed.

3CC.3

Understanding Cloud Condensation Nuclei Mixing States from Flow Tube Experiments. DIEP VU, Shaokai Gao, Jeffrey Pierce, Akua Asa-Awuku, *University of California, Riverside*

Cloud condensation nuclei (CCN) data analysis of single component aerosols, such as ammonium sulfate, $(NH_4)_2SO_4$, are well understood. The activation of a single known component yields a simple sigmoidal activation curve. However ambient aerosols generally exist as complex heterogeneous mixtures of organic and inorganic species. CCN data sets from ambient and chamber studies, which consist of these aerosol mixtures, may not show a single clean activation curve but instead can exhibit multiple activation curves not associated with doubly charged particles.

To characterize and modify mixing states, a new laminar flow tube apparatus has been developed to control the extent of mixing of organic and inorganic fractions. Increasing the residence time can increase the extent of internal mixing. Preliminary data suggests that aerosol water is a significant factor; under dry conditions, the aerosols were externally mixed and humid conditions promoted internal mixing. For example, $(NH_4)_2SO_4$ and $C_4H_6O_4$ (succinic acid) when dry, maintain an external mixture, multiple activation curves are constant, and can be reproduced with Köhler theory. We have successfully recreated data sets yielding multiple activation curves by mixing multiple compounds that are representative of different anthropogenic and biogenic sources in the flow tube. The data agree well with Köhler Theory and single parameter (kappa) theory thermodynamic predictions of droplet activation. Data sets are also compared with a diffusion based coagulation particle model to predict mixing behavior. The method of analysis and the effect of mixing states of multiple components on the supersaturated hygroscopic properties of aerosols are presented. Results suggest that the aerosol morphology can be observed in CCN activation data and can be revisited in complex aerosol data sets to understand the extent of mixing.

3CC.4

Cloud Condensation Nuclei Activity of Secondary Organic Aerosol: Kappa Values for a Range of VOCs, Individually and Combined. Josh Custer, William Madry, Dabrina Dutcher, TIMOTHY RAYMOND, *Bucknell University*

The activation of cloud condensation nuclei (CCN) depends on both particle chemistry and initial particle size. Kappa, a hygroscopicity parameter, relates a particle's dry diameter to its critical supersaturation[1]. In this study, we determined the kappa value for an extensive list of volatile organic compounds (VOCs). The VOCs that were studied were both biogenic and anthropogenic in nature. The VOCs were primarily monoterpenes, although a few sesquiterpenes were also studied. These VOCs were oxidized in a small Teflon smog chamber using ozone to form secondary organic aerosols. The total aerosol number and activated CCN number concentrations were measured. From these measurements an activation diameter (Dp50), the particle size at which half of all particles activate, was calculated using SMCA[2]. These results represent the largest data-set of the Dp50 of pure and mixed aerosols done using one experimental set-up. In addition to measuring the kappa values, it was also observed that activation diameters decrease as the SOA ages. When multiple VOCs were combined in the smog chamber before oxidation, the measured kappa values showed very little variance and settled into a narrow range independent of the initial VOC mixture composition. This result has significant implications for computational models of radiative transfer and cloud formation.

[1] Petters, M. D., and S. M. Kreidenweis. "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity." Atmospheric Chemistry and Physics 7, no. 8 (2007): 1961-1971.

[2] Moore, Richard H., Athanasios Nenes, and Jeessy Medina. "Scanning mobility CCN analysis—A method for fast measurements of size-resolved CCN distributions and activation kinetics." Aerosol Science and Technology 44, no. 10 (2010): 861-871.

3CC.5

Relating Volatility, Size and Cloud Condensation Nuclei Activation Properties of Longifolene SOA. ASHLEY VIZENOR, Akua Asa-Awuku, *University of California, Riverside*

Longifolene is a sesquiterpene found in pine resin and emitted to the ambient air. Compared to similarly emitted biogenic compounds, it has a longer atmospheric lifetime. This longer lifetime makes it an ideal compound to study in atmospheric chamber experiments as its decay and reactivity can be observed over a greater time with less reactant. Here, longifolene secondary organic aerosol (SOA) was formed upon reaction with hydroxyl radical in dual $90m^3$ Teflon reactors at the University of California, Riverside College of Engineering-Center for Environmental Research and Technology Environmental Chamber. A Volatility Tandem Differential Mobility Analyzer was used during the experiments to observe changes in the volatilities of the SOA formed. Volume Fraction Remaining (VFR) data suggests that upon nucleation, longifolene SOA volatility varies significantly with temperature. The VFR doubles when the thermal denuder temperature is decreased by fifteen degrees Celsius. When reacted with hydroxyl radical, the mode of particles shifts from 50nm to over 200nm within 240 minutes. During this time, the particles begin to decline in volatility, leading to a logarithmic trend between temperature and VFR. The volatility appears to be correlated to particle size, and cloud condensation nuclei (CCN) activation was observed. As the particles grow and their volatility decreases, the supersaturation required for CCN activation decreases from approximately 1% to 0.2%, indicating that the more volatile longifolene SOA species are hygroscopic. These trends were compared to the SOA chemistry of other sesquiterpenes. Furthermore, a lower volatile pre-cursor, isoprene was added to longifolene experiments. Isoprene can produce more volatile products that can influence the overall particle hygroscopcity. The contributions of isoprene and longifolene decay in the gas-phase are observed to determine how the volatility of mixed-phase particles compares with single-phase pre-cursor SOA.

3CC.6

Aerosol Size Distribution Response to Anthropogenically Driven Historical Changes in Biogenic Secondary Organic Aerosol Formation. STEPHEN D'ANDREA, Juan-Camillo Acosta Navarro, Salvatore Farina, Catherine Scott, Delphine Farmer, Ilona Riipinen, Jeffrey Pierce, *Colorado State University*

Emissions of biological volatile organic compounds (BVOC) have changed in the past millennium due to changes in land use, temperature and CO_2 concentrations. A recent model reconstruction of BVOC emissions over the past millennium predicted the changes in the three dominant secondary organic aerosol (SOA) producing BVOC classes (isoprene, monoterpenes and sesquiterpenes). The reconstruction predicted that global averages in isoprene emissions have decreased (land-use changes to crop/grazing land dominate the reduction), while monoterpene and sesquiterpene emissions have increased (temperature increases dominate the increases); however, all three show both increases and decreases in certain regions due to competition between the various influencing factors. These BVOC changes have largely been anthropogenic in nature, and land-use change was shown to have the most dramatic effect by decreasing isoprene emissions.

We use these modeled estimates of these three dominant BVOC classes' emissions from the years 1000 to 2000 to test the effect of anthropogenic changes to BVOC emissions on SOA formation and global aerosol size distributions using the GEOS-Chem-TOMAS global aerosol microphysics model. With anthropogenic emissions (e.g. SO_2, NOx, primary aerosols) held at present day values and BVOC emissions changed from year 1000 to year 2000 values, decreases in the number concentration of particles of size D_p > 80 nm (N80) of >25% in year 2000 relative to year 1000 were predicted in regions with extensive land-use changes since year 1000. This change in N80 was predominately driven by a shift towards crop/grazing land that produces less BVOC than the natural vegetation. Similar sensitivities to year 1000 vs. year 2000 BVOC emissions exist when anthropogenic emissions are turned off. This large decrease in N80 could be a largely overlooked and important anthropogenic aerosol effect on regional climates.

3IA.1

Shorter People May Be Exposed to More Influenza Viruses in Resuspended Dust. Peeyush Khare, LINSEY MARR, *Virginia Tech*

Resuspended floor dust constitutes up to sixty percent of the total particulate matter in indoor air. This fraction may also include virus-laden particles that settle on the floor after being emitted by an infected individual. This research focuses on predicting the vertical concentration gradient of influenza viruses in resuspended dust, generated by people walking in a room. Using a sonic anemometer, we measured the velocity field from floor to ceiling at 10-cm intervals to estimate the magnitude of turbulence generated by walking. The resulting eddy diffusion coefficients were maximal at 0.14-0.20 $m^2 s^{-1}$, depending on the number of people walking, at a height of ~0.75 m above the floor. This height corresponds to where the hand swings during walking. We used these coefficients in an atmospheric transport model to predict concentrations of influenza viruses in resuspended dust as a function of the carrier particle size and height in the room. Results indicate that the concentrations of resuspended viruses at heights of 1 m and 1.5 m are 7 times and 4 times higher, respectively, than at 2 m. Thus, shorter people may be exposed to higher concentrations of viruses in resuspended dust.

3IA.2

Biofilms and Bioaerosols in Showers. MARIA D. KING, Alexandra Caya, Chloe Wooldridge, Juan Pedro Maestre, Michal Ziv-El, Yassin Hassan, Kerry Kinney, *Texas A&M University*

The aim of this study is to delineate potential human allergens and pathogens in the bioaerosols that are released during a shower event and potentially form a biofilm on the shower stall and showerhead surfaces. Diverse fungal and bacterial microorganisms have been detected in municipal water that can become aerosolized during showering. We are currently analyzing the microorganisms that colonize residential water lines and showers; including an experimental double shower unit in controlled environment with two showerheads of different flow rates to determine the difference in waterborne, airborne and biofilm forming microbes.

In residential showers on different water supplies, bioaerosol samples were collected before, during and after shower operation with a high throughput (100 L/min) wetted wall cyclone (WWC). Biofilm (from showerhead, shower stall walls, floor and ceiling) and tap water samples were also collected. QPCR using 16S and ITS2 amplification was performed for bacteria and fungi. Periodic (weekly for eight weeks then once a month) sampling was also performed in the experimental shower units. The microbiomes are being delineated using Illumina sequencing.

The results indicate that bacteria are released into shower air during shower operation. QPCR of the DNA extracted from bioaerosol samples indicate that bioaerosol levels on the order of $1x10^6$ bacterial 16S gene copy numbers per m^3 are present during shower event. The samples from the residential shower units are currently being sequenced to delineate the microorganisms present and to assess potential sources of the recovered microbial community. Results indicate that the Mycobacterium genus represents a significant fraction of the bacterial sequences recovered in some residential shower units. Results of the experimental shower studies indicate that showerheads with different flow rates affect the microbiome composition.

This study is assessing the composition of shower bioaerosols as well as the source and magnitude of this potential human exposure risk.

3IA.3

The Influence of Residential Environmental Factors on the Indoor Microbiome. KAREN C. DANNEMILLER, Janneane Gent, Brian Leaderer, Jordan Peccia, *Yale University*

Through aerosol inhalation and direct contact, the microbial community in house dust represents an important human exposure to bacteria and fungi. While it is known that specific features of microbial communities can affect human health, the influence of housing factors on microbial communities remains unclear. In this study, we determine the effect of residential factors on fungal and bacterial community content. We utilized house dust from 198 southern New England homes of children with asthma and used next-generation DNA sequencing to quantify fungal and bacterial richness and taxa distribution. Considered residential environmental factors included number of people and children in the home, town type (suburban vs. urban), house type (single family vs. multifamily), reported visible mold, reported water leaks, air conditioning use, and presence of pets. We determined that microbial richness was influenced by number of people and children, pets, reported water leaks, length of air-conditioning use, and town type ($p<0.05$). Specific taxa previously associated with human health effects, including members of the genera Acinetobacter, were shown to have associations with crowded living conditions and the presence of pets. When coupled with emerging information on the effects of microbial exposures, these results provide insights for how homes can be designed, operated, and occupied in order to encourage an indoor microbiome that contributes to human wellness.

3IA.4

Assessing Building Penetration Challenges by Subalpine Wildfires: Juxtaposing Airborne Biomarker Profiles with Microbial Community Analysis. ALINA M. HANDOREAN, Bharath Prithiviraj, Odessa Gomez, Jane Turner, Mark T. Hernandez, *University of Colorado Boulder*

Wildfires are becoming more frequent in temperate regions, as is their proximity to (sub)urban building complexes. Profiles of biochemical and genetic biomarkers were assessed for their ability to serve as selective penetration indicators when buildings were challenged with aerosols generated by a sub-alpine wildfire. This profile included airborne carbohydrates, phospholipids and phylogenetic profiles of microbes associating with airborne particulate matter.

Twenty-four hour, size segregated composite samples were collected indoors and outdoors of a building complex before and during a wildfire event and compared with baselines collected from a similar environment not impacted by wildfire. 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 and PCR amplicons were generated using 515F / 806 R primers specific to the V4 region of 16S rRNA. These primers amplified Archaeal and Bacterial hypervariable 16S regions and amplicons were barcode tagged with linker sequences. Paired end Illumina reads were obtained from the sequencing run. Data was analyzed using the Quantitative Insights Into Microbial Ecology (QIIME) and taxonomic structure, alpha (within site) and beta (between site) diversity were derived using the Unifrac phylogenetic diversity metric. Microbial heat maps were constructed indicating intensity of aerosol loads and statistical correlation established with biopolymer loads. Metagenomic gene content was analyzed using PICRUSt based on copy number of 16S bioaerosols. This enabled assessment of metabolic potential for fire generated bioaerosols, and its influence on the indoor environment as the fire progressed. While more abundant in the outdoor samples, patterns of biopolymer contribution to indoor and outdoor organic carbon loads, suggest building penetration mode which could not be elucidated by conventional PM analysis.

3IA.5

Assessing Pollutant Exposures in Rural Homes Using a Filter Forensics Approach. JUAN PEDRO MAESTRE, Shahana Khurshid, Kelli Royse, Sharon Horner, Jeffrey Siegel, Kerry Kinney, *The University of Texas at Austin*

Delineating biological and chemical exposures in residential homes is an essential step toward understanding the effects of these exposures on the prevalence and severity of asthma and allergy in children. The filter forensics approach uses the heating, ventilation and air conditioning (HVAC) filters installed in homes as integrated, long-term samplers of particle-bound contaminants, such as phthalates, microorganisms – bacteria and fungi-, endotoxins, and allergens. The objective of this study is to evaluate the use of HVAC filters for assessing housing-related contaminant exposures in rural homes.

In this study, over 20 low-income houses located in rural Texas are being sampled. Airborne dust samples are being collected from the home HVAC filters as well as settled dust samples from two locations within the household including the childrens' bedroom. The phthalate, endotoxin, and allergen (cat, dog, mite) concentrations are being determined in the dust samples recovered from the HVAC filter samples and compared to the levels recovered from the settled dust samples. In addition, microbial DNA is being extracted and total fungal and bacterial loads analyzed by quantitative PCR. Fungal and bacterial communities are being delineated via high-throughput Illumina sequencing, targeting the bacterial 16S region and the fungal ITS-1 region. After quality control, operational taxonomic units, alpha-diversity and beta-diversity indices were calculated to compare the molecular results.

Results to date indicate that the dust samples obtained from HVAC filters and from settled dust identified different microbial species. Phthalates, endotoxins and allergens were detected in both types of dust samples. Allergen composition in dust samples might be influenced by the intrinsic characteristics of the allergens, like particle weight. The analysis of both types of dust samples suggests that HVAC filter dust when combined with HVAC characterization, offers a more controlled way of detecting and assessing indoor air contaminants present at low concentrations in homes.

3IA.6

Contextualizing Particles on HVAC Filters. JEFFREY SIEGEL, Juan Pedro Maestre, Ying Xu, Shahana Khurshid, Kerry Kinney, *University of Toronto*

One way of assessing the presence and composition of indoor particles is to collect and analyze samples from heating, ventilation, and air conditioning (HVAC) filters. HVAC filters have been used to reveal the presence of a variety of particle-bound contaminants including fungi and bacteria, viruses, semi-volatile organic compounds (SVOCs), and metals. The promise of the HVAC sampling approach is that it can be used to measure spatially and temporally integrated airborne concentrations of particle-bound contaminants. In order to use HVAC filters to assess the exposure relevant indoor concentrations, the mass of contaminant collected from a filter has to be connected to the average airborne concentration. This presentation provides methodologies to measure the system run-time, air flow rate and filter efficiency that can be used to contextualize HVAC filter samples. For all of these parameters, we present multiple measurement approaches, provide comparisons for the accuracy and usability of each approach, and present measured data. For a sample of approximately 30 homes, we found HVAC run-times that ranged from a few percent (in homes during temperate times of the year) to over 60% in homes during the winter in homes in cold climates. Airflow rates were generally more consistent and ranged from 600 m3/hr for smaller systems to over 2400 m3/hr for larger systems. Manufacturer's reported filter efficiency was generally an overestimate of in-situ measured filter efficiency, but represented a reasonable estimate of the size resolved efficiency for PM10 and PM2.5. These parameters, in combination with analysis of HVAC filter dust, were then used to assess the airborne concentrations of 36 fungal specifies and several allergens in a subsample of 12 homes. Clear differences in allergen and fungal concentrations were seen in different homes suggesting that it is necessary to characterize HVAC concentrations to use the HVAC filter sampling technique effectively.

3NP.1

Field Deployment of a Size-Resolved Nano CPC Battery to Infer the Composition of Freshly Formed Atmospheric Nuclei in the Boreal Forest. 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 field measurements and modeling studies indicating that freshly nucleated particles can contribute significantly to the global population of cloud condensation nuclei. Our understanding of atmospheric nucleation and its influence on climate, however, is limited, as few ambient measurements have been made of either the nucleation rate or the chemical composition of the freshly formed clusters, both of which are necessary to gain process-level understanding. Recently, a nano condensation particle counter battery (nano CPCb) was developed and characterized in the laboratory to infer the size-resolved composition of nanoparticles down to diameters of 1 nm. The nano CPCb is composed of CPCs optimized for the detection of sub 3 nm particles, using diethylene glycol, water, and butanol as the working fluids. The nano CPCb was also integrated as a particle detector in a Nano-SMPS (scanning mobility particle spectrometer) system optimized for nanoparticle detection down to 1 nm. By sampling mobility-classified particles, the nano CPCb accounts for the strong dependence of CPC detection on particle size and charge below 3 nm, so that any measured differences in CPC response can be attributed to composition-specific interactions between the particle and the various working fluids. The integrated system was then deployed during an intensive field campaign in the Spring of 2013 to study atmospheric nucleation and initial growth at a long-term measurement site in the boreal forest in Hyytiälä, Finland. Preliminary measurements of freshly nucleated aerosol size distributions will be presented, along with the corresponding size-resolved composition-dependent responses of the nano CPCb.

3NP.3

Chemical Ionization of Sulfuric Acid Clusters Containing Basic Molecules. COTY JEN, Jun Zhao, Peter McMurry, David Hanson, *University of Minnesota*

Sulfuric acid clusters are detected by chemical ionization mass spectrometry whereby reagent ions exchange protons with the neutral clusters to form ions. Neutral clusters can also be ionized by these product ions in a process known as ion-induced clustering (IIC). IIC contributions to observed ion signals must be known to obtain accurate measurements of neutral clusters that appear at the same masses. Chemical ionization and IIC of sulfuric acid and its clusters have been previously studied and modeled as chemical reactions between ions and clusters primarily composed of sulfuric acid and water. However in the atmosphere and laboratory measurements, these clusters also contain basic molecules that alter the proton affinities of the clusters. The purpose of this study is to experimentally explore how various basic gases, such as ammonia, methylamine, dimethylamine, trimethylamine, and triethylamine, interact with sulfuric acid clusters, take up protons, and thus potentially alter the ionization reactions and their rate constants. The University of Minnesota Cluster Chemical Ionization Mass Spectrometer (Cluster CIMS) was used to measure cluster response as a function of the basic gas, its concentration, and the ionization reaction time. Experiments were performed inside a continuously purged, glass flow reactor using a well characterized sulfuric acid source. Results indicate that the strongest basic gases neutralize sulfuric acid clusters to the point that they are not efficiently chemically ionized by nitrate ions or by product ions containing sulfuric acid and basic molecules. These results signify that bare sulfuric acid IIC cannot be used for all sulfuric acid/base systems. Ionization rate constants were fitted from data and compared to the collision rate constant of the nitrate/sulfuric acid ionization reaction.

3NP.4

Enhancement in the Production of Nucleating Clusters Due to Dimethylamine and Large Uncertainties in the Thermochemistry of Amine-enhanced Nucleation. ALEXEY NADYKTO, Jason Herb, Fangqun Yu, Yisheng Xu, *Moscow State University of Technology; SUNY at Albany*

The enhancing effect of dimethylamine (DMA) on the production of stable ternary clusters have been studied using the Density Functional Theory (DFT) and large uncertainties in the thermochemistry of amine-enhanced nucleation have been pointed out and discussed [1]. It has been pointed out that the DMA concentrations of 1-10 ppt are needed in order to achieve a considerable enhancement in production of sulfuric acid-water clusters under typical atmospheric conditions and that the relative humidity (RH) plays a significant role at the early stages of the gas-to-cluster conversion. The present study leads us to conclude that: (a) At RH typical for the atmosphere most of the small DMA-containing clusters are hydrated; (b) Thermodynamics of ternary homogeneous nucleation (THN) involving ammonia and amines is similar in terms of both composition dependencies of base and acid affinities and hydration; (c) The uncertainties in the effect of DMA on nucleation thermochemistry are very large and largely associated with the description of interactions of the sulfuric acid, the key atmospheric nucleation precursor, with nucleating clusters. It has been pointed out that conventional ab initio RI-MP2/CBS and present PW91PW91/6-311++G(3df,3pd) methods are in much better agreement with experiments than the locally developed multi-step BLRIMPP2 and B3RICC2 methods [2-3], on which the current conclusions about the THN involving amines are based; (d) The uncertainties in the catalytic effect of the DMA on production of stable sulfuric acid clusters are very large and may affect conclusions about the importance of amine-enhanced nucleation in the Earth's atmosphere.

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3NP.5

Novel Methods for Determining Free Energies of Molecular Clusters of Water and Sulphuric Acid. Gabriel Lau, Jake Stinson, Shawn Kathmann, IAN FORD, *University College London*

A microscopic model of the nucleation of atmospheric particles must involve the following elements: (a) the identification of the molecular species that form the critical cluster under prevailing conditions; (b) a force field that is capable of representing the interactions between these species; and (c) a procedure for calculating growth and evaporation rates of clusters, and combining them in a suitable kinetic framework, bearing in mind that their structures are disordered, and their evaporative lifetimes are relatively short. With regard to (a), the consensus view is that sulphuric acid is the central species in the process, condensing in association with water, ammonia, amines and perhaps other molecules. But the practical implementation of elements (b) and (c) is less settled. We shall describe the development of a new empirical valence bond (EVB) force field suitable for sulphuric acid/water mixtures that allows for the possibility of proton transfer. The scheme is classical and therefore computationally cheap: it is essentially an empirical fit to higher level force fields but crucially includes mixing between patterns of molecular bonding. Furthermore, we have developed a mechanical procedure of cluster disassembly in molecular dynamics that provides an estimate of the cluster excess free energy. This is a generalisation of a surface term and is a thermodynamic equivalent of the relevant growth and evaporation rates that lie at the heart of nucleation kinetics. The excess free energy may be related to the nonquasistatic mechanical work of disassembling the cluster into separate molecular constituents, by way of the Jarzynski equality. In contrast, it is more usual to determine free energy differences associated with individual growth and evaporation events, or to employ a high temperature reference state for each cluster, in comparison with which the disassembly method is more direct. We shall describe the essential ideas behind these developments.

3NP.6

New-particle Formation, Growth and Climate-relevant Particle Production in Egbert, Canada: Analysis from one Year of Size-distribution Observations. JEFFREY PIERCE, Daniel Westervelt, Samuel Atwood, Elizabeth Barnes, Richard Leaitch, *Colorado State University*

Aerosol particle nucleation, or new-particle formation, is the dominant contributor to particle number in the atmosphere. However, these particles must grow through condensation of low-volatility vapors without coagulating with the larger, pre-existing particles in order to reach climate-relevant sizes (diameters larger than 50-100 nm), where the particles may affect clouds and radiation. In this paper, we use one year of size-distribution measurements from Egbert, Ontario, Canada to calculate the frequency of regional-scale new-particle formation events, new-particle formation rates, growth rates and the fraction of new particles that survive to reach climate-relevant sizes. Regional-scale new-particle formation events occurred on 14-31% of the days (depending on the stringency of the classification criteria), with event frequency peaking in the spring and fall. New-particle formation rates and growth rates were similar to those measured at other mid-latitude continental sites. We calculate that roughly half of the climate-relevant particles (with diameters larger than 50-100 nm) at Egbert are formed through new-particle formation events. With the addition of meteorological and SO2 measurements, we find that new-particle formation often occurred under synoptic conditions associated with high surface pressure and large-scale subsidence that cause sunny conditions and clean-air flow from the north and west. However, new-particle formation also occurred when air flow came from the polluted regions to the south and southwest of Egbert. The nucleation rates tend to be faster during events under the polluted south/southwest flow conditions.

3UA.1

How To Achieve Further PM2.5 Reductions in a Midwestern City? A Combined Modeling and Measurement-Based Analysis of Iowa City, IA. ROBERT BULLARD, Elizabeth Stone, Charles Stanier, Ashish Singh, Can Dong, Chathurika Rathanyake, Thilina Jayarathne, Scott N. Spak, *University of Iowa*

The Iowa City, IA metropolitan area has regionally representative annual average $PM_{2.5}$ concentrations, with levels measured by the local EPA monitor ranging 10-12 micrograms/m^3 in recent years. However, this monitor is located 3.5 km from the downtown area, which has the highest population density and pedestrian exposure to air pollutants. The downtown also includes a majority of anthropogenic emissions from vehicles, cooking, local power generation, and medical waste incineration. To better understand population exposure to air pollution, we (a) chemically characterized $PM_{2.5}$; (b) evaluated the absolute and relative impacts of electric generation, industry, motor vehicles, residential emissions, and regional transport using CMB and chemical transport modeling (CTM); and (c) used the CTM with high resolution (0.4 km) emissions to generate spatially-resolved concentration maps of $PM_{2.5}$, O_3, and their precursors.

In 2011 and 2012, $PM_{2.5}$ samples were collected and analyzed for organic and elemental carbon (OC and EC), inorganic ions, and molecular markers at two locations. OC and EC averaged 2.5 and 0.3 micrograms/m^3, respectively, and exhibited seasonal patterns. Particle phase polycyclic aromatic hydrocarbons and the coal tracer picene peaked in winter. CMB modeling indicated that biomass burning and then non-catalyzed gasoline engines were the greatest contributors to primary $PM_{2.5}$ OC. The downwind site was enhanced in tracers for coal combustion tracer (factor of ~3), biomass burning (factor of ~1.5), and motor vehicles (factor of ~1.3). A two-week mobile field study was conducted to measure the aerosol concentration, aerosol size distribution, NO_x, and SO_2 concentrations in the power plant plume. Under breezy summer conditions, the plume contained about 10 ppb each of NO, NO_2, and SO_2, when it reached ground level in downtown Iowa City, and high concentrations of ultrafine particles. High resolution (0.4 km) WRF-CMAQ model was run for one year corresponding to the filter sampling period.

3UA.2

Investigation of the Sources and Evolution Processes of Severe Haze Pollution in Beijing in January 2013.

YELE SUN, Qi Jiang, Zifa Wang, Pingqing Fu, Jie Li, Ting Yang, Yan Yin, *Institute of Atmospheric Physics, CAS*

China experienced severe haze pollution in January 2013. Here we have a detailed characterization of the sources and evolution mechanisms of this haze pollution with a focus on four haze episodes that occurred during 10-14 January in Beijing. The average PM_1 mass concentration during the four haze episodes ranged from 144 – 300 µg m^{-3}, which was more than 10 times higher than that observed during clean periods (14 µg m^{-3}). All submicron aerosol species showed substantial increases during haze episodes with sulfate being the largest. Secondary inorganic species played enhanced roles in the haze formation as suggested by their elevated contributions during haze episodes. Positive matrix factorization analysis resolved six organic aerosol (OA) factors including three primary OA (POA) factors from traffic, cooking and coal combustion emissions, and three secondary OA (SOA) factors. The OA compositions varied greatly among different haze episodes. Overall, SOA contributed 41 – 59% of OA with the rest being POA. Coal combustion OA (CCOA) was the largest primary source, on average accounting for 20- 32% of OA, and showed the most significant enhancement during haze episodes. A regional SOA (RSOA) was resolved for the first time which showed a pronounced peak only during the record-breaking haze episode (Ep3) on 12-13 January. The regional contributions estimated based on the steep evolution of air pollutants were found to play dominant roles for the formation of Ep3. The regional contribution on average accounted for 66% of PM_1 during the peak of Ep3 with sulfate, CCOA and RSOA being the largest fractions (>~75%). Our results together suggest that stagnant meteorological conditions, coal combustion, secondary production, and regional transport are four main factors driving the formation and evolution of haze pollution in Beijing during wintertime.

3UA.3

Outdoor and Indoor Black Carbon at Multiple Schools in Salt Lake City, Utah.

Jennifer DeWinter, Steven Brown, David Vaughn, PAUL ROBERTS, *Sonoma Technology, Inc*

To help understand pollutant concentrations inside classrooms in relation to ambient (outside) concentrations under existing air handling and ventilation systems, black carbon (BC) was measured indoors and outdoors at four schools in Salt Lake City, Utah, during March-June 2014. The schools are within 2,100 feet of a planned major freeway, and two of them will abut the freeway. The data generated by this monitoring will inform us of the existing air handling systems' filtration effectiveness for removing BC. BC is a frequently used surrogate for diesel particulate matter (DPM), which has been shown to have significant health effects in near-road environments. DPM, as measured by BC, is the focus of this effort, as 84% of the cancer risk at one of the schools was attributed to DPM (on the basis of MATES II cancer risk values and ambient air monitoring of BC and gaseous air toxics during 2013). In addition to BC, PM2.5 was measured indoors and outdoors at one school. We will present results describing indoor and outdoor concentrations, diurnal and weekday/weekend variations, filtration efficiency at each school, and how outdoor concentrations compare to near-roadway concentrations elsewhere. Results will assist the Utah Department of Transportation's Air Working Group and the school district in determining the best mitigation measures for indoor air pollution.

3UA.4

Sources and Chemical Composition of Atmospheric Fine Particles in Rabigh, Saudi Arabia.

HAIDER A KHWAJA, Omar S Abu-Rizaiza, Azhar Siddique, Shedrack R Nayebare, Mirza M Hussain, Jahan Zeb, *King Abdulaziz University, Saudi Arabia*

Air pollution is a major environmental problem of public concern in several developing countries of the world. Research into air pollution in Saudi Arabia and the whole of Middle East region is at its inception. There are significant gaps in policy guidelines related to air pollution control in the region, which has worsened the air quality over the years. This study presents the first detailed data on fine particulate matter (PM2.5) concentrations of Black Carbon (BC) and trace metals (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Cd, Sb, and Pb) at Rabigh, Saudi Arabia, and assesses their sources. Analytical results showed several characteristics aspects of air pollution at Rabigh area. Sulfur and BC mass concentrations ranged from 68.6 to 642 ng/m3, and from 0.39 to 1.31 µg/m3, respectively, while the PM2.5 mass concentration ranged from 12.2 to 75.9 µg/m3 with significant temporal variability. More than 90% of the time, the daily PM2.5 levels exceeded the 24 h WHO guideline of 20 µg/m3 . An Air Quality Index (AQI) was calculated for PM2.5 at Rabigh, with any PM2.5 level beyond moderate, reported as a “level of health concern” (good: <=12 µg/m3, moderate: 12.1 – 35.4 µg/m3, unhealthy for sensitive groups: 35.5–55.4 µg/m3, unhealthy: 55.5 – 150.4 µg/m3, very unhealthy: 151 – 250 µg/m3, and hazardous: 251 – 350 µg/m3). Based on the AQI, there were 44% days of moderate air quality, 33% days of unhealthy air quality for sensitive groups, and 23% days of unhealthy air quality throughout the study period. Two broad categories of aerosol trace metal sources were defined: anthropogenic (S, V, Cr, Ni, Cu, Zn, Br, Cd, Sb, and Pb) and naturally derived elements (Si, Al, and Fe). The extent of anthropogenic contribution was estimated by the degree of enrichment of these elements compared to the crustal composition. Soil resuspension and/ or mobilization appear to be the important source of “natural” elements, while "anthropogenic" elements originate primarily from fossil fuel combustion and industries. Ni and V correlated strongly pointing to combustion of heavy fuel oil as the likely source. A factor analysis method, positive matrix factorization (PMF), was used to obtain information about possible sources of aerosol.

3UA.5

Chemical Characterization of Time Resolved Haboob Samples from Phoenix, AZ.

AURELIE MARCOTTE, Jershon Eagar, Denise Napolitano, Pierre Herckes, *Arizona State University*

During the summer months in Arizona, very intense dust storms, or haboobs, can occur. These dust storms can last from minutes to hours and can alter the aerosol content greatly on short time scales. Monsoon-like storms sometimes follow haboobs, which can scavenge the aerosol particles that were brought in by the dust storm. Understanding haboobs is of great importance in the Phoenix area as they can increase particulate matter (PM) and bring an influx of PM material from other locations. Deposition of PM may alter soil and water chemistry in the affected areas. In this work, we chemically characterize haboobs and their effect on the air quality in the Phoenix area. During the summer of 2013, background urban PM samples and the PM of haboob events (PM2.5 and PM>2.5) were collected on the Arizona State University Tempe Campus. Samples were collected before, during, and after haboobs to determine the time resolved effect of haboobs on PM in the Phoenix area. Samples were analyzed for trace metals by inductively coupled plasma mass spectrometry (ICP-MS), soluble iron content by a ferrozine/UV-Vis method, and major inorganic species by ion chromatography (IC). Additional analyses included thermal optical transmittance to determine organic and elemental carbon concentrations and gas chromatography mass spectrometry (GC-MS) to identify organic tracer compounds such as alkanes and polycyclic aromatic hydrocarbons (PAH). Changes in composition with a focus on differences and communalities between haboob and non-haboob aerosols will be discussed. The duration of a haboob’s effect on ambient PM concentrations will also be examined. A more complete understanding of the effect of haboobs on the Phoenix area could be helpful in making health recommendations for residents during the summer months.

3UA.6

Silicon is a Nearly Ubiquitous Component of Ambient Nanoparticles. BRYAN R. BZDEK, M. Ross Pennington, Andrew J. Horan, Christopher A. Zordan, Murray Johnston, *University of Delaware*

This work presents quantitative elemental composition measurements of individual 20-25 nm atmospheric nanoparticles using the Nano Aerosol Mass Spectrometer. Measurements were conducted in urban (Wilmington, Delaware), suburban (Pasadena, California), rural (Lewes, Delaware), and remote (Hyytiälä, Finland) environments. The nonmetal silicon was found to be present in a low but substantial abundance in a surprisingly large fraction of the nanoparticles measured in environments impacted by humans. For example, more than 48% of the nanoparticles studied during a summertime campaign in Lewes, DE, contained Si with an abundance greater than 1% elemental mole fraction. A campaign in Pasadena, CA, found that more than 40% of the nanoparticles studied contain Si > 1% elemental mole fraction. On the other hand, nanoparticles analyzed in the remote boreal forest contained barely any Si. These observations suggest that nanoparticulate Si tends to be observed more frequently in impacted (rather than remote) environments. Diurnal trends indicate that Si is more abundant during the daytime, suggesting photochemical formation of low-volatility Si-containing compounds from higher volatility precursors. Measurements made in the same location during different seasons show substantial seasonal dependencies on Si content. Combined with meteorological data, these observations suggest local (rather than regional) sources for the Si. In summary, these observations indicate nearly ubiquitous, local sources of Si in environments impacted by human activity. By making assumptions about the molecular species contributing to nanoparticulate Si (e.g. assigning Si to SiO2 or various siloxanes), the atmospheric burdens of these species can reach several tens of ng/m3. These observations suggest a more refined understanding of the sources, reaction pathways, and sinks of organosilicon compounds in the atmosphere is required.

4AC.1

Explicit Modeling of Multi-generational Aging of Organic Aerosol in an Air Quality Model. SHANTANU JATHAR, Anthony Wexler, Christopher Cappa, Michael Kleeman, *University of California, Davis*

Climate and air quality models lack or incorporate a simple and unconstrained treatment of the multi-generational aging of organic gases, a pathway that could improve organic aerosol (OA) model performance and bears heavily on OA's climate- and health-relevant properties. Here we implement an explicit oxidation scheme (Cappa and Wilson, ACP, 2012) parameterized using recent experimental data in a regional air quality model to simulate the influence of multi-generational aging of OA. The scheme includes a resolved treatment of carbon size and molecular structure (linear, branched, cyclic) for alkanes and a lumped treatment for aromatics and biogenics. We use the air quality model to simulate two summertime episodes over Southern California for which comprehensive air quality measurements are available: July-August 2005 (SOAR) and May-June 2010 (CalNex). Results will be compared to measurements to determine if multi-generational aging substantially enhances region-wide daily-averaged OA concentrations. Evaluations at Riverside, CA and Pasadena, CA based on measurements will be used to determine if the model improves predictions of OA's diurnal profile, degree-of-oxygenation and fossil-versus-modern fraction.

4AC.2

Modeling Secondary Organic Aerosol Formation via Partitioning and Aerosol Phase Reactions under Two Phase States: Liquid-liquid Phase Separated and Homogeneously Mixed. ROSS BEARDSLEY, Myoseon Jang, *University of Florida*

The Unified Partitioning-Aerosol phase Reaction (UNIPAR) model was used to investigate the influence of aerosol phase state on secondary organic aerosol (SOA) formation from the photooxidation of volatile organic compounds (VOC). UNIPAR employs an explicit gas phase kinetic model to predict the gas phase oxidation products of VOC that are subsequently lumped into 8 volatility and 5 reactivity bins using mass stoichiometric coefficients($a_{i,j}$) as a function of VOC/NO_x ratio. SOA formation is then predicted via partitioning and aerosol phase reactions (oligeomerization, acid-catalyzed reactions, and organosulfate formation) assuming either liquid-liquid phase separation (LLPS) or a single homogeneously mixed phase (SHMP). Day long NOx photooxidation experiments were performed using the large, outdoor UF-APHOR chambers for isoprene, benzene, toluene, or alpha–pinene in the presence and absence of SO_2. The oxidation products of isoprene are primarily polar and hydrophilic inducing SHMP SOA, while the non-polar, hydrophobic α–pinene oxidation products characteristically form LLPS SOA under ambient conditions. The phase states of benzene and toluene SOA are not as distinct and will vary based on aerosol composition and RH. The phase state of SOA significantly impacts the rate of aerosol phase reactions and partitioning and needs to be handled appropriately by models. In this study, all of the mentioned VOC/NO_x systems were simulated using both phase state options of UNIPAR in order to determine the implications of phase on SOA model performance.

4AC.3

Understanding the Sensitivity of SOA Formation to Various Uncertain Modeling Parameters Using a Variance-Based Statistical Approach. MANISHKUMAR SHRIVASTAVA, Chun Zhao, Yun Qian, Richard Easter, Alla Zelenyuk, Jerome Fast, *Pacific Northwest National Laboratory*

Several physical and chemical processes affect the formation of secondary organic aerosol (SOA), one of the most important but uncertain fraction of fine particles in the atmosphere. Models typically select a set of parameters to represent various processes such as dry deposition, the emissions of volatile organic compounds (VOCs), NOx, SOA precursor emissions and SOA yields. But all these parameters have a big range of uncertainty, which are not accounted in the models. In addition, there are complex non-linear interactions among these parameters e.g. changing the emissions of volatile organic compounds (VOCs) and NOx would change oxidant fields and NOx regimes, which affect SOA yields. Also, the sensitivities of SOA formation to VOC and NOx regimes may depend on the properties of SOA such as its low volatility, phase and viscosity. In this study, we investigate the sensitivity of SOA to seven parameters related to the emissions of anthropogenic and biogenic VOC and NOx, as well as anthropogenic semi-volatile and intermediate volatility species (SIVOC), phase and volatility changes of SOA particles, and dry deposition parameters of SOA precursors. We perform an ensemble of 128 simulations using the Weather Research and Forecasting Model coupled to Chemistry (WRF-Chem), and simulate SOA using our modified volatility basis-set (VBS) approach over the domain where the CARES field study in Sacramento, CA was conducted in June 2010. We adopt a quasi-Monte Carlo (QMC) sampling approach to effectively sample the high-dimensional parameter space and conduct a variance-based sensitivity analysis to quantify the contribution of each parameter to the overall SOA loading uncertainty. We also characterize the spatial and temporal statistical significance of these parameters. Finally we investigate how the interactions between these parameters affect the variance of SOA formation in the atmosphere. Results are expected to provide insights that would help better constrain the SOA modeling to improve model-measurement agreement.

4AC.4

1D Nanodusty Pulsed Plasma Sectional Chemistry Model for the Study and Control of Particle Generation and Growth. CARLOS LARRIBA-ANDALUZ, Steven Girshick, *University of Minnesota*

Plasmas can be a valuable tool in the production of nanostructured materials if the formation, growth and transport of nanoparticles in reactive plasmas can be controlled. Plasmas containing nanoparticles are termed “nanodusty” and present impelling opportunities for nanosynthesis of materials such as silicon nanocrystals used in solar panels. The drawback is that particles of a few nm in size are difficult to detect in situ and characterize and thus require elaborate experimental systems as well as complicated numerical schemes. The modeling of low temperature plasmas for fundamental investigations and equipment design is challenged therefore by conflicting goals: 1)the need to address subtle physical phenomena and 2)the flexibility to expand a wide range of conditions. Here we try to numerically explore the ability of plasmas to produce nanocrystals by combining a silane low temperature plasma chemistry model with a nanoparticle sectional model. A 1D model simulates an RF capacitive argon plasma in a parallel-plate reactor with the injection of silane for nanoparticle formation. Spatial profiles of instantaneous electron and positive ion concentrations, electron temperature, plasma potential, and electric field are determined using a continuum formulation while nanoparticles are calculated using a Sectional Model that includes Coagulation, Nucleation, Surface Growth and Charging. A drift-diffusion approximation is applied to the electron, ion and nanoparticle flux. The combination of continuum and sectional models provide a fast and self-consistent reliable tool to study plasmas and their production of particles. We go a step further by looking into the possibility of controlling the size and particle production through pulsing and afterglow of plasmas. We will demonstrate that one can produce different sized nanoparticles by tuning the frequency and duty-cycles of the pulse. Simultaneously, we will show that the need to provide accurate chemistry is key to providing reliable results when compared with the experimental results.

4AC.5

Modelling of Amines in the Global Atmosphere: Impacts of Oxidation and Aerosol Uptake. FANGQUN YU, Gan Luo, *University at Albany*

Amines have received increasing attention in recent years as theoretical, laboratory, and field measurements indicate that amines may considerably enhance particle formation and growth. Recent measurements taken in the CLOUD (Cosmics Leaving Outdoor Droplets) chamber experiments at CERN indicate that dimethylamine concentration ([DMA]) of several pptv can substantially enhance nucleation rates but such an enhancement drops significantly as [DMA] decreases below a few pptv. In order to determine the contribution of ternary nucleation involving amines to the atmospheric particle production, it is critical to know the concentrations of key amines and their spatiotemporal variations in the atmosphere. In the present work, we attempt to simulate the global distributions of amines in the air with a global chemistry transport model (GEOS-Chem). The key processing controlling amines concentrations (including emission, deposition, transport, oxidation, and aerosol uptake) are considered and the simulated results are compared to the limited measurements. Our simulations indicate that amines have a very short lifetime (as short as 1-2 hours over some regions) due to oxidation and aerosol uptake. As a result, relatively high concentrations of amines are generally confined to the source regions. With the estimated global DMA emission flux from the literature, our simulations indicate that the annual mean [DMA] is generally less than 1 pptv in the boundary layer over major continents and below 0.1 pptv over oceans and above boundary layer. Total concentrations of methylamines amines (including monomethylamine, dimethylamine, and trimethylamine) are about one order of magnitude higher. The uncertainty in the model simulations, sensitivity of simulated amines concentrations to aerosol uptake coefficients, and implications of results to atmospheric new particle formation will be discussed.

4AC.6

Simulation of the Volatility-Oxygen Content Distribution of Organic Aerosol during the PEGASOS Campaigns. ELENI KARNEZI, Benjamin Murphy, Spyros Pandis, *Carnegie Mellon University*

The two-dimensional volatility basis set (2D-VBS) is used for the simulation of the OA distribution as a function of its volatility and oxygen content. A one-dimensional Lagrangian chemical transport model (PMCAMx-Trj) is used as the host model for the simulations. PMCAMx-Trj simulates the chemical evolution of a column of air as it travels towards a user-selected receptor site. The Hybrid Single Particle Lagrangian Integrated Trajectory HYSPLIT model (Draxler et al., 2009) is used to calculate 72 h back trajectories arriving at the receptor sites in the heavily polluted from both industrial and agricultural sources Po Valley in Northern Italy. We evaluate different parameterizations of secondary organic aerosol formation and processing of the 2D-VBS with the measurements of OA collected in the PEGASOS field campaign using among other airborne measurements collected by a Zeppelin. The predicted vertical profiles of the OA concentration are rather sensitive to the evaporation enthalpy and the chemical aging mechanism. This state-of-the-art dataset allow us to constrain further the different parameterizations and mechanisms of OA chemical aging used in the 2D-VBS scheme. The simplest approach parameterizing the chemical aging of anthropogenic compounds assuming a reduction of volatility by one bin during every aging step accompanied by an increase of one or two oxygen atoms with an equal probability is the most successful. The model shows remarkable skill in reproducing the observations of quite oxidized OA with little diurnal variation in O:C during the day.

4AC.7

Dynamic Simulation of Atmospheric Chromium Speciation.

MEHDI AMOUEI TORKMAHALLEH, Soudabeh Gorjinezhad, *Middle East Technical University Northern Cyprus Campus*

The two chromium oxidation states found in ambient atmospheric particulate matter are trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium. Cr(III) is a trace element essential for the proper function of living organisms. However, Cr(VI) is toxic and exposure to Cr(VI) may lead to cancer, asthma and bronchitis. Therefore, it is important to accurately discriminate between these two species in atmospheric particulate matter (PM) samples. Since 1995 when first study on the simulation of atmospheric chromium chemistry was published by Seigneur and Constantinou (Environ. Sci. Technol, 29, 222-231), no such study has been added to the literature to improve our understanding on atmospheric chromium speciation. The simulation results published by Seigneur and Constantinou showed how fast Cr(III) and Cr(VI) inter conversion would occur in the atmosphere. However, the impact of chromium reactions with atmospheric gases and organic carbon, on the overall direction of chromium speciation was not studied. More importantly, the model did not employed experimental or field data as input or for validation. Since 1995, few experimental data on atmospheric chromium chemistry have been published by Amouei Torkmahalleh et al. (Atmospheric Environment (2013), 71, 92-94; Aerosol Science and Technology (2012), 46(6), 690-696) and other researchers which can be employed together with atmospheric chromium concentration data to improve the proposed model by Seigneur and Constantinou. The current study performs a computer simulation of atmospheric chromium speciation. We found that for liquid-coated particles with pH of 1 the half life of chromium is around 1 minute, and it increases to almost 3 minutes if lack of some heavy metals such as Pb2+, Cu2+ and Zn2+ exists in the solution. The system attains steady state after approximately 15 minutes. The effects of pH and liquid water content which is controlled by the deliquescence of ambient PM were found to be significant on chromium speciation.

4AP.1

Classical Nucleation Theory Does Not Correctly Predict the Dependence of Nucleation Rate on Supersaturation.

STEVEN GIRSHICK, *University of Minnesota*

While it is well known that classical nucleation theory (CNT) does not correctly predict the temperature dependence of the stationary rate of homogeneous nucleation, it is commonly asserted that CNT does at least correctly predict the supersaturation dependence. In this work we reexamine this claim in light of a number of experimental studies in which homogeneous nucleation rates of various substances (water, several 1-alcohols, argon and nitrogen) were measured over ranges of temperature and saturation ratio, and the measured supersaturation dependence of nucleation rate was used to infer critical cluster sizes by means of the Nucleation Theorem. In general, the inferred critical sizes agree poorly with those predicted by CNT, implying that the supersaturation dependence of nucleation rate is poorly predicted, contrary to what is commonly believed.

If one considers the expression for the stationary nucleation rate in summation form, before any assumption is made regarding the form of the free energy change (delta-G) for formation of a cluster from the monomer vapor, one finds that every term in the summation has a supersaturation dependence that arises purely from well-established thermodynamics (the dependence of Gibbs free energy on pressure) and kinetics (the dependence of molecular collision rates on number densities of the collision partners). Superficially, it thus seems that CNT, or any other theory that accepts the summation expression for the nucleation rate as valid, must correctly predict the supersaturation dependence. However, the model used to predict delta-G does affect the value of the critical size, and, since the summation is dominated by terms close to the critical size, the model for delta-G in turn affects the dependence of nucleation rate on saturation ratio. Therefore, we can conclude that CNT's incorrect model for delta-G for small clusters leads to an incorrect prediction of the supersaturation dependence of nucleation rate.

4AP.2

Resolving the Surface and Bulk Accommodation of Atmospherically Relevant Compounds with Molecular Dynamics Simulations. JAN JULIN, Paul M. Winkler, Neil Donahue, Paul E. Wagner, Ilona Riipinen, *Stockholm University*

The condensational growth of aerosol particles needs to be accurately understood in order to correctly predict cloud condensation nuclei (CCN) concentrations. A large fraction of the condensable vapors partaking in the growth process are different organic compounds with a variety of structural features. The CCN in turn grow to cloud droplets by condensation of water vapor. The quantity describing the vapor uptake ability of the aerosol particles is the mass accommodation coefficient, defined as the fraction of gas phase molecules that will accommodate to the condensed phase. The coefficient has proven to be challenging to determine experimentally. A further complication arises from the fact that the experiments are interpreted using aerosol dynamic models which do not distinguish between aerosol bulk and surface, yet the coefficient can be defined either as surface or bulk accommodation coefficient. The difference between the two is whether surface adsorption or bulk absorption is required for accommodation.

We present molecular dynamics (MD) simulation results on the condensation of various organic molecules on organic surfaces, as well as water on ice. MD simulations provide information on mass accommodation coefficient directly from the fates of individual molecules as they arrive on a surface, and MD can distinguish between surface and bulk accommodation. We find that for nonane MD simulations and expansion chamber measurements agree well. We have examined the effect of both the molecular structure of the organic compounds and the phase-state of the condensed phase on the mass accommodation process. Our results highlight both the sensitivity of the bulk accommodation coefficient to the division between surface and bulk, and the necessity to include a time-dependence in the definition of the bulk accommodation coefficient. Consequently, our results emphasize the need for experimental methods that can probe aerosol surface and bulk separately to reliably constrain the mass accommodation coefficient.

4AP.3

Experimental Study of Light Scattering from Irregularly Shaped Particles. YULI WANG, Amit Chakrabarti, Chris Sorensen, *Kansas State University*

Light scattering has been a subject of enduring scientific interest for a long time. An important application of light scattering concerns the role that aerosols play in affecting our climate. We built our own setup to determine scattering matrix elements from irregularly shape particles. The novelty of our experimental apparatus is using photodiode arrays to detect simultaneously at many angles. We also use some angles that quite small which is necessary for accurate characterization of large particles. We tested our setup with water droplets from a nebulizer. Here, we present measurements from soot particles produced from homemade burner. We apply q-space analysis which provides a comprehensive description of scattering in terms of power laws with quantifiable exponents.

4AP.4

Surface Freezing of n-alkanes. VIRAJ MODAK, Mitchell Thayer, Barbara Wyslouzil, Sherwin Singer, *The Ohio State University*

Crystallization is a common physical process encountered in the chemical industry as well as in natural environments. For liquids with free surfaces, whether the nucleation event occurs at the surface or in the bulk, has been a subject of controversy, especially in the atmospheric science community. For straight chain n-alkanes, however, there is experimental evidence to suggest surface freezing occurs. This phenomenon was first observed for intermediate chain length alkanes (15<i

4AP.5

Experimental Bipolar Diffusion Charging of Spherical and Cylindrical Aerosol Particles with Detailed Characterization of the Charging Ions. Ranganathan Gopalakrishnan, Peter McMurry, CHRISTOPHER HOGAN JR., *University of Minnesota*

The results of bipolar diffusion charging experiments performed using spherical and cylindrical aerosol particles are presented here. Gold nanoparticles (spheres of nominal diameters 50 and 70 nm; cylinders of nominal length to diameter ratios of 2.2 to 14.3) are generated by electrospraying colloidal solutions. The mass and mobility distributions of the charging ions (formed by ionization of gas phase species by a Po-210 source) are measured using a high resolution DMA coupled to a time-of-flight Mass spectrometer. Using a tandem-DMA setup, the fraction of neutral particles and ratios of the singly to doubly charged particles of positive and negative polarities are measured in Ultra-high purity air and Carbon dioxide. Measured charge distributions are compared to predictions of a previously developed Brownian Dynamics based charging model that takes into account the exact geometric size distribution of the particles as inferred from electron microscopy and the mass-mobilities of the ions with minimal simplifying assumptions, while also separately accounting for the operating conditions (transfer function) of the DMAs. From measured charge distributions of cylinders, it is seen that particles that are highly nonspherical (ratio of the orientation averaged Projected Area to the diffusion based surface area of 0.70 and 0.63) attain higher charge levels than mobility equivalent spheres (at 65 nm). The effect of mobility diameter was also studied, and for the particles considered here (aforesaid ratio=0.84) behave akin to mobility equivalent spheres (<65 nm). The measured and simulated charge distribution for spheres show good agreement in air, while in carbon dioxide the presence of high mobility negative charge carriers that escaped detection by our measurement systems are hypothesized to be one of the reasons for differences. The ions generated by radioactive neutralizers were traced to the tubing material based on the measured mass-mobility spectra.

4AP.6

Understanding the Drag Force and Mobility of Nonspherical Particles in the Free Molecular Regime.

MINGDONG LI, George Mulholland, Michael Zachariah, *University of Maryland*

An approach to obtain the mobility of nonspherical particles is proposed by averaging the drag force orientationally, and two other widely used approaches in the literature, the averaged-collision-integral and averaged-drift-velocity methods, are summarized and extended. The concept of orientationally averaged collision integrals based on Chapman-Enskog theory for small gas-phase ions is re-examined for macromolecular ions whose surface cannot be treated as specular, but with inelastic interactions. A well accepted collision model considering inelastic collisions is Epstein's theory, which has been extended to include long-range potential forces by Li and Wang [Phys. Rev. E 68, 061206 (2003)] for spherical particles. This work extends Li and Wang's spherical particle theory to convex nonspherical particles considering long-range potential, and simplifies this collision integral to a product of the averaged projection area and an enhancement factor for short-range interactions (hard collisions), which is independent of convex particle shape and is identical to the value for a sphere that people are using. We also show that the averaged projection area of a convex particle in free molecular regime for hard collisions is equal to its mobility diameter. The second approach is the averaged-drift-velocity approach using the friction coefficient in a tensor form, which is often employed in aerosol science. We extend this approach in our previous work for axisymmetric particles to develop an expression for the mobility of nonspherical particles in a general form. Furthermore, it is pointed out that this approach is only valid when the particle Brownian rotation is slowcomparedwith the particle translational relaxation time. If the particle Brownian rotation is fast, usually so in the case of very small ions and particles, we propose an "averaged-drag-force" approach. The three approaches are then compared for a randomly oriented rod and the protein GroEL. We show that for a cylinder rod in the free molecular regime at random orientation, the averaged-drag-force approach is identical to the averaged-collision-integral approach for short-range interactions (hard collisions). We then summarize the relationship between collision-integral based approach and tensor based approaches. For readers only interested in implementation of the theory, we provide useful expressions in Tables I and II.

4AP.7

Evaporation Loss of PM2.5 during Filter Sampling.

CHUEN-JINN TSAI, Chun-Nan Liu, Sih-Fan Lin, Guo-Rui Lee, *National Chiao Tung University*

The evaporation loss of PM2.5 in a filter-based sampler was evaluated experimentally by a home-made multi-filter PM10-PM2.5 sampler. Results show that the evaporation loss is severe during sampling process, accounting for 5.8 to 36.0% of the corrected PM2.5 concentration and the percentage increased with decreasing loaded particle mass and increasing filtration velocity. In the present study, this issue was evaluated theoretically. The model of Cheng and Tsai (1997) which can only be used to calculate the evaporation loss of monodisperse NH4NO3 particles was modified allowing for calculating the evaporation loss of PM2.5 particles. In this modified model, the evaporation losses of particles in different particle size ranges below 2.5 μm sampled by the 4th to the after filter stages of the MOUDI were calculated separately and then integrated to obtain the total PM2.5 evaporation loss. Results show that when the collected particles are nearly neutral with a pH equals to 7 to 8, the evaporated concentrations predicted by the present model agree well with the experimental data with an average difference of < 10%. However, for acid aerosols with a pH less than 3.5, the predicted evaporation loss is less than experimental data. This is because in the acid condition, nitrate and chloride particles can also be lost due to chemical interactions between collected particles and strong acids which is not calculated. The theoretical model was used to examine the effect of PM2.5 concentration, ambient temperature and relative humidity on the extent of evaporation loss. Results show that evaporated PM2.5 concentration increases with an increasing temperature and with a decreasing relative humidity and PM2.5 concentration.

4AQ.1

Overview of the NOAA SENEX Field Mission. JOOST DE GOUW, Aikaterini Bougiatioti, Jerome Brioude, Steven G. Brown, William P. Dube, Peter Edwards, David Fahey, Jessica Gilman, Timothy Gordon, Martin Graus, Tom Hanisco, John Holloway, Jennifer Kaiser, Frank Keutsch, Daniel Lack, Daniel Law, Ben Lee, Brian Lerner, Jin Liao, Jack Lin, Felipe Lopez-Hilfiker, Milos Markovic, Ann M. Middlebrook, Kyung-Eun Min, et al., *NOAA ESRL*

The NOAA Southeast Nexus of Air Quality and Climate Change (SENEX) study was focused on biogenic and anthropogenic emissions in the Southeastern United States, and their interactions to form oxidants and aerosol. For SENEX, the NOAA WP-3D research aircraft was deployed out of a regional airport in Smyrna, Tennessee during June and July of 2013. The aircraft carried an extensive suite of instruments to characterize the gas- and aerosol-phase composition of the atmosphere, as well as the climate-relevant properties of the aerosol. The SENEX study was performed in close collaboration with several other studies in the framework of the Southeast Atmosphere Study.

Some highlights of the measurements will be presented. Vertical distributions of aerosol, and gradients below, within and above clouds, were carefully examined for evidence of aqueous-phase chemistry. Measurements downwind from power plants gave insight into particle formation and growth into CCN-active size ranges. Power plant plumes over isoprene and monoterpene emitting regions yield insight into the formation of organic aerosol from biogenic precursors in air masses with enhanced NOx and SO2. Measurements over urban areas were used to study the formation of secondary organic aerosol from anthropogenic emissions. Organic aerosol correlated closely with CO and other species emitted from mobile sources. However, the enhancements in CO and organic aerosol downwind from major cities were small relative to a region-wide enhancement in these species explained from emissions in the eastern U.S. accumulated over many days. Nighttime flights were conducted to look for evidence of organic aerosol formation from the reaction between biogenic VOCs and nitrate radicals. Finally, agricultural fires in the Mississippi delta region were widespread during the mission and their emissions were sampled on two flights. The SENEX data will be useful to constrain the sources and climate-relevant properties of aerosol in the southeast U.S.

4AQ.2

DISCOVER-AQ Investigation of Aerosol Impacts on Air Quality over Houston. RICHARD FERRARE, James Crawford, Robert Griffin, Chris Hostetler, Bruce Anderson, Sharon P. Burton, Brent Holben, Andreas Beyersdorf, Luke Ziemba, *NASA Langley Research Center*

The NASA Deriving Information on Surface Conditions from Column and VERtically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) mission is focused on improving the interpretation of satellite observations related to air quality. DISCOVER-AQ provides systematic and concurrent observations of column-integrated, surface, and vertically-resolved distributions of aerosols and trace gases relevant to air quality using two NASA airborne platforms (LaRC King Air and Wallops P-3B) as well as re-locatable and fixed surface networks and a mobile van. During September 2013, DISCOVER-AQ deployed these assets and investigated the air quality over Houston. The P-3B conducted extensive in situ profiling of trace gases and aerosols, and the King Air conducted passive and active remote sensing of the atmospheric column below the aircraft. Ground-based instruments included lidar measurements of aerosol distributions as well as an extensive network of AERONET Sun photometers. The DISCOVER-AQ measurements are used to examine the relationships between surface concentrations of PM2.5, aerosol extinction values near the surface and within the boundary layer, and column aerosol optical thickness (AOT). These measurements revealed the presence of elevated smoke layers produced by agricultural fires over the southeastern U.S. These elevated layers complicate efforts to deduce surface PM2.5 concentrations from column measurements. Airborne in situ measurements indicated significant differences in aerosol optical and microphysical properties between the surface and these elevated smoke layers. Both remote sensing and in situ measurements show evidence of periodic higher concentrations of localized dust near the Houston ship channel. Mobile surface measurements indicate enhancement of organic aerosol during pollution episodes, particularly overnight, likely due to in situ formation. These mobile surface measurements also show the importance of isolated, yet very high impact, primary aerosol sources distributed throughout Houston.

4AQ.3

Highlights from the St. Louis Air Quality Regional Study (SLAQRS) 2013. BRENT WILLIAMS, Dhruv Mitroo, Raul Martinez, Yaping Zhang, Michael Walker, Christopher Oxford, Xiaochen Zuo, David Hagan, Steven Dhawan, Li Du, Jay Turner, Gavin McMeeking, Laura King, Hongyu Guo, Rodney Weber, Munkhbayar Baasandorj, Lu Hu, Dylan Millet, *Washington University in St. Louis*

The St. Louis Air Quality Regional Study (SLAQRS) took place at the previous EPA Midwest Supersite in East St. Louis, IL between August 4th - October 11th 2013. A wide range of particle physical and chemical characterization techniques were employed as well as a number of gas phase detectors and high-resolution meteorological equipment. Additionally, a potential aerosol mass (PAM) reaction chamber was utilized to perturb oxidation states of ambient mixtures. Several highlights of this project include a comparison of 4 different black carbon measurement techniques, high time resolution correlations between particle volatility, hygroscopicity, and chemical data at the molecular level, and establishment of the St. Louis region as a highly interesting measurement site for future studies of the impact on secondary aerosol production from mixed anthropogenic/biogenic sources. Compared to other southeastern U.S. cities that are continuously impacted by isoprene emissions during the summer months, the St. Louis region, being situated at the northern edge of the Ozark Mountains, is only periodically impacted by isoprene emissions (at very high concentrations), but local anthropogenic emissions remain fairly constant regardless of specific regional air masses.

4AQ.4

Comparison of the Observed Organosulfates (IEPOX Sulfate and GA Sulfate) in the Southeast US to the Western US during DC3 and SEAC4RS. JIN LIAO, Karl D. Froyd, Daniel Murphy, Frank Keutsch, Ge Yu, Paul Wennberg, Jason St. Clair, John Crounse, Armin Wisthaler, Tomas Mikoviny, Jose-Luis Jimenez, Pedro Campuzano-Jost, Douglas Day, *CU CIRES- NOAA ESRL*

Organosulfates are important secondary organic aerosol (SOA) components and are good tracers for aerosol heterogeneous reactions. However, quantification of organosulfates is challenging, and as a result our knowledge about their spatial distribution, formation conditions, and environmental impact is limited. In this study, we report the airborne measurements of two organosulfates, a relatively well-known isoprene derived IEPOX-sulfate and a newly identified and quantified glycolic acid (GA) sulfate, by the NOAA Particle Analysis by Laser Mass Spectrometer (PALMS) onboard the NASA DC8 aircraft over the continental US during DC3 and SEAC4RS campaigns. IEPOX sulfate accounted for about 1-1.5% of aerosol mass loading on average near the ground in the Southeast US and decreased dramatically in the western US (0.2-0.4%) and in upper troposphere and lower stratosphere (<0.2%). Compared to IEPOX sulfate, the observed GA sulfate is more uniformly distributed, present from lower troposphere (0.2-0.6% of aerosol mass) to upper troposphere (0.7%), to even lower stratosphere (0.7%). Considering the spatial distribution, GA sulfate may be even more abundance than IEPOX sulfate globally. Ambient measurements confirmed that IEPOX sulfate is formed from isoprene oxidation and is an indicator for isoprene SOA formation. Acidity is critical for both organosulfates and largely drives GA sulfate formation at high altitudes. The organic precursors of GA sulfate may include glycolic acid and likely have both biogenic and anthropogenic sources. GA sulfate in the upper troposphere and lower stratosphere is probably formed in situ and provide ambient evidence for the formation of SOA at high altitudes. This study suggests that besides the emission of organic precursors, emission control of SO2 and NH3, which largely govern the aerosol acidity, would largely affect the formation of SOA compounds such as organosulfates.

4AQ.5

Particle Formation in Power Plant Plumes in the Southeastern United States. CHARLES BROCK, Steven G. Brown, Timothy Gordon, Joost de Gouw, John Holloway, Jin Liao, Ann M. Middlebrook, J. Andrew Neuman, John B. Nowak, Jeff Peischl, Ilana Pollack, Thomas Ryerson, Michael Trainer, Nick Wagner, Jeffrey Pierce, Robin Stevens, André Welti, *NOAA Earth System Research Laboratory, Boulder, CO*

Measurements of particle size distribution and composition and of gas-phase particle reactive and precursor species were made in the plumes downwind of more than 30 power plants in the southeastern United States in summer 2013 as part of the Southeast Atmosphere Study. Substantial reductions in emissions of SO2 from many of these sources over the last two decades have resulted in smaller regional sulfate concentrations, as is evident in compositional measurements at long-term surface monitoring sites. Despite the impressive reductions in sulfate mass production, however, large numbers of submicron particles are still generated in power plant plumes. In addition to being a potential human health hazard, these particles may also grow to sizes large enough to be active as cloud condensation nuclei (CCN), subsequently affecting cloud microphysical properties, extent, and lifetime. Airborne measurements made on the NOAA WP-3D aircraft are used to quantify the number of particles of cloud-active size formed as a function of plume age and chemical processing. A systematic relationship between chemical age of the plume and CCN-sized particle abundance is evident. Enhanced number concentrations of ultrafine particles were found in some of the plumes emitted after sunset that were measured during SAS and earlier projects, suggesting direct emissions of SO3 or ultrafine particles in these cases. These cases of nighttime particle production will be examined for their importance to downstream particle size and number and for evidence of formation of secondary organic species.

4AQ.6

Characterization of Nocturnal Aerosol Formation in Houston during DISCOVER-AQ. H. William Wallace, Yu Jun Leong, Basak Karakurt Cevik, Madeline Camp, James Flynn, Barry Lefer, ROBERT GRIFFIN, *Rice University*

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer was deployed aboard a mobile laboratory during the NASA DISCOVER-AQ mission in Houston, Texas during September 2013 and during several shorter periods through late 2013 and early 2014. Additional measurements included black carbon using an aethalometer, relevant trace gases including ozone (O3), nitrogen oxides (NOx), sulfur dioxide, volatile organic compounds (VOCs), and carbon monoxide (CO), and meteorological parameters. Based on previous (2006) observations in Houston of a local nocturnal peak in the CO-scaled diurnal profile of the sampled sub-micron oxidized organic particulate matter, analysis focused on characterization of nighttime aerosol in this study. This focus also was motivated by enhanced organic aerosol loadings at night during more polluted periods within the DISCOVER-AQ timeframe. The nocturnal organic aerosol during such periods was characterized spectrally by a small relative degree of oxidation of the organic material (based on the relative contributions of the signals of mass-to-charge ratio (m/z) 44 and m/z 43). The material also displayed an enhanced ratio of the signal of m/z 30 to that of m/z 46, from which it can be inferred that the aerosol is influenced strongly by organic nitrates. Estimates indicate that organic nitrates comprised approximately 25% of the organic aerosol during periods of enhanced organic aerosol at night. Estimates of the rate of formation of nitrate radical, which is expected to be large due to the high levels of NOx and O3 in the Houston atmosphere, correlate with increases in organic aerosol loading, implying that nitrate radical oxidation of VOCs followed by phase partitioning of the resulting products is responsible for the local increases in particulate mass concentration. Analyses from measurements made near primary aerosol sources also will be highlighted.

4AQ.7

Organic Aerosol from Nocturnal Oxidation of Biogenic VOCs: Results from Night Flights in the Southeast U.S. during SENEX 2013. STEVEN G. BROWN, Peter Edwards, Benjamin Ayres, Charles Brock, Joost de Gouw, Martin Graus, William P. Dube, Juliane L. Fry, Jessica Gilman, John Holloway, Ben H. Lee, Brian Lerner, Jin Liao, Felipe Lopez-Hilfiker, Ann M. Middlebrook, Kyung-Eun Min, J. Andrew Neuman, Ilana Pollack, James Roberts, Thomas Ryerson, Joel A. Thornton, Patrick Veres, Carsten Warneke, Robert Wild, Reed Wommack, *NOAA ESRL*

Oxidation of biogenic hydrocarbons, BVOC, by the nitrate radical, NO3, represents an important but highly uncertain mechanism by which anthropogenic (i.e., NO¬x) and biogenic emissions interact. For example, some model studies suggest large organic aerosol mass attributable to NO3-BVOC reactions, but estimates from different models vary widely. One key uncertainty is the nighttime oxidation of BVOC in the residual boundary layer, where a large mass of BVOC from the previous day’s emission resides, but where measurements are extremely sparse.

The SENEX campaign took place in June and July of 2013 in the southeast U.S., a region with large biogenic and anthropogenic emissions. There were several nighttime research flights of the NOAA P-3 aircraft that extensively sampled the residual layer, and that occasionally probed the nocturnal boundary layer during low approaches to airfields. Measurements included speciated BVOC, nighttime oxidants (NO3 and O3), BVOC oxidation products and aerosol mass and composition. This presentation will examine budgets for nighttime BVOC oxidation, particularly in the residual layer. It will address competition between NO3 and O3, the potential for organic nitrate and organic aerosol formation, and the changes in nighttime oxidative capacity that has resulted from declining anthropogenic emissions of NO¬x in the U.S.

4HA.1

Exposure of Workers to Mixed Aerosols. EMANUELE CAUDA, Luca Stabile, Giorgio Buonanno, Teresa Barone, *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 Diesel Particulate Matter (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 DPM typically present in underground mines. Real time monitors were used to assess the characteristics of the mixed aerosol during each experiment. 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.

This work was submitted to the AAAR2013 conference but not presented because of government shutdown.

4HA.2

Comparison of Personal Sampling and Robotic Sampling Platform to Estimate Personal Exposures in Young Children. JESSICA SAGONA, Marta Hernandez, Zuocheng Wang, Maya Ramagopal, Stuart Shalat, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Exposure to particulate matter (PM) is considered one of potential causes for asthma development, but measuring personal exposure in young children is often difficult due to the weight and bulkiness of the sampling equipment. To address this concern, the Pre-toddler Inhalable Particulate Environmental Robotic sampler (PIPER), was developed. PIPER is designed to mimic the average movements and breathing height of children up to age 3 as they play, including sitting, standing, and running, to provide a realistic proxy for personal exposure to PM when using personal sampling equipment is not feasible. Our earlier studies have consistently shown that PIPER measures higher PM concentrations than traditional stationary samplers.

As further development of the method, we compared filter-based PM mass concentrations measured by PIPER to those from samplers worn by 2-year old children. 68 homes were sampled. Each child wore a backpack with the pump and Button aerosol sampler for two hours while playing as normal. The child then left the room and PIPER ran for two hours with two Button samplers operated at 4 and 10 L/min. Results show that PIPER's PM mass measurements are systematically lower than those from the backpack. This may be in part due to the large variations in activity level among 2 year olds. Correlations between PIPER and personal samplers are highest ($r^2 = 0.41$) for children who spent less than a third of the time standing and running, suggesting that PIPER is most accurate for children who spend more time playing on the floor. Additionally, the mass concentrations measured by Button samplers on PIPER (operated at 4 and 10 L/min) were highly correlated ($r^2 = 0.84$). Further work is needed to determine the relative importance of factors that may contribute to the differences seen between the two samplers.

4HA.3

Internal Airway Percussion (IAP) for Lung Infection Diagnostics. NIMA AFSHAR-MOHAJER, Chang-Yu Wu, Hsiu-Wen Tsai, Erin Silverman, Paul Davenport, Satyanarayan Hegde, *University of Florida*

There is a great need for a direct but non-invasive sampling of aerosolized particles originating in the lungs, for the purpose of diagnosis of lung infections. In this study, a novel technique of Internal Airway Percussion (IAP) involving the transmission of acoustic sound waves into the lower respiratory tract, for effective vibration of the lung, was developed and optimized. Acoustic waves produced by IAP vibrate both the upper and lower respiratory tracts, thus increasing the release of aerosolized particles into the exhaled breath (EB). The IAP device consists of two separate channels: the inhalation channel which is connected to a sound wave generator to produce and deliver sound waves directly into the lungs, and the exhalation channel which is connected to a sterile Tedlar® bag for storing EB-containing aerosolized particles for concentration and particle size distribution analysis using an Aerodynamic Particle Sizer (APS). IAP optimization was conducted through statistical analysis of the obtained results at four different sound frequencies (15, 30, 60 and 100 Hz), and three different intensities (0.75, 1.5 and 3 cm H_2O) on 24 healthy adult participants.

Preliminary results at 15 Hz indicated an average increase in concentration of the aerosolized particles by 24%. An increase in (1) average particle size and (2) particle concentration was observed with increases in the frequency of the vibration delivered by the IAP device, at a constant intensity. In all cases, IAP was well tolerated and no adverse side effects were reported. Full results of this experiment will be presented at the conference.

4HA.4

The Association of National Air Toxics Assessment Exposures and the Risk of Childhood Autism Spectrum Disorder: A Case Control Study. EVELYN TALBOTT, Lynne Marshall, Judith Rager, Vincent Arena, Ravi Sharma, *University of Pittsburgh*

Background: Autism spectrum disorders (ASD) constitute a major public health problem, affecting one in every 68 children. There is little understanding of the cause of ASD despite its serious social impact. Air pollution contains many toxicants known to have adverse effects on the developing fetus.

Methods: We conducted a population-based case control study in six southwestern PA counties estimating the association between ASD and USEPA census tract modeled NATA levels for 30 neurotoxicants. Cases were recruited from local ASD treatment centers. There were two different control groups: 1) Interviewed controls with complete residential histories from pre-pregnancy through age two recruited through mailings using the Pennsylvania Department of Health birth registry (2005-2009). 2) 5,007 non-interviewed controls from a random sample of the birth records using residence at birth. Logistic regression analysis was conducted using quartiles of exposure, adjusting for age of mother, smoking, race, and education.

Results: There were a total of 217 cases. For the first group of 224 controls, median levels of chromium, styrene, cyanide, and polycyclic aromatic hydrocarbons were higher in cases compared to controls ($p<.05$). Women in the highest quartile of exposure to styrene had an odds ratio of 1.78 (95% CI: 1.035-3.068) of having a child with ASD compared to the lowest quartile, after adjustment for covariates. In the second control group, each increase of interquartile range exposure to cyanide resulted in a 16% higher odds (95%CI; 1.04-3.46) of ASD in the adjusted logistic model. Additionally, women with the highest quartile of exposure to chromium had 1.65 (95%CI; 1.10-2.47) times the odds of having a child with ASD compared to the women in the lowest quartile of chromium exposure.

Conclusions: Chromium, cyanide and styrene exhibited elevated odds ratios using two different control groups. These findings need to be verified with exposure assessment at the individual level.

4HA.5

Reformulation of Abandoned Wortmannin into Biodegradable Nanoparticles for Lung Cancer Treatment. HSI-WEI YEH, Da-Ren Chen, *Virginia Commonwealth University*

Lung cancer is the most ordinarily diagnosed cancer worldwide. Despite the continuous advancement of therapies for various cancers, the development of effective ones against lung cancer remains stagnant. The efficacy of currently available medicines is unsatisfactory because of the late appearance of symptoms. Alarmingly, these medications could even be toxic when applied to patients at high doses via either improper administration routes or pharmaceutical dosage forms. Safer and more effective new therapies are in high demand for lung cancer patients. To meet such unmet medical needs, much efforts have been made for the development of brand new chemical entities. However, the decreasing success rate of these compounds during clinical development, and the time and capital consumption in the development process impede the industry to efficiently translate the research results into drug products. Reformulating abandoned drugs which have been proven with excess toxicity yet with great therapeutic effects could be one strategy to the answer of the aforementioned challenge. Because of the unique properties of nanoparticles (NPs) to target tumors, they are promising drug carriers to reformulate abandoned drugs and to release them in controlled manner for the lowest toxicity. The feasibility of the concept has been proven by encapsulation of Wortmannin in biodegradable NPs generated in liquid phase for radiation therapy. However, the concept hasn’t been studied for lung cancer treatment. Electrospray (ES) technology is a promising tool for generating drug carriers (in the particle form) with superior controlled release performance compared with those generated by liquid-phase systems. In this study, we encapsulated Wortmannin with Poly(Lactide-co-Glycolide) (PLGA) NPs generated by a dual-capillary ES System to reduce the side effect while keeping sufficient drug dose concentration at the site of action. The release profiles of as-produced nanoparticles in various sizes were characterized. The detail of this study will be given in this presentation.

Keywords: Lung cancer treatment, Nanoparticles, Wortmannin, Biodegradable polymer

4HA.6

Variability of Lung Targeted Aerosol Delivery during High Flow Nasal Cannula Therapy. ROSS WALENGA, Geng Tian, Michael Hindle, Worth Longest, *Virginia Commonwealth University*

Patients that receive high flow nasal cannula (HFNC) therapy may benefit from lung targeted pharmaceutical aerosol administration, but results in the literature indicate that drug deposition and variability are likely to be high in both the delivery system and the nasal cavity. For this study, conventional and enhanced excipient growth (EEG) aerosol delivery methods were assessed with respect to variability of delivery through a nasal cannula interface. Adult nasal cavity dimensions from CT scan measurements and previously published data were compiled and used to select four models that represent a physiological range of nasal surface area-to-volume ratios (SA/V). Predictions at a steady state flow rate of 30 L/min through a streamlined cannula and the four nasal models were produced using validated computational fluid dynamics (CFD) methods. Conventional and EEG approaches were assessed with droplets (initial 5 micrometer aerodynamic diameter) and solid particles (0.9 micrometer and 1.5 micrometer), respectively. While the use of a conventional approach with 5 µm droplets showed a range of aerosol deposition efficiency of 15.5-64.1% (95% confidence interval (CI)) in the four geometries, the range of deposition for the EEG method with 0.9 µm particles was 2.3-3.1% (95% CI). Delivered dose, as expressed by penetration fraction (PF) through the nasopharynx, was predicted to be improved by a factor of four when using EEG as opposed to the control case. Additionally, the use of EEG as compared with a conventional aerosol reduced variability of PF by a factor of five, as expressed by the coefficient of variation. Surface area-to-volume ratio (SA/V) showed a strong correlation with PF for larger aerosols, but PF for smaller aerosols showed some dependence on nasopharyngeal exit hydraulic diameter. In summary, predictions using four newly created nasal airway models showed that lung targeted aerosol delivery was greatly improved by use of the EEG technique, while variability was significantly reduced.

4HA.7

Detecting Respiratory Infection by 3D Microbial Fingerprints from Exhaled Breath. Fangxia Shen, Xiaoguang Li, Zhuanglei Zou, Jie Xu, Chang-Yu Wu, MAOSHENG YAO, *Peking University*

Every year, respiratory tract infection costs a tremendous human toll worldwide. However, available methods fall short or are cost-prohibitive of providing quick and accurate bedside diagnosis of flu. This study investigated flu microbiota and fluorescent particle size, concentration and fluorescence strength-“3D microbial fingerprints” from exhaled breath for rapid and accurate diagnosis of clinical respiratory infections. Fifty-five patients with respiratory infections and 11 healthy subjects were recruited, and throat swab specimens from a subset were also taken. Bacterial species profiles for these samples were further obtained using 454 GS-FLX pyrosequencing. In addition, the recruited were advised to exhale toward a biological aerosol detector, and 3D microbial fingerprints from exhaled breath were produced instantly. Sequence data revealed a high abundance and diversity of bacteria (more than 400 unique bacterial species including many human pathogens such as Streptococcus pneumoniae) in the specimens, and significant microbial distribution shifts were observed compared to the control. The hemoglobin (HGB) levels for those confirmed with bacterial infections were shown significantly lower than those suspected with viral infections (p-value= .043). A pronounced contrast was observed between the 3D microbial fingerprints that were collected from the same patients when they were ill and healed later. For some cases, fluorescent peaks were observed in much larger particle size ranges (>5 µm), implying a possible fungal infection. Our data suggest that use of the 3D microbial fingerprints from exhaled breath can revolutionize the diagnosis of respiratory infection at virtually no cost in a clinical setting.

4IM.1

Liquid Atomization via a Newly Designed, Multi-notched Electrospray Head. JINGJIE ZHANG, Da-Ren Chen, *Virginia Commonwealth University*

The capability of generating monodisperse particles in the sizes ranging from nanometers to micrometers gives the electrohydrodynamic atomization (often called electrospray) the unique advantage over other mechanical techniques. The low mass throughput of single-capillary electrospray, however, limits its industrial applications. Several variations of spray heads have been recently reported to increase the mass throughput of electrospray, such as spray heads with a number of nozzles arranged in linear or 2-D array (i.e., multiplex electrospray). Unfortunately, none of them is practical for industrial scale applications. It is because of the complexity of multiplex systems.

To increase the mass throughput of electrospray, we had previously proposed to electrospray liquid sheet instead of liquid jets. We reported a spray head design allowing ones to vary the number of notches to implement the concept of liquid sheet electrospray. Based on the early version of the nozzle and experience collected during the performance evaluation, we developed a new electrospray head in this study. The new spray head design ensures the uniformity of annual spacing of fluid channel and minimizes the dead volume of the liquid reservoir built in the spray head. The shape of notches is also re-designed to prevent liquid from bridging between two adjacent teeth during the spray operation. The operational envelope and I-V curve of this newly designed multi-notched spray head, and particle sizes produced were characterized in the spray head performance evaluation. The result of this study will be presented in this presentation.

4IM.2

A Non-Specific Monodisperse Aerosol Generation System. JONATHAN ESHBAUGH, Francisco Romay, Shanna Ratnesar-Shumate, Paul Dabisch, *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 ranges of interest was designed and evaluated. The design coupled an ultrasonic atomizer to a series of clean air core virtual impactors designed by MSP to generate a monodisperse or near-monodisperse aerosol at three discrete particle sizes from a biological suspension. Airflow for the entire system was controlled and monitored with valves, laminar flow elements, and differential pressure gauges. Characterization tests with minimum essential media demonstrated production of aerosol count distributions with modes of 1.4, 6.3, and 11.4 micro-meters and geometric standard deviations of 1.3, 1.2, and 1.3, respectively. The system design as well as experimental results will be presented.

4IM.3

Performance Study of Miniature Cyclones with Multiple Inlets.

DI LIU, Zhenzhong Zhang, Ta-Chih Tsiao, Da-Ren Chen, *Virginia Commonwealth University*

Epidemiological studies showed the adverse heath effect of ultrafine particles, leading to the development of portable and cost-effective particle sizers for spatial measurements of ultrafine particles. The devices based on DMA/EAA or OPC techniques have been proposed to measure size distribution of particles in ultrafine size range. However, the performance of these devices affects by the presence of large particles in the sampled stream. Miniature cyclones have been proposed as the size-selective inlet to remove large particles. In addition, single-inlet cyclones may encounter the issue of directional sampling when used as the size-selective inlet. Miniature cyclones with multiple inlets are thus proposed in this study to minimize the above issues.

A group of miniature cyclones with different numbers of inlets (i.e., single-, dual- and quarto-inlets) were designed and made in this study. The pressure drop and particle cut-off curves of miniature cyclones were characterized at various operational flow rates. With the pressure drop data collected, a semi-empirical model stemmed from the Chen-Shi's model was developed. A CFD modeling was also applied to calculate the flow field and the pressure drop across these cyclones. More, a new relationship between the pressure drop and cutoff size of these multi-inlet cyclones was observed in this study. The detail of this study will be presented in this talk.

4IM.4

Collection of Airborne Particles by a High-Gradient Permanent Magnetic Separator.

MENG-DAWN CHENG, Steve Allman, Larry Avens, Gerard Ludtka, *Oak Ridge National Laboratory*

We report on the use of magnetic force in collection of airborne particles by a high-gradient permanent magnetic separation (HGPMS) device. Three aerosol particles of different magnetic susceptibility (NaCl, CuO, and Fe3O4) were generated in the electrical mobility size range of 10 to 200 nm and were used to study HGPMS collection. One HGPMS matrix element, made of stainless steel wool, was used in the device configuration. Magnetic force was found to exhibit an insignificant effect on the separation of NaCl particles, even in the HGPMS configuration. Diffusion was a major mechanism in the removal of the diamagnetic particles; however, diffusion is insignificant under the influence of a high-gradient magnetic field for paramagnetic or ferromagnetic particles. The HGPMS showed high-performance collection (> 99%) of paramagnetic CuO and ferromagnetic Fe3O4 particles for particle sizes greater than or equal to 60 nm. As the wind speed increases, the influence of the magnetic force weakens, and the capability to remove particles from the gas stream diminishes. The results suggest that the HGPMS principle could be explored for development of an advanced miniaturized passive aerosol collection.

4IM.5

Performance of Inertial Impactor with Varying Geometries. HUAN LI, William Faulkner, John Haglund, *Texas A&M University*

Inertial impactors are extensively used in air quality monitoring. Nozzles for inertial impactors can be challenging to machine. Those that require the simplest tooling often converge quickly near the nozzle exit, which may affect impactor performance. In present study, the nozzles with two kinds of profiles and two standoff distances were placed into an impactor, and the performance of inertial impactors was tested in a wind tunnel using solid ammonium fluorescein particles with Stoke's numbers from 0.09 to 0.59. The effectiveness of impactor for each particle size was obtained by fluorometric analysis. The rate of nozzle convergence significantly impacted the slope of the impactor effectiveness profile. Effects of standoff distance are being evaluated.

4IM.6

Trapping of Individual Airborne Absorbing Particles Using a Counterflow Nozzle and Photophoretic Trap for Continuous Sampling and Analysis. YONG-LE PAN, Chuji Wang, Steven Hill, Joshua Santarpia, *US Army Research Lab*

There is a need for improved on-line instruments for studying and monitoring aerosols. We describe an integrated opto-aerodynamic system and demonstrate that it enables us to trap absorbing airborne micron-size particles from air, hold them and then release them, and to repeat this sequence many times as would be appropriate for continuous sampling of particles from air. The key parts of the system are a conical photophoretic optical trap and a counter-flow coaxial-double-nozzle that focus, concentrates and then slows particles for trapping. This technology should be useful for on-line applications that require monitoring (by single particle analyses) of a series of successively arriving particles (e.g., from the atmosphere or pharmaceutical or other production facilities) where the total sampling time may last from minutes to days, but where each particle must be held for a short time for measurements (e.g., Raman scattering). This new system overcomes the trapping difficulty in air caused by the moving air current that focuses, concentrates and carries the aerosol particles into the small trapping region, greatly increases the trapping rate comparing to the passively launching methods generally used.

4IM.7

Collection of Droplets by Centrifugal Filter. HIROAKI MATSUHASHI, Shusuke Nakajima, Mikio Kumita, Takafumi Seto, Hidenori Higashi, Yoshio Otani, *Kanazawa University*

Many collection devices have been used for the removal of micrometer sized droplets from air, such as air filter, mist eliminator, cyclone, and scrubber, etc. However, these devices cannot collect submicron sized droplets at a high efficiency because none of the mechanical collection mechanisms exert effectively for the removal of droplets in submicron range. In addition, the re-entrainment of collected droplets is of serious concern for these conventional collection devices. In this study, we introduced centrifugal force for the collection of submicron droplets by air filter, a new type of collection device; centrifugal filter. The basic idea of the centrifugal filter is to capture submicron droplets by rotating filter element. For example, if we attach a filter on the blades of a fan, the filter actively collect particles as a "bug collecting net", not passively waiting for the collision of bugs (particles) on the net (air filter). Moreover the use of centrifugal force is advantageous for the cleaning of air filter. If the centrifugal force acting on the particle deposits on the filter fibers is larger than the air drag, the deposited particles can be detached in the radial direction so that the re-entrained droplets no longer enter the filtered air. In the present work, we investigated the influence of rotation speed and radial thickness filter on the collection performance. In our estimation, the centrifugal filter consisting of 10 micro-meter fibers can collect 0.3 micro-meter particles at 50% collection efficiency when the filter outer radius is 40 mm, the rotation speed is 1000 rpm and the flow rate is 10 L/min. By introducing the centrifugal force to air filters, we can have one additional design parameter for air filter, which should broaden the application of air filters.

4UA.1

Contribution of Biomass Use for Renewable Energy to Particulate Matter Formation. MARC CARRERAS-SOSPEDRA, Donald Dabdub, Jack Brouwer, Rob Williams, *University of California, Irvine*

Biomass contributes to 19% of California’s instate renewable power, which is nearly 2% of full California power mix. Current operating biopower capacity is about 900 Megawatt (MW), including approximately 550 MW of woody biomass solid fuel combustion, 280 MW of landfill gas-to-energy and 75 MW from wastewater treatment biogas. It is estimated that there is sufficient in-state 'technically' recoverable biomass to support another 2,800 MW of capacity. While most biomass energy is derived from woody material from urban wood waste, forest and agricultural residue, there is a growing interest in using municipal solid waste, food processing waste, increased use of animal manures and applying co-digestion techniques at wastewater treatment facilities to generate electricity and renewable fuels. Increasing production of bioenergy contributes to energy sustainability while reducing greenhouse gas emissions and could affect direct pollutant emissions, and secondary particulate formation.

This study assesses the emissions from a variety of pathways for biomass utilization, from direct use for biopower generation, to processing to produce biofuels. The resulting emissions from the various biomass use pathways are used as input to the Community Multiscale Air Quality model (CMAQ) to predict regional and statewide temporal impacts on particulate matter formation from the biopower scenarios. This investigation provides a consistent analysis of increasing electricity generation from biomass in California. The findings will help inform policy makers and industry with respect to further development and direction of biomass policy and bioenergy technology alternatives needed to meet energy and environmental goals in California.

4UA.2

Atlanta Rail Yard Study (ARYS): Evaluation of Local-scale Air Pollution Trends and Emissions Quantification Using Stationary and Mobile Monitoring Strategies.

GAYLE HAGLER, Halley Brantley, Boris Galvis, Scott Herndon, Armistead Russell, Michael Bergin, Paola Massoli, Edward Fortner, Jonathan Franklin, Lu Xu, Nga Lee Ng, *ORD-US EPA, RTP, NC*

Intermodal rail yards are important nodes in the freight transportation network, where freight is organized and moved from one mode of transport to another, critical equipment is serviced, and freight is routed to its next destination. Rail yard environments are also areas with multiple sources of air pollutant emissions (e.g., heavy-duty vehicles, locomotives, cranes), which may affect local air quality in residential areas nearby. In order to understand emissions and related air quality impacts, two field studies took place over the time span of 2010-2012 to measure air pollution trends in close proximity to the Inman and Tilford rail yard complex in Atlanta, GA. One field study involved long-term stationary monitoring of black carbon, fine particles, and carbon dioxide at two stations nearby the rail yard. In addition, a second field study performed intensive mobile air monitoring for a one month period in the summer of 2012 at a roadway network surrounding the rail yard complex and measured a comprehensive array of pollutants. Real-time mobile particulate measurements included particle counts, extinction coefficient, black carbon via light-absorption and particle incandescence, and particle composition derived by aerosol mass spectrometry. Gas-phase measurements included oxides of nitrogen, sulfur dioxide, carbon dioxide, and air toxics (e.g., benzene). Both sets of measurements determined detectable local influence from rail yard-related emissions. Preliminary analysis of mobile monitoring data indicates that pollutants directly emitted by diesel emissions had moderate to high inter-pollutant correlation spatially and elevated concentrations downwind of the rail yard area.

4UA.3

Total Particulate Matter from Mobile Sources in Los Angeles.

TIMOTHY GORDON, Albert A. Presto, Andrew May, Mang Zhang, Christine Maddox, Hector Maldonado, William Robertson, Ngoc Nguyen, Eric Lipsky, Matti Maricq, Daniel S. Tkacik, Neil Donahue, Sulekha Chattopadhyay, Shantanu Jathar, John Massetti, Tin Truong, Pablo Cicero-Fernandez, Kwangsam Na, Paul Rieger, Keshav Sahay, Alvaro Gutierrez, Allen Robinson, *NOAA*

While progress has been made in quantifying primary particulate matter (PM) emissions from combustion sources, fewer studies have characterized the secondary PM formed from the emissions from these sources, and fewer (if any) experimental studies have holistically examined the link between tailpipe emissions from mobile sources and ambient PM. In this study dilution and smog chamber experiments were performed to characterize the primary emissions and secondary organic aerosol (SOA) formation from gasoline and diesel vehicles and gasoline small off-road engines (SOREs). We then calculated the total PM (primary+secondary) contribution of these mobile sources to ambient PM in L.A. by combining primary emission, SOA production and fuel consumption data.

Substantial SOA formed during every experiment with 15 gasoline vehicles. The emissions from some vehicles generated as much as five times the amount of SOA as primary PM, suggesting that ambient PM from gasoline vehicles is likely dominated by SOA. Tests with two heavy-duty diesel vehicles (HDDVs) equipped with catalyzed diesel particulate filters (DPFs) produced negligible primary PM and SOA. Therefore, catalyzed DPFs appear to be very effective in reducing both primary PM and SOA formation from HDDV exhaust. A HDDV without a DPF emitted large amounts of primary PM but generated relatively small amount of SOA—comparable with the newest gasoline vehicles. Therefore, the ambient PM contribution of HDDVs without aftertreatment is likely dominated by primary PM emissions. Gasoline SOREs emit extremely high levels of primary PM, and their emissions also generate many times more SOA per kg of fuel than any of the other mobile sources. However, the vastly greater fuel consumption of on-road vehicles renders them (on-road vehicles) the principal mobile source of ambient PM in the Los Angeles area.

4UA.4
Atmospheric Intermediate-volatility Organic Compounds: A Small Fraction of Atmospheric Hydrocarbons and a Large Contribution to Secondary Organic Aerosol.

YUNLIANG ZHAO, Allen Robinson, Christopher Hennigan, Andrew May, Joost de Gouw, Jessica Gilman, Bill Kuster, Agnes Borbon, *Carnegie Mellon University*

Understanding the abundance, volatility distribution and chemical composition of atmospheric intermediate-volatility organic compounds (IVOCs) is crucial to predicting their secondary organic aerosol (SOA) production and identifying their major primary sources. In our study, atmospheric IVOCs collected in Pasadena, CA during the CalNex campaign are analyzed comprehensively. The concentrations of IVOC hydrocarbons average 6.3±1.9 µg/m-3 and 7.4 ± 1.2% of the concentrations of speciated volatile organic compounds (VOCs). Only 8.6 ± 2.2% of IVOC hydrocarbons are speciated. The remaining IVOC hydrocarbons are reported as two lumped groups of branched alkanes and unspeciated IVOC hydrocarbons and are determined as bins corresponding to n-alkanes (C12-C21). These binned and lumped groups allow more constraints on both OH reaction constant rates and SOA yields of atmospheric IVOCs. The estimated lower bound of SOA production from IVOC hydrocarbons accounts for ~30% of enhancement in SOA during the day and is over four times that from the traditional SOA precursors, light single-ring aromatics. Other primary sources in addition to on-road vehicles are indicated to significantly contribute to atmospheric IVOCs and to be petroleum-related sources.

4UA.5
Assessing Aerosol Mixing State through Single Particle Mass Spectrometry and Particle-Resolved Modeling.

NICOLE RIEMER, Swarnali Sanyal, Robert Healy, Greg J. Evans, John Wenger, *University of Illinois at Urbana-Champaign*

The mixing state of the aerosol population is the distribution of chemical compounds across the particle population. Recent field observations using single-particle measurement techniques have revealed that the mixing states of ambient aerosol populations are complex. Even freshly emitted particles can have complex compositions by the time they enter the atmosphere, and the initial particle composition is further modified in the atmosphere as a result of aging processes including coagulation, condensation of secondary aerosol species, and heterogeneous reactions. Considering this, it becomes clear that the frequently used terms “external mixture” and “internal mixture” are rarely sufficient to characterize the mixing state of ambient aerosol populations.

In this work, a newly developed framework for quantifying aerosol mixing state based on information-theoretic entropy is applied for the first time to single particle mass spectrometry field data combined with process modeling using the particle-resolved model PartMC-MOSAIC. Single-particle composition estimates for black carbon, organic aerosol and inorganic ions are derived for data collected at an urban site in Paris, France. The composition of each particle is described in terms of its species “diversity” and compared to the composition of the bulk aerosol to derive a quantitative mixing state index. This index is a single parameter representation of how internally or externally mixed a particle population is at a given time, and describes a continuum, with values of 0% and 100% representing full external and internal mixing, respectively. The mixing state index of ambient aerosol in Paris is 59% on average, but changes as a function of time of day and air mass origin between 40% and 70%. This approach represents a new means by which to compare and contrast aerosol chemical mixing state in various environments globally, and the process modeling elucidates the mechanisms of aging in the particular environment.

4UA.6

On the Importance of New Particle Formation Events as a Source for Cloud Condensation Nuclei in an Urban Environment.

ANNA WONASCHUETZ, Julia Burkart, Anselm Demattio, Carmen Dameto de Espana, Robert Wagner, Georg Reischl, Gerhard Steiner, Regina Hitzenberger, *University of Vienna*

New particle formation (NPF) events have been observed in many remote, urban and rural environments. The newly-formed particles are suspected to contribute significantly to cloud condensation nuclei (CCN) concentrations, after growing into the appropriate size range. Due to the relative lack of long-term CCN measurements, quantifications of this souce often rely on CCN concentrations calculated from the size distributions alone. In this calculation, the choice of activation diameter is crucial. In this study, we combine size distribution and CCN measurements from a period of several years (10 months of overlapping measurements) to quantify the contribution of NPF events to CCN concentrations. The measurements were taken at an urban background location in Vienna, Austria. Consistent with other locations, NPF events occur most frequently in the warm season (23% of all days in summer), suggesting the largest contribution in that season. Previous results from the same location have shown that the estimate of the activation diameter from these measurements strongly depends on the assumed mixing state of the aerosol (Burkart et al., 2011, 2012). Here, we investigate the importance of the NPF source for CCN based on different estimates of the activation diameter, and compare it to other factors (local sources, meteorological conditions) influencing CCN concentrations.

4UA.7

Influence of the Manaus Plume on Aerosol Size Distribution and Cloud Condensation Nuclei (CCN) during GoAmazon – Preliminary Results.

FAN MEI, Jian Wang, Jason Tomlinson, Jennifer Comstock, John Hubbe, Mikhail Pekour, John Shilling, Chongai Kuang, Karla Longo, Scot Martin, 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 a result of our incomplete understanding of the ability of particles to form cloud droplets under atmospherically relevant supersaturations. One of the objectives of the US Department of Energy (DOE) Green Ocean Amazon Project (GoAmazon) is to understand the influence of the emission from Manaus, a tropical megacity, on aerosol size, concentration, and chemical composition, and their impact on aerosol cloud condensation nuclei (CCN) spectrum.

During the GOAmazon study, size distributions, CCN spectra and chemical composition of aerosols both under pristine conditions and inside Manaus plume were measured in-situ from the DOE Gulfstream 1 (G-1) research aircraft during two Intensive Operations Periods (IOPs), one conducted in the wet season (Feb 22- March 24, 2014) and the other in dry season (Sep 1 – Oct 10, 2014). Aerosol size distributions were measured by a Fast Integrated Mobility Spectrometer (FIMS) and compared with the merged size distribution from two other instruments, an Ultra High Sensitivity Aerosol Spectrometer – Airborne (UHSAS-A, DMT), and a Passive Cavity Aerosol Spectrometer Probe (PCASP-200, DMT). Aerosol chemical composition was characterized using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Inc.). CCN number concentration was measured by a DMT dual column CCN counter at two supersaturations 0.25% and 0.5%. Based on the aerosol properties mentioned above, CCN closure is carried out. In addition, the sensitivity of calculated CCN spectrum to organic aerosol hygroscopicity is examined. The differences in aerosol/CCN properties between two seasons will be discussed.

5AC.1

Heterogeneous Reaction Kinetics of Isoprene-Derived Epoxides. THERAN P. RIEDEL, Cassandra Gaston, Sri Hapsari Budisulistiorini, Ying-Hsuan Lin, Zhenfa Zhang, Avram Gold, Joel A. Thornton, Jason Surratt, *University of North Carolina at Chapel Hill*

Isoprene (2-methyl-,1,3-butadiene) is the most abundant nonmethane hydrocarbon present in the atmosphere and has large potential effects on air quality and radiative forcing. The formation of secondary organic aerosol (SOA) from the photochemical oxidation of isoprene represents a significant source of aerosol loadings, especially in the southeastern United States. Epoxides formed from isoprene oxidation have been shown to be a critical precursor to isoprene-derived SOA. However, the heterogeneous reactions of these epoxides required for subsequent SOA formation remain poorly constrained. We use this as motivation to investigate the heterogeneous kinetics of two isoprene-derived epoxides, methacrylic acid epoxide (MAE) and trans-β-IEPOX (IEPOX) using a glass flow reactor coupled to a chemical ionization mass spectrometer (CIMS) and a scanning electrical mobility sizing system (SEMS). Gas-aerosol reaction probabilities, also called reactive uptake coefficients, are calculated for MAE and IEPOX on 1 - 2 component aerosols under various aerosol compositions and environmental conditions. Compositions and conditions are chosen in order to probe potential chemical drivers of epoxide uptake and put experimental constraints on epoxide-aerosol reaction probabilities that might be encountered in the ambient atmosphere. The obtained reaction probabilities are also incorporated into a simple 0-D, time-dependent box model in order to compare modeled SOA yields with experimental results obtained from chamber studies.

5AC.2

Reactions of Condensed Phase Alkoxy Radicals. ANTHONY CARRASQUILLO, Kelly Daumit, Jesse Kroll, *MIT*

Our understanding of the major processes that influence the chemical evolution of organic aerosol derive from experimental observations of organic radical reactivity in the gas phase. The reactivity of these radicals in the condensed organic phase, however, is poorly understood due to a lack of experimental observations. Additional and potentially important reactions not accessible in the gas phase are possible in the bulk organic phase, including bimolecular reactions. Here we consider the reactions of long chain alkoxy radicals generated by the photolysis of corresponding alkyl nitrites within organic matrices. Experiments were conducted in both bulk organic solvents (followed by atomization to aerosol instrumentation), as well as a smog chamber within submicron isotopically labeled squalane particles. Characterization of the chemical composition was completed with on-line measurements using the Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer. We observed the formation of an alcohol species, indicative of a bimolecular H-abstraction reaction with the bulk organic phase. Spectral subtraction of the alcohol mass spectrum from that of the bulk allows for determination of the branching ratios for unimolecular and bimolecular pathways. The identification and evolution of key product ions from unimolecular reactions as well as changes to the elemental ratios (O/C, H/C, N/C) of the products provides additional insight into the major pathways influencing in-particle oxidation processes.

5AC.3

Hydrolysis and Gas-particle Partitioning of Organic Nitrates Formed in Environmental Chamber Experiments. JEFFREY BEAN, Lea Hildebrandt Ruiz, *University of Texas at Austin*

Understanding the partitioning and hydrolysis of organic nitrates is important in understanding their role as NOx sinks and sources in the atmosphere. Organic nitrates are abundant, and thus important in predicting the formation of ozone and the eventual fate of NOx in the atmosphere. We report both the hydrolysis rate and the partitioning coefficient for alpha-pinene derived organic nitrates formed under varying conditions. Experiments were performed in a 12 m^3 atmospheric chamber at the University of Texas at Austin with initial concentrations of alpha-pinene from 26 to 128 ppb and initial VOC/NOx ratios of ~1.

An Aerosol Chemical Speciation Monitor (ACSM) is used to determine aerosol composition with a Scanning Electron Mobility System (SEMS) used to find the total organic aerosol concentration throughout experiments. A High Resolution Chemical Ionization Time of Flight Mass Spectrometer (HR-ToF-CIMS) is used to identify specific organic nitrates formed from alpha-pinene oxidation in high NOx conditions. The SAPRC model is used to find HNO_3 concentrations throughout experiments so that a mass balance can be used to estimate total gas-phase organic nitrate concentration. We find that the ratio of particulate nitrate to total SOA decreases with increasing relative humidity, consistent with an increased level of hydrolysis as particles contain more water. The gas/particle partitioning is dependent on total OA concentrations consistent with absorptive partitioning theory.

5AC.4

Reactions Between Water-Soluble Organic Acids and Nitrates in Atmospheric Aerosols: Recycling of Nitric Acid and Formation of Organic Salts. BINGBING WANG, Alexander Laskin, *Pacific Northwest National Laboratory*

Atmospheric aerosol particles often include a complex mixture of inorganic and organic materials. Nitrate as an important inorganic component can be chemically formed in the atmosphere. For example, formation of sodium nitrate ($NaNO_3$) and calcium nitrate ($Ca(NO_3)_2$) occurs when nitrogen oxides and nitric acid (HNO_3) react with sea salt and calcite, respectively. Organic acids contribute a significant fraction of photochemically formed secondary organics that can condense on the preexisting particles. We present here a systematic microanalysis study on chemical composition of laboratory-generated particles composed of water soluble organic acids and nitrates ($NaNO_3$ and $Ca(NO_3)_2$) using elemental X-ray analysis and fourier transform infrared micro-spectroscopy analysis. Results show that water soluble organic acids can react with nitrates and release gaseous HNO_3 during the dehydration process. These reactions are attributed to acid displacement of nitrate with weak organic acids driven by the evaporation of HNO_3 into gas phase because of its relatively high volatility. The reactions result in significant nitrate depletion and formation of organic salts in mixed organic acids/nitrate particles that, in turn, may affect their physical and chemical properties relevant to atmospheric environment and climate. The results indicate a potential mechanism of HNO_3 recycling that may further affect atmospheric chemistry.

5AC.5

Organic Peroxide Formation from Photooxidation of Methylglyoxal in the Aqueous Phase.

YONG LIM, Barbara Turpin, *Rutgers University*

Aqueous chemistry in atmospheric waters (e.g., cloud droplets or wet aerosols) is well accepted as an atmospheric pathway to produce secondary organic aerosol (SOAaq). Water-soluble organic compounds with small carbon numbers (C2-C3) are precursors for SOAaq and products include organic acids, organic sulfates, and high molecular weight compounds/oligomers. Fenton reactions and the uptake of gas-phase OH radicals are considered to be the major oxidant sources for aqueous organic chemistry. If these are the only sources, aqueous oxidation chemistry will be oxidant-limited. However, sources and availability of oxidants in atmospheric waters and their reactions with dissolved organic compounds in the aqueous phase are still not well understood.

In this work, laboratory experiments and ultra high resolution Fourier Transform Ion Cyclotron Resonance electrospray ionization mass spectrometry (FTICR-MS) are used to demonstrate that organic peroxides form during aqueous photooxidation of methylglyoxal. It is already well known that organic peroxides form and recycle OH in the gas-phase. And that these organic peroxides partition into particles forming secondary organic aerosol (SOAgas) We argue that photolysis of organic peroxides in clouds and wet aerosols provides a source of OH radicals (OH recycling) for aqueous chemistry and SOAaq formation. Organic peroxides formed through aqueous chemistry could be a yet unrecognized source of light absorbing "brown" carbon in aerosols.

5AC.6

Uptake and Transformation of Glyoxal on Mineral Dust Particles.

Xiaoli Shen, Yue Zhao, Dao Huang, ZHONGMING CHEN, *Peking University*

Glyoxal plays a crucial role in the formation of secondary organic aerosols (SOA) because of its plenty and highly reactivity in the atmosphere. The mineral dust particle, a significant constituent of atmospheric particles, may provide a reaction medium for glyoxal. We investigate the uptake and transformation of glyoxal on fresh and acidic gas-aged SiO2, alpha-Al2O3, and CaCO3 particles, as the models of atmospheric mineral dust particles. A series of products, including oligomers, organosulfate and organic acids, which can contribute to SOA, are detected. It is found that water vapor favors the uptake of glyoxal, and the formation of oligomers and organosulfate, whereas suppresses the formation of organic acids. This finding demonstrates that the mineral dust particle has a special reactivity towards glyoxal.

5AC.7

Effect of Ammonia on Glyoxal SOA in Inorganic Aqueous Seed Particles. ELEANOR WAXMAN, Alexander Laskin, Jay Slowik, Aurelia Maxut, Siyuan Wang, Jian Zhen Yu, Theodore Koenig, Julia Laskin, Andre Prévôt, Urs Baltensperger, Barbara Noziere, Josef Dommen, Rainer Volkamer, *University of Colorado*

Glyoxal (C2H2O2) is a small molecule that is observed in the terrestrial biogenic, urban, marine and arctic atmosphere. It forms secondary organic aerosol (SOA) as a result of multiphase chemical reactions in water. The rate of these reactions is controlled by the effective Henry’s law partitioning coefficient (Heff) which is enhanced in the presence of inorganic salts by up to 3 orders of magnitude (Kampf et al., 2013, ES&T). Aerosol particles are among the most concentrated salt solutions on Earth and the SOA formation rate in aerosol water is strongly modified by this ‘salting-in’ mechanism. We have studied the effect of gas-phase ammonia on the rate of SOA formation in real particles composed of different inorganic salts (sulfate, nitrate, chloride). A series of simulation chamber experiments was conducted at the Paul Scherrer Institut in Switzerland during Summer 2013. The SOA formation rate in experiments with added gas-phase ammonia (NH3) was found to be greatly accelerated compared to experiments without added NH3. Product analysis of particles included online HR-ToF-AMS and offline nano-DESI and LC-MS. We find that imidazole-like oligomer compounds dominate the observed products, rather than high-O/C oligomers containing solely C, H, and O. We further employed isotopically labelled di-substituted 13C glyoxal experiments in order to unambiguously link product formation to glyoxal (and separate it from chamber wall contamination). We present a molecular perspective on the reaction pathways and evaluate the effect of environmental parameters (RH, particle pH, seed chemical composition) on the formation of these imidazole-like oligomer compounds. The implications for SOA formation from photosensitized oxidation chemistry is discussed.

5AC.8

Molecular Composition of Aged Secondary Organic Aerosol Generated from a Mixture of Biogenic Volatile Compounds Using Ultrahigh Resolution Mass Spectrometry. IVAN KOURTCHEV, Chiara Giorio, Brendan Mahon, Jean-François Doussin, Nicolas Maurin, Aline Gratien, Edouard Panqui, Sebastien Morales, Manuela Cirtog, Juho Aalto, Taina Ruuskanen, Markku Kulmala, Markus Kalberer, *University of Cambridge*

A considerable lack of knowledge exists concerning the chemical composition of natural aerosols. Field observations over the past decade revealed that a significant fraction of ambient remote organic aerosol (OA) is highly oxidised (Kroll et al., 2011). The oxidation reactions (ageing) leading to formation of highly oxidised OA involve heterogeneous uptake of oxidants and multigenerational oxidation of vapours by OH radicals (Henry and Donahue, 2012). The objectives of this work were (i) to examine photochemical ageing of SOA generated from a precursor mixture containing BVOCs (i.e. α and β-pinene, Δ-3-carene, and isoprene) that are most abundant at a remote boreal forest site Hyytiälä, Finland; (ii) to characterise the aged SOA using novel ultrahigh resolution mass spectrometry (UHR-MS) that allows detection of thousands of individual SOA constituents at once providing their elemental formulae from accurate mass measurements (Nizkorodov et al., 2011); and (iii) to compare elemental composition of laboratory generated SOA with that of ambient. The laboratory experiments were performed in the CESAM (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber) chamber, which is specifically designed to investigate multiphase processes and simulate atmospheric aerosol ageing due to relatively low wall loses of the OA. The applied experimental conditions (e.g., RH, VOC ratios) were selected to represent those at the boreal sampling site during the summer period. The influence of the UV radiation and/or OH radicals and acidic aerosol seed on the organic aerosol composition of the SOA was investigated. Ageing effects in the chamber were observed over 3-9 hours. The elemental composition of the complex compound mixtures from SOA samples were compared with field samples using statistical data analysis methods.

Henry and Donahue, 2012 Journal of Physical Chemistry A 116, 5932-5940.
Kroll et al., 2011. Nature Chemistry 3, 133-139.
Nizkorodov et al., 2011. Physical Chemistry Chemical Physics 13(9), 3612-3629.

5AQ.1

BVOC Oxidation Products Measured by SV-TAG Reveal Differences in Chemistry and Partitioning between Natural and Polluted Environments Forming Secondary Organic Aerosol (SOA). ALLEN H. GOLDSTEIN, Gabriel Isaacman, Lindsay Yee, Nathan Kreisberg, Suzane Simoes de Sa, Scot Martin, Lizabeth Alexander, Brett Palm, Weiwei Hu, Pedro Campuzano-Jost, Douglas Day, Jose-Luis Jimenez, Thien Khoi Nguyen, Annmarie Carlton, Juarez Viegas, Antonio O. Manzi, Rodrigo A. F. Souza, Maria Oliveira, Paulo Artaxo, Joel Brito, Eric Edgerton, Karsten Baumann, Susanne Hering, *University of California, Berkeley*

Anthropogenic pollutants affect biogenic SOA formation, but the impacts and details of this interaction are still poorly understood. Though laboratory studies have characterized oxidation chemistry of isoprene and monoterpenes, few time-resolved atmospheric measurements of organic tracers are available to constrain the relative importance of chemical pathways. We present ambient hourly measurements of oxidation products of biogenic emissions in two locations: the Southeastern U.S. (SOAS 2013) and Amazonia, Brazil (GoAmazon 2014). In both of these measurement locations, high levels of biogenic emissions interact with plumes from nearby cities, enabling the study of anthropogenic-biogenic interactions in aerosol formation. A Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SV-TAG) was modified to include simultaneous collection of particle-phase and total gas- and particle-phase compounds, and derivatization of hydroxyl groups prior to GC analysis. Using SV-TAG, concentrations and gas-particle partitioning of BVOC oxidation products were measured, providing ratios of tracers for different chemical pathways (i.e. with and without NOx influence) and compared to traditional partitioning models. Generally, traditionally-used tracers are found to exist in the particle-phase more than that predicted by equilibrium partitioning, but most compounds are found in both phases. Methyl tetrols, an oxidation product of isoprene, are traditionally considered to be primarily in the particle phase but are observed here to have a significant day-time gas-phase component. The measured concentration of these products in both the gas- and particle-phase is found to be strongly correlated with particle-phase sulfate, indicative of anthropogenic influence in the formation or partitioning processes. Consequently, due in part to large differences in sulfur emissions, concentrations as well as partitioning of measured isoprene products vary between the sites. We explore this dynamic further for traditional and new oxidation tracers of isoprene and monoterpenes to yield broader insight into the chemical processes behind biogenic SOA formation.

5AQ.2

Processes Influencing the Organic Aerosol Mass during SENEX. ANN M. MIDDLEBROOK, Wayne Angevine, Jerome Brioude, Charles Brock, Joost de Gouw, Jessica Gilman, Martin Graus, John Holloway, Brian Lerner, Jin Liao, J. Andrew Neuman, Michael Trainer, Carsten Warneke, Jennifer Kaiser, Glenn Wolfe, Tom Hanisco, Frank Keutsch, Jingqiu Mao, Larry Horowitz, André Welti, *NOAA ESRL*

The NOAA Southeast Nexus (SENEX) project occurred during the summer of 2013 over the southeastern United States and involved studying the interactions between natural and anthropogenic emissions at the nexus of climate change and air quality. As part of the project, a suite of instruments for aerosol and gas–phase species was deployed on the NOAA WP-3D aircraft and models were used to calculate trace gas and aerosol species in the region and along the aircraft flight tracks. Throughout the study, the measured non-refractory submicron aerosol mass was dominated by organic material (58% +/- 9%) with smaller contributions from sulfate (27% +/- 8%), ammonium (10% +/- 3%), nitrate (3% +/- 1%), and chloride (0.1% +/- 0.1%). Here we examine the influence of urban emissions on the organic aerosol (OA) mass in regions characterized by higher and lower biogenic emissions. For the air around and downwind of urban areas, OA mass is highly correlated with carbon monoxide (CO), a tracer of anthropogenic emissions as well as an oxidation product of isoprene, a biogenic species. The slope of this correlation is roughly 0.15 micrograms per standard cubic meter per ppbv, which is significantly higher than observed in prior studies. The enhancement in OA mass relative to the enhancement in CO is independent of the concentration of biogenic species. In contrast, formaldehyde enhancements are clearly higher in the presence of biogenic species in agreement with the NOAA GFDL AM3 model. Downwind from the urban areas, CO and OA were not strongly enhanced relatively to a region-wide enhancement in these species that can only be explained from the accumulation of emissions in the eastern U.S. for several days. Back-trajectories of air parcels with emissions from biogenic and anthropogenic sources will be examined to elucidate the impact of both sources on OA mass.

5AQ.3

Seasonal Characterization of Atmospheric Organic Aerosol at the Look Rock Site, Great Smoky Mountains National Park during 2013 Using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM). SRI HAPSARI BUDISULISTIORINI, Xinxin Li, Philip Croteau, Manjula Canagaratna, Solomon Bairai, Roger Tanner, Stephanie Shaw, Eladio Knipping, John Jayne, Zhenfa Zhang, Avram Gold, Jason Surratt, *University of North Carolina at Chapel Hill*

Ambient PM_1 at the Look Rock site, Great Smoky Mountains National Park was continuously measured using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) during 2013. In addition, filter samples were collected using a Tisch $PM_{2.5}$ High-Volume Sampler for 1.5 months during the 2013 Southern Oxidant and Aerosol Study (SOAS). The organic mass spectra measured by the ACSM were analyzed with the Multi-linear Engine (ME-2) program using a-value equation for source apportionment. Two factors were identified during winter, spring, and fall: biomass burning organic aerosol (BBOA) and low-volatility oxygenated organic aerosol (LV-OOA). In summer, two factors were identified: isoprene epoxydiol-derived organic aerosol (IEPOX-OA) and LV-OOA. Identification of the IEPOX-OA factor in summer was confirmed by comparison with molecular tracers of IEPOX-derived secondary organic aerosol quantified by gas chromatography-electron ionization mass spectrometry (GC/EI-MS) and ultra-performance liquid chromatography-negative electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-Q-TOFMS). Contributions of each factor vary by season, with BBOA making the largest contribution in winter (~20%) and IEPOX-OA in summer (~50%). The LV-OOA remained constant (~80%) throughout, except in summer when the number decreases due to large IEPOX-OA contribution.

5AQ.4

Sources of primary and secondary organic aerosol during the Southeast Atmosphere Study. ELIZABETH STONE, Anusha Priyadarshani Silva Hettiyadura, John Groenenboom, Thilina Jayarathne, *University of Iowa*

To evaluate anthropogenic influences on secondary organic aerosol (SOA) formation in the southeastern United States, ambient PM2.5 samples were collected in Centerville, Alabama from June 1 to July 15 in 2013. Elemental and organic carbon (EC and OC) and organic molecular markers were measured on daytime (08:00-19:00) and nighttime (20:00-07:00) samples. OC levels ranged from 0.9 – 6.0 ug/m3 (averaging 3.0 ug/m3) while EC ranged from < 0.05 to 0.4 ug/m3 (averaging 0.14 ug/m3). The average OC to EC ratio was 22, reflecting a strong contribution from non-combustion (i.e. secondary) sources. Levoglucosan, a marker for biomass burning, concentrations ranged from 3 – 106 ng/m3; the six concentration maxima occurred during the nighttime due to more stable boundary layer conditions. Assuming that biomass burning emissions were open-burning in nature, this source was estimated to account for 1.3 to 45% of OC (averaging 8%). Alkanes, reminiscent of vegetative detritus, revealed an odd-carbon preference (ranging from 1.4 – 7.7 and averaging 3.1), reflecting the presence of primary biogenic aerosol in PM2.5. Tracers for isoprene-derived SOA (i.e. 2-methylglyceric acid and 2-methyltetrols) were among the most abundant organic species detected. Pinonic acid, a tracer for monoterpene-derived SOA, revealed a striking diurnal variation with peak concentrations observed during the day, indicative of their photochemical origin. Aromatic acids and dicarboxylic acids also peaked during the daytime. Results from molecular-marker based source apportionment to quantify absolute and relative contributions of primary and secondary sources to ambient OC will also be discussed.

5AQ.5

Chemical Characterization of Organic Aerosol during SOAS Using High Resolution Aerosol Mass Spectrometer.

LU XU, Hongyu Guo, Christopher Boyd, Kate Cerully, Aikaterini Bougiatioti, Laura King, Rodney Weber, Athanasios Nenes, Nga Lee Ng, *Georgia Institute of Technology*

Secondary organic aerosol (SOA) has important impacts on climate, visibility, and human health. However, SOA formation is controlled by complex processes which are not well understood. Specifically, to what extent do human activities affect SOA formation and SOA evolution is highly uncertain. The interaction between anthropogenic and biogenic emissions was investigated in Southern Oxidant and Aerosol Study (SOAS) by deploying a High-Resolution Time-of-Flight Mass Spectrometer (HR-ToF-AMS). Positive Matrix Factorization (PMF) analysis on organic aerosol (OA) resolved three SOA factors, including isoprene-derived organic aerosol (Isop_OA), semi-volatile oxygenated organic aerosol (SVOOA), and low-volatility oxygenated organic aerosol (LVOOA). It is found that all OA factors are correlated with at least one anthropogenic component. The formation of Isop_OA is greatly controlled by sulfate level. SVOOA can be related to reaction between monoterpenes and NO3 radicals. LVOOA shows association with black carbon, where back trajectory analysis indicates that both can arise from long range transport. Analysis will be discussed to reveal the detailed interactions between anthropogenic and biogenic emissions on SOA formation.

5AQ.6

Chemical Characterization of Isoprene- and Monoterpene-Derived SOA Tracers in PM2.5 Collected from Centerville, AL, during SOAS 2013.

MATTHIEU RIVA, Lindsay Yee, Sri Hapsari Budisulistiorini, Eric Edgerton, Stephanie Shaw, Eladio Knipping, Allen H. Goldstein, Zhenfa Zhang, Avram Gold, Jason Surratt, *University of North Carolina at Chapel Hill, Chapel Hill, NC*

Secondary organic aerosol (SOA) formed from the atmospheric oxidation of biogenic volatile organic compounds (BVOCs) accounts for a substantial mass fraction of fine particulate matter (PM2.5). Isoprene is the most abundant non-methane hydrocarbon and BVOC emitted into the Earth’s atmosphere and is mainly present (along with monoterpenes) in the southeastern U.S. during summer. Recent work has shown that anthropogenic pollutants, such as sulfate aerosol, enhance oxidation products of isoprene and monoterpene as a source of SOA. For isoprene SOA formation, acidified sulfate aerosol enhances the reactive uptake of isoprene-derived epoxides, whereas monoterpene SOA appears to be enhanced by sulfate aerosol via heterogeneous reactions. Ozonolysis can enhance nucleation monoterpenes. However, impact of environmental conditions (NOx level, aerosol acidity, sulfate, and primary aerosol) on biogenic SOA formation arising from isoprene and monoterpene oxidation remains unclear. Improving our knowledge of isoprene and monoterpene SOA formation will be the key to improving existing air quality models in order to elucidate impacts of anthropogenic activities on SOA formation from biogenic VOCs.

In order to investigate the impacts of anthropogenic activities on BSOA and confirm previous laboratory findings, PM2.5 samples were collected during the Southern Oxidant and Aerosol Study (SOAS) in summer 2013 at the Centerville, AL, site using high-volume samplers. Filters were collected at least twice per day on regular sampling days, and four times per day on intensive sampling days. We present the chemical characterization of these samples using ultra performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-QTOFMS) and gas chromatography interfaced with electron ionization mass spectrometry (GC/EI-MS) with prior trimethylsilylation. Real-time gas- and particle-phase chemical data obtained from collocated instruments have been used in order to investigate the detailed linkages between anthropogenic activities and biogenic SOA.

5AQ.7

Initial Field Deployments of a Volatility and Polarity Separator (VAPS) for Organic Aerosol Characterization.

RAUL MARTINEZ, David Hagan, Yaping Zhang, Dhruv Mitroo, Michael Walker, Lu Hu, Munkhbayar Baasandorj, Dylan Millet, Brent Williams, *Washington University in St. Louis*

The Volatility and Polarity Separator (VAPS) was deployed during two field campaigns in the summer and fall of 2013 – Centerville, Alabama and East St. Louis, Illinois. VAPS was used to obtain hourly measurements of chemically resolved organic aerosol (OA) detected using high-resolution time-of-flight mass spectrometry (HR-ToFMS). This novel instrument increases the mass throughput of ambient OA in comparison to traditional GC by utilizing shorter transfer paths and passivated coatings. Chemical separation resolution is sacrificed for this increased mass transfer, but the high-resolution mass spectral data recovers information such as chemical classes and even some individual compounds along with elemental composition to determine aerosol oxidation states.

The ambient data sets are explored by using high resolution mass spectral analysis and positive matrix factorization (PMF). Different techniques for interpreting and representing VAPS data are considered and PMF factors are compared to meteorological and chemical data from other co-located instruments. Differences and similarities between the two sites are also presented.

5AQ.8

Measurements of Atmospheric Amines and Ammonia with a Chemical Ionization Mass Spectrometer (CIMS).

SHANHU LEE, Yi You, Roxana Sierra-Hernández, Joost de Gouw, Abigail Koss, Karsten Baumann, Eric Edgerton, *Kent State University*

Amines and ammonia play critical roles in new particle formation, via acid-base reactions at the initial stage of aerosol nucleation. Nitrogen-containing base compounds also contribute to the SOA formation, by forming salts or via condensation of amine photo-oxidation reactions. However, atmospheric measurements of amines with fast response detection methods are very limited. Here, we report ambient concentrations of amines and ammonia measured with a chemical ionization mass spectrometer (CIMS) in an Alabama forest and a moderately polluted Midwestern site (Kent). In the Alabama forest, mostly C3-amines (pptv and tens pptv) and ammonia (up to 2 ppbv) were detected at the daily base, but other amines were usually within the CIMS detection limits. C3-amines and ammonia showed similar diurnal trends and similar temperature and wind direction dependences, and they were not associated with the transported CO and SO2 plumes. These results indicate these base compounds were emitted likely from the same natural sources (such soils and trees) at this forest site and they were also affected by the theromodynamic equilibrium between the gas and aerosol phases. When there were transported biomass burning plumes, various amines (C1-C6) were measured at the pptv level, indicating that biomass burning can be a substantial source of amines even in the Southeast U.S. In the moderately polluted Kent site, higher concentrations of amines (C1-C6 at pptv and tens pptv) and ammonia (up to 6 ppbv) were detected. Diurnal variations of C1- to C3-amines and ammonia closely followed the ambient temperature. But C4- to C6-amines showed frequent and abrupt rises during the nighttime, suggesting that they were emitted from some local sources. These abundant amines and NH3 may in part explain the high frequency of new particle formation events reported from Kent.

5BB.1

The Current State and Future of Wildfire Smoke and Air Quality Modeling. TIMOTHY BROWN, Narasimhan (Sim) Larkin, Pete Lahm, *Desert Research Institute*

Smoke is a consequence from biomass burning, and starting in the 1970s, has been an increasingly prominent issue for wildland fire management agencies. The Environmental Protection Agency (EPA) Clean Air Act of 1970, and subsequent regulatory amendments have provided a mandate to monitor and manage smoke. In response to the management planning needs, numerous smoke model guidance products have been developed over the years starting in the 1990s. The primary problem is that there has been little scientific objective evidence that any wildland fire smoke model to date provides sufficiently desired accurate and reliable results. This is a critical knowledge gap given the regulatory and decision-making needs surrounding smoke and air quality management. The same information needs has lead to new monitoring for wildfire smoke. This presentation will give a perspective from a research partnership at the interface of science and operations for smoke and air quality. An overview will be provided of the current status of operational smoke modeling and monitoring. A discussion will be provided on key scientific questions and knowledge gaps for the next generation of smoke and air quality models.

5BB.2

Constraining Emissions from Open Burning Sources and Their Atmospheric Impacts. CHRISTINE WIEDINMYER, Serena H. Chung, Robert J. Yokelson, Elena McDonald-Buller, Tomohiro Oda, Christopher Elvidge, Louisa Emmons, John Orlando, *National Center for Atmospheric Research*

Open burning of biomass and other materials contributes significantly to the atmospheric aerosol budget. However, estimates of emissions from these sources are highly uncertain, posing challenges to quantifying their impacts in the atmosphere. Uncertainties in the estimates are associated with fire location, timing and area, as well as the vegetation burned and the amount consumed. Changes in the model inputs can lead to factors of two to 10 differences in regional emission estimates. For example, in the western United States, monthly fire emissions can vary by as much as three when different land cover and burned area inputs are applied. Recent satellite products, such as the VIIRS, can provide data on fire location, timing and area burned, particularly for smaller fires that are challenging to detect. These new products have been implemented within the Fire Inventory from NCAR to provide emission estimates in Indonesia and results will be shown.

Uncertainties in the impacts of the fire emissions on atmospheric aerosol are also associated with estimates of primary particulate emissions as well as the gas-phase constituents that can react and form secondary particles in the fire plume. Recent efforts to more accurately represent the volatile organic compound emissions from burning improve the modeled plume chemistry and can lead to better predictions of the atmospheric impacts of biomass burning emissions.

5BB.3

Satellite Characterization of Biomass-Burning Aerosol Emissions for Regional Modeling. CHARLES ICHOKU, Luke Ellison, Jun Wang, Feng Zhang, *NASA Goddard Space Flight Center*

Satellite remote sensing has become an indispensable technique for characterizing smoke aerosol emissions from open biomass burning, especially at regional to global scales, because of the transient and widespread nature of fires. These fires are detected from space because of the intense heat energy they generate and the corresponding smoke plumes that comprise different species of aerosols and trace gases. However, because of the inherent difficulty in quantifying these emissions in a timely fashion using traditional methods, it has hitherto been challenging to parameterize them accurately in models used for biosphere-atmosphere interaction studies or air-quality monitoring and forecasting. Fortunately, a series of recent studies have revealed that both the biomass consumption and emission of aerosol particulate matter by open biomass burning are directly proportional to the fire radiative energy (FRE), whose instantaneous rate of release or fire radiative power (FRP) is measurable from space. We have leveraged this relationship to generate a global, gridded smoke-aerosol emission coefficients (Ce) dataset based on FRP and aerosol optical thickness (AOT) measurements from the MODIS sensors aboard the Terra and Aqua satellites. Ce is a simple coefficient to convert FRE to smoke aerosol emissions, in the same manner as traditional emission factors are used to convert burned biomass to emissions. The first version of this Fire Energetics and Emissions Research (FEER.v1) global Ce product is available at http://feer.gsfc.nasa.gov/. This gridded Ce product at 1°x1° resolution was used in conjunction with satellite measurements of FRP to derive smoke aerosol emissions, which were applied to WRF-Chem fully-coupled meteorology-chemistry-aerosol model simulations in Northern su-Saharan Africa. The results reveal that these FRE-based emissions are able to capture some important regional smoke distribution patterns that may not be adequately represented by using other major emissions inventories, when compared to satellite AOT retrievals.

5BB.4

Constraints on Smoke Injection Height, Source Strength, and Transports from MISR and MODIS. RALPH KAHN, Maria Val Martin, Mariya Petrenko, Mian Chin, *NASA Goddard Space Flight Center*

Multi-angle and multispectral satellite observations have produced some constraints on smoke source characteristics and downwind transports, globally. Injection height and source strength are the two key quantities used to parameterize aerosol sources in chemical transport and climate models. We are able to map smoke injection height near-source by applying stereo retrieval techniques to multi-angle imaging from MISR. These maps, combined with downwind smoke plume layer height from the space-based CALIPSO lidar, provide fairly strong constraints on smoke vertical distribution for transport modeling. However, important questions remain about how to physically model the injection height process, for which the dynamical heat flux of the fire, the atmospheric stability structure, and the plume entrainment process must be represented with sufficient accuracy.

We also compared snapshots of near-source smoke plume aerosol optical depth (AOD) from MODIS and MISR with GoCART aerosol transport model runs, initialized with different smoke emission inventories. Systematic, regional consistency regarding the places where the model AOD, sampled at satellite overpass times and initialized with different inventories, underestimate, overestimate, and agree with the observations. These results provide a useful guide to source strength representation by the inventories used, at least in the context of the GoCART model. We are developing full-year data sets for both the injection height and plume-specific AOD retrievals, to be used in a more extensive modeling exercise with the AeroCom group. One remaining question asks about the large-scale environmental impacts of smoke from numerous, small fires that cannot be detected from space.

5BB.5

The Joint Fire Sciences Program Smoke Science Plan: Progress toward Goals. DOUGLAS G. FOX, Cindy Huber, Allen Riebau, *Nine Points South Technical Pty. Ltd., Australia*

The Joint Fire Sciences Program (JFSP), a multiagency research program created by the National Fire Plan to support research in wildland fire, developed a Smoke Science Plan to help guide its research in smoke and smoke management from 2008-2015. The Plan has focused research in four themes: Emissions Inventory, Smoke Model validation, Smoke and Populations and Smoke and Climate Change. This paper will identify specific "end points" for this research and outline some specific research projects that have been undertaken. We will also present results from a recent survey and Workshop of JFSP investigators undertaken, in part, as an assessment of the effectiveness of the Smoke Science Plan and an evaluation of how well it is likely to achieve these "end points."

5BB.6

Projecting the Impacts of Climate Change on Wildfire-driven Air Quality over the Southeastern U.S. UMA SHANKAR, Jeffrey Prestemon, Aijun Xiu, Kevin Talgo, Bok Baek, Dongmei Yang, Mohammad Omary, *University of North Carolina at Chapel Hill*

Under the Forest and Rangeland Renewable Resources Planning Act (RPA) of 1974, the Forest Service and other federal agencies are required to generate national RPA Assessment reports on a ten-year cycle, describing projected conditions of the US forest and rangeland in the next 50 years. In support of this goal, analyses were conducted to project the impacts of climate change on annual areas burned (AAB) using global climate model projections of fire weather parameters corresponding to the latest projection time frame, 2010-2060. The climate data were remapped to a modeling domain over the Southeastern U.S. to develop statistical models that project fire activity in contemporary and future periods. These theoretically based models recognize not only the changes in driving climate variables but also those in biophysical, socioeconomic, and land use variables that have been shown to explain wildfire historical variations in time and space. They have been applied to yield corresponding wildfire AAB projections, gridded over the spatial domain, at 5-year intervals from 2015 to 2060. The AAB projections have been used in a stochastic model to constrain estimates of daily burned areas for the eventual estimation of wildfire emissions in selected years. Air quality simulations are being conducted in these years with the coupled WRF-CMAQ model to examine the impacts of wildfires on air quality, and on the feedback of aerosols formed in wildfires to the atmospheric dynamics. Results are presented for available years on the ambient concentrations of aerosols and ozone, and boundary layer characteristics.

5BB.7

Quantify the Impact of Biomass Burning Aerosols on Regional Climate over the Southeastern USA. PENG LIU, Yongtao Hu, Athanasios Nenes, Armistead Russell, *Georgia Institute of Technology*

Biomass burning has been and will continue to be a major contributor to the particulate matter over the southeastern USA. In order to quantify the direct effects of biomass burning aerosols on the regional climate, we employ the WRF and coupled WRF-CMAQ (Wong et al., 2012), both of which are driven by NARR data and downscale to 12km resolution covering the southeastern USA.

Ensemble of one-year long (year of 2007) simulations will be conducted with one control run and two emission scenarios for biomass fire emissions. For the control run, both biogenic and anthropogenic emissions of the year 2007 will be used except that there is no emission from fire. Then with base emissions for the control run, the first fire emission scenario includes the multi-year average fire emission, which serves as a representative regional climate forcing from biomass burning. The second fire emission scenario is the actual fire emission for the year 2007, when extreme wildfires occurred in the region. Hence, the second emission scenario will represent an extreme regional climate forcing from biomass burning.

By comparing WRF and coupled WRF-CMAQ (control run with no fire emissions), we will be able to quantify when feedback being considered the background of the impact of emissions other than fires on regional climate. In addition, we will separate the impacts into two parts. The first part is due to the aerosol direct effect and the second part is due to bulk property change of clouds. By comparing the results from control and emission scenarios, we are interested in first, how the regional climate (especially, surface temperature, cloud coverage and precipitation) would change due to the extra forcing from biomass burning, and second, to what extent the relative contributions from aerosol direct effect and bulk cloud change would alter due to extreme conditions.

5BB.8

WRAP Fire Tools and Support for Smoke Management Programs, Land Managers, and Air Quality Planning in the Western U.S. TOM MOORE, Chen Bin, *WRAP/WESTAR*

I will provide an overview of current and future work by the Western Regional Air Partnership (WRAP) through WRAPTools (https://wraptools.org/), related to smoke management and air quality planning in the western U.S. and beyond. I will discuss two recent and ongoing Joint Fire Sciences Program projects and their implications for smoke management, the next chapter for regional fire / air quality analysis and planning support by the WRAP, and the future of the Fire Emissions Tracking System.

5CH.1

Effect of Particle Loading Rate on Flat Filter Medium Performance.

QIANG WANG, Xiuli Lin, Da-Ren Chen, *Virginia Commonwealth University*

Filter media have been well used in a variety of industrial applications, where the dust concentration and system velocity are always different and varying. Thus, it is important to understand the effect of different application environments on filter performance in order to help guiding the filter media and test methods design. A series of experiments have been carried out to study the effect of different dust loading rates on filter pressure drop. The objective was to figure out if there is any influence of dust loading rate on affecting the pressure drop over filter media with loaded mass. High efficiency filter media have been utilized in this study. Two different filter media loaded with medium size dust under two different face velocities (10 cm/s and 20 cm/s) and four different dust loading rates were studied here. For each combination of dust loading rate, face velocity and filter media, one curve indicating pressure drop vs. dust mass loaded was obtained. The study verifies the dust feeding rates do have effects on filter pressure drops evolution with loaded dust mass. Membrane filter media has a much stable pressure drop under different dust feeding rates, but glass fiber filter has an obviously distinct pressure drop under different dust feeding rates. Besides, dust loading rate brings a much significant difference on pressure drop for glass fiber filter under low face velocity than higher face velocity.

5CH.2

Effect of Nanofibers on Collection Performance of Air Filters.

HISASHI YUASA, Takashi Yoshitake, Takafumi Seto, Yoshio Otani, *Kanazawa university*

Air filters composed of nanofibers are of great interest in the field of air filtration as a new medium to improve the filtration performance. The filtration theory predicts that nanofibers contribute to an increase in collection efficiency and a reduction in pressure drop, compared to the conventional micrometer sized fibers. However, the filtration efficiency of actual nanofibers filters is often lower than the predicted based on the single fiber filtration theory because uniform packing of nanofibers is quite difficult for the mass production. This study investigated the effects of nanofibers on filtration performance when they are laminated on or dispersed in micrometer sized filters. The test filters were prepared by a wet process with nanofiber and micrometer sized fiber. As a result, for the nanofiber laminated filters, the inhomogeneity factor of nanofiber layer ranged from 2 to 10 and the measured filtration efficiency was fairly in good agreement with the predicted accounting for the inhomogeneous packing of nanofiber layer, suggesting that the correction with inhomogeneous factor is valid for the nanofiber layered filters. The collection performance difference by lamination and dispersion of nanofibers on/in micrometer fiber filters is discussed according to the filtration theory.

5CH.3

Artifacts in Filter Penetration Measurements Associated with Multiple Charging of Particles. MEILU HE, Suresh Dhaniyala, Matthew Wagner, *Clarkson University*

A critical characteristic of filter performance is its size-dependent particle capture efficiency. The capture efficiency of a filter is usually established by challenging the filter with mono-mobility particles from a differential mobility analyzer (DMA) and determining change in particle concentrations upstream and downstream of the filter. It's often assumed that the particles exiting the DMA are singly charged, and hence monodisperse in size. The contribution of multiply-charged particles to the filter efficiency measurements can, however, be important under some conditions. This is particularly the case when the test particles entering the DMA have a peak size larger than the most penetrating particle size of the test filter. Under such a test condition, even a small number of multiply-charged particles corresponding to a highly penetrating size can significantly skew filter particle capture results. In our presentation, we will highlight the role of multiple charging on filter penetration measurements and propose solutions to eliminate this problem and ensure accurate measurements.

5CH.4

Evaluation of Metallic Filter Media for High Temperature Filtration Application. QISHENG OU, James Warner, Matti Maricq, David Y. H. Pui, *University of Minnesota*

Filtration is considered the most economical control technique to effectively remove airborne particles in nanometer size range. Many filtration systems are operated at high temperature, such as in advanced coal power plants, engine exhaust after-treatment, and chemical and petrochemical processes. Besides the conventional fabric bag and ceramic filter media, metallic filter media is seeing more applications because of its high porosity and strength, good thermal resistance, and good optimization between efficiency and back pressure.

In this study, the pressure drop and collection efficiency of metallic filter media were characterized under a variety of flow temperatures with soot particles as challenging aerosols. Two types of metallic filter media were tested: one is a sintered metal type media with similar structure as conventional ceramic filter media used in automobile exhaust after-treatment, and the other is a type of non-woven metal fiber media with higher porosity and specific area, which has similar microstructure as fiberglass fibrous filter media used in low temperature filtration applications. The pressure drop and collection efficiency of both clean and soot-loaded filter media were measured. The effects of media characteristics and flow temperature were investigated under a variety of filtration velocities. The filter media quality factor, which represents the tradeoff between collection efficiency and pressure drop, as well as its implications for high-temperature filtration system design will be reported and discussed.

5CH.5

Impact of Relative Humidity on HVAC Filters Loaded with Hygroscopic and Non-hygroscopic Particles. JAMES MONTGOMERY, Sheldon Green, Steven Rogak, *University of British Columbia*

The key characteristics of an air filter – flow resistance and filtration efficiency – are strongly affected by captured particles. The impact of exposing loaded HVAC air filters to a relative humidity (RH) other than that experienced during loading is investigated to develop an understanding of the role of RH throughout filter operation. Flat sheets of commercial filter media were loaded with hygroscopic, non-hygroscopic, or a mixture of particles, in a laboratory apparatus. When a filter loaded with hygroscopic particles in dry air is exposed to an elevated relative humidity of 20% or 40% the flow resistance reduces by up to 10% and 45%, respectively, depending on the filter being tested. Investigation of filter efficiency against 130nm particles before and after changes in RH in the same samples shows reductions of 5 and 20 percentage points, respectively. Further increasing RH causes additional drops in flow resistance and efficiency whereas reverting back to a lower humidity does not change the filter characteristics. Exposing an unloaded filter medium to the same RH changes produces a negligible change in flow resistance and filtration efficiency. The irreversibility of the particle-loaded filter characteristics implies that the RH increases are associated with an irreversible change in the particle structure. The response to humidity is similar, but with a lower dependence on RH, when a 50:50 mixture of hygroscopic and non-hygroscopic particles is used. Exposure of filters loaded with only non-hygroscopic particles does not show the same dependence on RH. Imaging of agglomerates of hygroscopic particles captured on filter fibers shows changes in agglomerate structure when RH is increased within the range of the experimental conditions. This observation supports the hypothesis that small increases in size of individual particles due to changes in relative humidity well below deliquescence can result in large changes to the filter performance.

5CH.6

Electrostatic Collection of Tribocharged Lunar Dust Simulants at Elevated Vacuum Levels. NIMA AFSHAR-MOHAJER, Chang-Yu Wu, Nicoleta Sorloacia-Hickman, *University of Florida*

Deposition of the naturally charged particles on the lunar surface was troublesome in previous NASA explorations. Developing control technologies for mitigating dust deposition in limiting condition of the lunar atmosphere is imperative for any future space exploration. This study reports experimental investigation of the collection efficiency of an electrostatic lunar dust collector (ELDC). A dual-functional remotely controlled particle charger/dropper was designed for tribocharging 20-µm lunar dust simulants using aluminum surfaces, and a system of Faraday cup connected to an electrometer working in nC charge range was used to measure the particle charges. First, tribochargeability of the lunar dust simulants at three vacuum levels was studied, and the process was found to be the most effective with the JSC-1A samples. Estimation of ELDC collection efficiency as a function of applied voltage was achieved through implementing two separate experimental designs to study the effect of low vacuum (~0.1 Torr) and high vacuum (~0.0001 Torr) on the created particle charge and the ELDC collection efficiency at four different voltages. For the tested range of electrostatic field strength (0.66 to 2.6 kV/m), the mass-based and charge-based approaches used in determining the collection efficiencies obtained the range of 0.25 to 0.75% and 0.35 to 1.05% for the low vacuum, and 9 to 42% and 12 to 54% for the high vacuum conditions. The linear relationship between the applied voltage and ELDC collection efficiency predicted by the previous model was confirmed, and the collection pattern of the collected particles over the collection plate was consistent with the previously computed charge distribution on the collection plate. Aside from validating the predictability of the developed theoretical model, this study offers a novel method of particle charging inside vacuum chambers with a variety of applications for studying chargeability of particles at different temperatures and pressures.

5CH.7

Nanoparticle Penetration through Facepiece Respirators. YUE ZHOU, Yung-Sung Cheng, *Lovelace Respiratory Research Institute*

The advances of nanotechnology have produced a diverse range of nanomaterials or “engineered nanoparticles,” including metal oxides, fullerenes, nanotubes, nanowires, and quantum dots. To prevent inhalation of nanoparticles, Respirators, including NIOSH-certified N95 and P100 particulate respirators, are recommended. However, there is no information on the behavior of engineered nanoparticles in respirators. Only preliminary laboratory tests of filtering efficiency using standard test aerosols have been reported in the literature. In this study, the performance of N95 and P100 respirators for engineered nanoparticles including TiO2, fullerenes, and carbon nanotubes (CNT) was evaluated. As a comparison, the respirator performance for NaCl particles was also conducted.

Different generation methods were used to generate test particles. CNT and TiO2 particles were generated using a laboratory vortex device, whereas fullerene particles were generated using an evaporation and condensation method. Also NaCl particles were generated using a Collison nebulizer. The experimental setup includes a test chamber, the nanoparticle generator, a manikin head, and monitoring equipment. The manikin head is placed at the bottom of the chamber with a test respirator. The manikin is equipped with a probe to sample the aerosol inside the face piece. The flow rates through the respirator were 30, 85, and 130 LPM. The 30 LPM represents inhalation during a low/moderate workload. The 85 LPM is used by NIOSH for certification test. The flow rate of 130 LPM matches the peak inspiratory flow by a cyclic flow with a mean inspiratory flow of 85 LPM. Aerosol penetration through the respirator was determined by the ratio of concentration measured inside and outside the face piece using a Wide-Range Particle Spectrometer.

Results show that the penetrations meet the NIOSH criteria for all N95 and P100 respirators when flow rate was below 85 LPM. However, when flow rate increased to 130 LPM. The penetrations were found above the NIOSH criteria in many cases. Our data also indicated that the performance of N95 and P100 respirators for nanoparticles are not as good as compared to NaCl standard test particles used for respirator certification.

5CH.8

How Small Can We Go: Exploring the Limitations and Scaling Laws of Air-Microfluidic Particulate Matter Sensors. OMID MAHDAVIPOUR, Ben Gould, Dorsa Fahimi, David Liederman, Son Duy Nguyen, David Woolsey, Paul A. Solomon, Richard White, Lara Gundel, Igor Paprotny, *University of Illinois at Chicago*

Air-microfluidics is a field that has the potential to dramatically reduce the size, cost, and power requirements of future air quality sensors. Microfabrication provides a suite of relatively new tools for the development of micro electro mechanical systems (MEMS) that can be applied to create sophisticated air-based lab-on-a-chip applications. Such devices have the potential to revolutionize the way we monitor air quality in a similar to how liquid lab-on-a-chip instruments revolutionized medical sciences. This presentation will provide a comprehensive overview of this technology, focusing on air-microfluidic sensors for particulate matter. It will describe some of the potential benefits, challenges, and limitations related to designing, building, and validating air-microfluidic circuits with particle-laden air as the working fluid. The examples shown in the presentation build on the continuing research of the Air-Microfluidic Group, a research consortium between University of Illinois at Chicago, Lawrence Berkeley National Laboratory, University of California Berkeley, and the U.S. Environmental Protection Agency. Challenges such as data validity and scalability will be addressed in the context of emerging citizen science initiatives.

5IM.1

Effect of Upstream Flow Mixing on Charging Capability of Aerosol Neutralizers. JAMES FARNSWORTH, Hans-Georg Horn, *TSI Incorporated*

Bipolar charge neutralizers (Kr-85, soft X-ray, Po-210, Am-241, Ni-63) are commonly used to predefine the charge distribution of an aerosol upstream of an electrostatic classifier. Charge equilibrium can be predicted depending on aerosol concentration, residence time, and the charger activity level. In practice however, charge equilibrium is assumed and not often verified, which can result in invalid data. In this study we show how a flow recirculation within a neutralizer of a typical experimental setup can result in inadequate neutralization, and how the issue can be mitigated by adding flow mixing elements to the flowpath.

A representative aerosol conditioning setup (generator, dryer, neutralizer) and SMPS were employed to compare the charging capacity of various neutralizers under typical experimental conditions (0.3-3 l/min aerosol flow, polydisperse NaCl, $<10^6$ #/cc total concentration). An apparent 2X difference in charging capability was observed at some flow rates when using a Kr-85 neutralizer (TSI Model 3077A) versus a soft x-ray neutralizer (TSI Model 3088). Further investigation revealed that internal geometry differences between neutralizer housings were the cause of the disparity; models indicated that particles along the edges of the flow profile were being recirculated by the Kr-85 neutralizer, while particles along the centerline were passed through at severely reduced residence times such that the exiting aerosol was insufficiently charged.

Various means were used to investigate the flow recirculation. By placing a flow restriction of dia. <2.5mm upstream of the neutralizer, or by adding a simple step change of tube diameter within 40mm of the neutralizer inlet, flow patterns inside the housing were sufficiently altered that flow recirculation did not occur.

Suggestions for the prevention of flow recirculation within neutralizers, from the perspective of both the manufacturer and the researcher, will be presented. Potential drawbacks of using flow mixing elements (i.e. diffusion losses) will also be discussed.

5IM.2

A New Device for Measuring Number Concentration of Solid Particulate Matter. AARON AVENIDO, Jason Johnson, Brian Osmondson, Hans-Georg Horn, *TSI Incorporated*

The significant reduction of particulate matter (PM) emissions from diesel engines since the introduction of diesel particulate filters (DPF) has made conventional mass based emissions measurement techniques impractical due to their inherently low sensitivity. To measure reduced PM emissions, a portable instrument capable of measuring the total number concentration of solid particles resulting from combustion sources has been developed.

The TSI Model 3795 Nanoparticle Emission Tester (NPET) consists of a sample dilution and conditioning system that removes condensation and large particles (greater than 1 micrometer) from the sample using a water trap and cyclone. Volatile particles are then removed using a built-in catalytic stripper (CS) and the resulting number concentration of solid particles is measured using an isopropanol based condensation particle counter (CPC). The instrument described here is capable of measuring number concentration from less than 1,000 to 5,000,000 particles per cubic centimeter; allowing for the measurement of solid PM number concentrations from engine configurations with, and to some extent, without DPF.

The built in CS volatile particulate removal efficiency has been determined to be greater than 99% by measuring the number concentration of 30nm geometric mean diameter tetracontane particles upstream of the CS using a TSI 3025A CPC and downstream of the CS using the built in isopropanol CPC of the NPET.

The instrument’s built in catalytic stripper and CPC have also been characterized by measuring exhaust particle emissions from a modern GM 2.0l turbocharged diesel engine and comparing NPET measurements to particulate size distributions with and without CS gathered by a TSI SMPS. In addition, NPET measured solid PM number concentrations have been compared to those as measured by a TSI 3790A engine exhaust CPC. The NPET performance characterization and comparison to 3790A CPC will be presented.

5IM.3

Statistical Comparison of Particle Counts. PATRICK O'SHAUGHNESSY, *University of Iowa*

Particle counters are now commonly used to provide measurements as part of a study to compare aerosol concentrations in different workplaces and ambient air settings. When two settings are to be compared, a t-test is applied to determine the statistical significance of the difference in mean levels of those areas. Proper application of a t-test relies on the assumption that the observations have been randomly obtained from a population and are independent and normally distributed. However, at the high sampling rates often applied when counting particles (< 1 min) there is an increased probability that subsequent observations are autocorrelated which violates the t-test assumptions. Applying a standard t-test to autocorrelated data inflates the probability of a type-1 error relative to its declared value – an increased chance of false rejections of the null hypothesis. Methods have been developed to compensate for autocorrelation that rely on theory associated with the field of time series analysis which requires substantial experience to apply correctly. The study objective was to develop an alternative method that retains the same analytical structure as the standard t-test so that it can be more universally applied by researchers in the aerosols community. The basis of the method is the adjustment of the standard error of the data time series to compensate for the actual increase in this statistic when data is autocorrelated. Methods employed when performing a standard t-test can then be used to compare, for example, the mean of a data series relative to an exposure limit, or the means of two data series. This method can also be applied, after proper adjustments, to lognormally-distributed data, which is very likely when measuring particle counts in occupational and ambient environments. The method was successfully applied to particle counts made in an occupational setting.

5IM.4

Laboratory Characterization of an Ultrafine Condensation Particle Counter Using a Perfluorinated Compound Working Fluid: Particle Size, Charge, and Composition Dependent Responses down to 1 nm. CHONGAI KUANG, Juha Kangasluoma, Daniela Wimmer, Jian Wang, Markku Kulmala, Tuukka Petäjä, *Brookhaven National Laboratory*

Recent advances in the development of condensation particle counters (CPCs) have enabled the detection of gas-phase single molecules and molecular clusters down to 1 nm diameter and below through the use of new working fluids and operating conditions. This new capability has enabled the direct measurement of aerosol nucleation from gaseous precursors in both laboratory experiments and the ambient environment, providing information necessary to constrain and probe the nucleation mechanism. While there are CPCs now that are capable of detecting nanoparticles down to 1 nm, the corresponding values for d50 (the particle diameter at which 50% of the sampled particles are counted) display a strong dependence both on particle charge state and particle composition. These strong sensitivities can lead to substantial uncertainties when calculating the actual number concentration of sampled aerosol, especially if the aerosol is of unknown composition. Prior studies have indicated that a perfluorinated compound working fluid could reduce the sensitivity of CPC detection efficiency to particle composition down to 3 nm. In this study, a commercial ultrafine CPC has been adapted to use a perfluorinated compound as the working fluid, with operating conditions optimized for the detection of sub 3 nm aerosol. Characterization results will be presented for compositionally diverse calibration aerosol of both negative and positive charge states.

5IM.5

A Portable Water Condensation Particle Counter.

SUSANNE HERING, Steven Spielman, Gregory Lewis, *Aerosol Dynamics Inc.*

A small, water-based condensation particle counter has been developed for portable monitoring of particle number concentrations. This instrument uses a three-stage, temperature-moderated laminar flow condensation method, with a self-sustaining wick. It has no fluid reservoirs, and may be operated in any orientation. Once wetted, it sustains operation for days to weeks. This self-sustained operation is enabled through a combination of recovery of evaporated water within the growth region, and capture of water vapor from the sampled air. The length of operation without addition of water depends on the absolute relative humidity of the sampled air stream, the thickness of the wick material, and operating temperatures. The aerosol flow rate is 0.2-0.3 L/min. The most recent design of the condensational growth section, which is the instrument without its optics head and control board, measures 7cm x 4cm x 11cm, weighs 320g. In tests with the first, somewhat larger, prototype, the detection efficiency for 6nm sodium chloride aerosols is 80%. For particles larger than 10nm the detection efficiency is above 90%. In comparison to the TSI-3788 ultrafine WCPC while sampling ambient air over a two day period, the the correlation between the portable WCPC gives R2>0.99, with regression slope of 0.95. For comparison over two weeks of unattended operation the correlation decreases to R2=0.97, with regression slopes of 0.89. Efforts are underway to incorporate this technology into portable device suitable for hand-held or personal monitoring.

5IM.6

A Filter Sensor for Determining the Fractal Dimension of Nanosized Agglomerates and Fibrous Carbon Nanotubes.

SHENG-CHIEH CHEN, Jing Wang, Heinz Fissan, David Y. H. Pui, *University of Minnesota*

Filtration techniques are used to mitigate PM emissions. The removal efficiency is the function of filtration conditions (filter types and properties and face velocities) and particle properties (size, morphology, concentration, etc.). Therefore, there exists a possibility to utilize the filtration method to differentiate particle shape. It has been found that there was a significant penetration difference between spherical particles and open agglomerates with the same mobility diameter through 1 micro-meter pore diameter Nuclepore filter due to the elongated shape and the accordingly enhanced interception deposition of agglomerates. A modified capillary tube model has been developed to predict the penetration accurately for aggregates and agglomerates by our previous studies. In this study, 1 micro-meter Nuclepore filter was challenged by classified monodisperse nanoparticles with different fractal dimension (determined by DMA-APM method) and carbon nanotubes. The modified capillary tube model was used to estimate the interception length (or effective length) by assuming the diffusion and impaction efficiencies are known. Results show that the calculated effective lengths of MWCNTs with different mobility diameters were close to the average values determined by the SEM analysis. The comparison of penetration between different fractal dimension Ag particles and CNT showed the higher fractal dimension the higher penetration. The penetration difference was significant between these particles. Nuclepore filter with the modified capillary tube model could be a sensor for determining particle fractal dimension.

5IM.7

Accurate Control of Relative Humidity for HTDMA Particle Growth Rate Measurements. STEVEN CEVAER, Suresh Dhaniyala, *Clarkson University*

Research on the interaction of aerosol particles with water vapor is important to determine particle lifetime, light scattering properties, and role in cloud formation. The hygroscopic tandem differential mobility analyzer (HTDMA) is an instrument commonly used to measure growth rate and deliquescence of particles as a function of relative humidity (RH). Particle growth rate measurements with the HTDMA can be used to determine particle compositions and to help differentiate the constituents of an externally mixed sample. Accurate particle size response to RH can only be achieved with an accurately controlled humidification process for the scanning DMA's sheath and aerosol flows. For particle sources that vary in space or time, it is also necessary that the RH control system quickly stabilize at desired RH values. We studied several humidification systems and evaluated their response times and ability to maintain long-term humidity control. The results of this study will be presented and implications for fast HTDMA measurements will be discussed.

5IM.8

Instrumental and Methodological Complex for Inhalation Intake Assessment of Radioactive Gas-Aerosol Mixtures. ANDREW KAREV, Alexander Tsovianov, *FMBC*

Report's subject is development instrumental and methodological complex which allows simultaneous conducting of particle-size distribution analysis and volume activity measurement of aerosol and gas fractions of radioactive gas-aerosol mixtures for further inhalation intake assessment. Importance of the report is concerned with fact that for measuring volume activity of radioactive air samples including gas and aerosol fractions it's necessary to measure volume activity of both fractions simultaneously because taking into account volume activity of only one fraction can result to decreasing of internal dose estimation. The presented method includes separation aerosol fraction of gas-aerosol mixture from gas fraction by inertial deposition of aerosol particles onto cascade impactor stages simulating human respiratory tract, the subsequent chemical transformation of gas fraction of gas-aerosol mixture to aerosol fraction by injection of reagent vapors into gas stream and sedimentation of the formed aerosol particles on filter. The device could be used in the atomic industry for radioactive pollution measurement of air environment.

5PH.1

Linking Air Pollution and Health Effects: The Role of Semi-volatile Components of Ultrafine Ambient Particles.

MICHAEL KLEINMAN, Andrew Keebaugh, David Herman, Vishal Verma, Payam Pakbin, Loyda Mendez, Constantinos Sioutas, *University of California, Irvine*

Air pollution exposure is associated with increased incidence of cardiovascular disease. Effects include increased daily mortality and hospital admissions. Urban airborne ultrafine PM contains semi-volatile organics (SVOCs) which have a high proportion of redox active compounds that can be bound to particles or can partition to the vapor phase after emission where they may be responsible for some of the observed exacerbation of PM-associated adverse cardiovascular health effects. Therefore, we hypothesized that the removal of SVOCs from an aerosol should decrease the ability of ultrafine PM to cause oxidative damage and reduce adverse cardiovascular effects including development of atherosclerotic plaque, induction of cardiac abnormalities measured by changes in electrocardiogram (ECG) waveform morphology and arrhythmias and losses of heart rate variability (HRV). Groups of genetically altered ApoE -/- mice (prone to developing atherosclerosis) were exposed to either purified air, quasi-ultrafine concentrated ambient particles (CAPs; under 0.18μm aerodynamic diameter), or to thermally denuded CAPs (deCAPs) from which SVOCs were removed from the particle core using a thermal denuder. The mice were exposed 5 hours/day, 4 days/week for 8 weeks in downtown Los Angeles, about 100m downwind of a major freeway. Implanted cardiac transducers monitored ECGs from the mice. The ECGs were analyzed to detect changes in HRV and abnormal waveforms including ischemia-related changes and arrhythmias. Histological and biochemical examination showed that CAPs exposed mice exhibited significantly more arterial atherosclerotic plaque than did deCAP or Air-exposed mice. They also exhibited progressive HRV losses that were accompanied by ischemia-related changes in ECG waveforms not seen in deCAPs or Air exposed mice. Losses of HRV and arrhythmias are common measures of myocardial dysfunction in humans associated with life-threatening cardiac events precipitated by atherosclerosis. Further investigation into the observed changes need be performed to explicate the mechanisms of the changes resulting from CAPs exposures.

5PH.3

Sources of Reactive Oxygen Species (ROS) Generation Properties of Atmospheric Aerosols in Southeastern United States.

VISHAL VERMA, Ting Fang, Laura King, Hongyu Guo, Rodney Weber, *Georgia Institute of Technology*

ROS generating properties of the ambient aerosols has emerged as a widely accepted mechanism responsible for the various health outcomes associated with particulate matter (PM) pollution. As part of a multi-institutional and collaborative center (Southeastern Center for Air Pollution & Epidemiology) study, we measured the potential of the atmospheric aerosols in southeast US to generate superoxide radicals. Ambient fine particles (Dp< 2.5 micro-meter) were collected on the quartz filters (23 hours integrated samples, N = 500) at multiple (N=7) sites representing different environmental settings from urban to rural environments, for one complete year from May 2012 to April 2013. Detailed chemical analyses including carbonaceous species (elemental and organic carbon, water-soluble organic and brown carbon), inorganic ions and water-soluble metals were conducted on all of the samples, and ROS-generation potential of the particles was measured using dithiothreitol (DTT) assay. The emission sources were identified using linear regression analysis between DTT activity and various chemical components and positive matrix factorization was applied to apportion the relative contribution of these sources in the PM ROS-generation potential. Four major emission sources, i.e. vehicular emissions, road dust resuspension, secondary photochemical formation and biomass burning, are identified significantly contributing to the ROS activity of the particles. The associations of the emissions sources with PM-ROS activity have strong spatial and seasonal trends. Primary vehicular emissions contribute throughout the year particularly in urban areas. In summer, resuspended dust makes a significant contribution in urban sites, but secondary organic aerosols dominate the ROS generation in both urban and rural areas. In winter, biomass burning is the major source contributing to the PM-ROS generation potential throughout southeast. Further statistical and mechanistic studies are underway to delineate the specific chemical components present in each source to drive the ROS responses and the subsequent health effect mechanisms in humans.

5PH.4

Isoprene-derived Secondary Organic Aerosol and Epoxide Intermediates Induce Altered Expression of Inflammation-associated Genes in Lung Cells. YING-HSUAN LIN, Maiko Arashiro, Zhenfa Zhang, Avram Gold, Ilona Jaspers, Rebecca Fry, Jason Surratt, *University of North Carolina at Chapel Hill*

Secondary organic aerosol (SOA) derived from OH-initiated oxidation of isoprene (2-methyl-1,3-butadiene) has been recognized as a substantial source contributing to the total ambient PM2.5 mass in isoprene-rich environments. Whether SOA derived from this source contribute to adverse health effects induced by exposure to ambient PM2.5 is unknown. To evaluate the toxicological potency of isoprene-derived epoxide intermediates and the resultant SOA constituents, cytotoxicity and proinflammatory cellular responses were examined using an in vitro model of human airway epithelial cells (BEAS-2B). Here, the release of lactate dehydrogenase (LDH), XTT-based cell proliferation assays, and inflammation-associated gene expression were assessed to study potential biological effects on lung cells. Isoprene-derived epoxides, including isoprene epoxydiols (IEPOX) and methacrylic acid epoxide (MAE), were synthesized, and the SOA constituents were generated from heterogeneous reactive uptake of IEPOX and MAE onto preexisting sulfate seed aerosols in a series of controlled smog chamber experiments under conditions simulating urban and downwind urban atmospheres impacted by isoprene emissions. SOA constituents were collected on Teflon membrane filters and extracted for subsequent cell exposure. Aliquots of the filter extracts were chemically characterized at the molecular level and quantified using ultra performance liquid chromatography interfaced to quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-Q-TOFMS) equipped with electrospray ionization (ESI), and electron impact gas chromatography-mass spectrometry (GC/EI-MS) following trimethylsilyl derivatization. Associations between identified SOA chemical compositions and biological/toxicological effects will be presented to discuss potential health risk induced by isoprene-derived SOA exposure.

5PH.5

Investigating the Health Effects of Fresh and Aged Traffic Aerosols: Linking Particle Oxidative Potential to Chemical Composition. NGA LEE NG, Matthew Kollman, Vasileios Papapostolou, Joy Lawrence, Sriram Suresh, Vishal Verma, Rodney Weber, Armistead Russell, Petros Koutrakis, *Georgia Institute of Technology*

Emissions from mobile sources are of substantial interest in health effects studies. Most studies have focused on the adverse effects of primary diesel and gasoline emissions. In contrast, studies on the toxicity of secondary mobile emissions, especially that involving gas-particle partitioning upon oxidation and secondary organic aerosol (SOA) formation, is extremely limited and their health effects remain poorly characterized. In this collaborative study between the EPA-funded SCAPE and Harvard Clear Air Centers, we systematically investigate the chemical composition and oxidative properties of primary and secondary particles from vehicular emissions. Measurements are conducted at a moderate-to-heavy traffic density tunnel in the Northeastern US equipped with photochemical chamber and animal exposure facility. The facility produces three test atmospheres: “primary particles” (P), “aged primary plus secondary organic aerosols” (P+SOA), or “secondary organics aerosols” (SOA). For each system, the near real-time chemical composition of the particles is characterized by an Aerosol Chemical Speciation Monitor (ACSM). The ACSM provides mass concentration and mass spectra of organics, sulfate, ammonium, nitrate, and chloride. Filter samples are taken from each system and analyzed for oxidative properties (reactive oxygen species generation properties) using dithiothreitol assay (DTT), as well as complementary chemical composition such as EC/OC, particle mass, and trace elemental concentrations. We apply Positive Matrix Factorization (PMF) to the ACSM organics data to deconvolve the mass spectra into different factors for linking to aerosol oxidative properties. The PMF factors are consistent with offline EC/OC measurements, where we resolve hydrocarbon-like OA and oxygenated OA that are surrogates for primary and secondary organic aerosols. It is found that SOA exhibits the highest intrinsic DTT activity among all test atmospheres. As SOA mass often dominates fine particle matter in the atmosphere, results from this study highlight the importance of understanding the health effects of SOA formed from the photooxidation of primary emissions.

5PH.6

Linking Nitrogen Oxide Chemistry and Aerosol over the Last Decade in San Joaquin Valley, California. SALLY PUSEDE, Ronald Cohen, *UC Berkeley*

Nitrogen oxide (NO_x) abundances across the U.S. have fallen steadily over the last fifteen years. Patterns in anthropogenic sources result in 2-fold lower NO_x on weekends than weekdays largely without co-occurring changes in other emissions. These trends taken together provide a near perfect NO_x constraint on the nonlinear chemistry of ozone, on key oxidants hydroxyl (OH) and nitrate radical (NO_3), and on secondary aerosol formation. We use this NO_x constraint to interpret trends in wintertime $PM_{2.5}$ over the last decade in San Joaquin Valley, California, a location with severe aerosol pollution and where a large portion of the total aerosol mass is ammonium nitrate (NH_4NO_3). We combine the 15-year routine monitoring record and the air- and ground-based DISCOVER-AQ-2013 data set to quantify the impact of NO_x emission controls on wintertime $PM_{2.5}$ concentrations. Nitrate ion (NO_3^-) is the oxidation product of NO_2 and is formed by distinct daytime and nighttime pathways, both of which are nonlinear functions of the NO_2 abundance. We present observationally derived decadal trends in both pathways and show that NO_x reductions have dually worked to increase and decrease NH_4NO_3 production over the last 15 years. The net effect is a substantial decrease in NO_3^- via decreased production in the nighttime residual layer. We quantify the impact of future NO_x controls on $PM_{2.5}$ exceedances.

5PH.7

Estimating Spatiotemporal Variations of $PM_{2.5}$ over the Pittsburgh Metropolitan Area Using Aerosol Optical Depth. Tao Xue, RICHARD BILONICK, Daniel Connell, Evelyn Talbott, Judith Rager, LuAnn Brink, *University of Pittsburgh*

Epidemiological studies have associated $PM_{2.5}$ with adverse health outcomes. Exposure assessment plays a critical role in estimating health risk of $PM_{2.5}$ but is limited by sparsely-distributed monitoring stations. Previous studies have applied satellite remote sensing of aerosol optical depth (AOD) to predict spatiotemporal variations of $PM_{2.5}$ mass concentration measurements but rarely considered the time-varying $PM_{2.5}$-AOD association and potentially complex spatiotemporal correlation. This study is a part of the Pittsburgh Aerosol Research and Inhalation Epidemiology Study (PARIES) and aims to predict $PM_{2.5}$ over the Pittsburgh metropolitan area from 2001-2008.

We collected $PM_{2.5}$ mass concentration measurements from 102 monitors at 47 sites and MODIS AOD (Level 2) measurements from the Terra satellite. Measurements were aggregated at the daily level resulting in 61,346 $PM_{2.5}$ measurements (square-root transformed) and 309,919 AOD observations. We designed a two-stage approach. First, AOD was smoothed using space-time kriging with a product-sum covariance structure to reduce spatial misalignment between $PM_{2.5}$ and AOD. Next, smoothed AOD was associated with $PM_{2.5}$ through a time-varying coefficient mixed effects model, producing best linear unbiased predictors of $PM_{2.5}$ at given spatiotemporal coordinates. We used cross validation (CV) to evaluate our models.

$PM_{2.5}$ had a mean of 15.2 mu-g/m^3 with a standard deviation of 9.6 mu-g/m^3 and was higher in autumn (19.8 mu-g/m^3) and summer (15.2 mu-g/m^3), lower in spring (13.1 mu-g/m^3) and winter (12.8 mu-g/m^3). Daily $PM_{2.5}$ was 1.7% more highly correlated with smoothed AOD (R^2=0.4466) than raw AOD (R^2=0.4392). $PM_{2.5}$-AOD association was found to vary seasonally and was higher in summer/autumn than in winter/spring. Ten-fold CV confirmed that space-time kriging with the varying-coefficient mixed effects model performed well with CV R^2 of 0.9882 and 0.9157 (CV RMSE 0.0313 and 0.4435), respectively, for smoothing AOD and predicting $PM_{2.5}$. We will present details of the statistical methodology and examples of the resulting daily exposure maps.

5PH.8

Mutagenicity of PAH and Nitro-Derived: An Assessment of Respirable Particulate Matter in Rio de Janeiro, Brazil.

Claudia Rainho, SERGIO CORREA, Jose Mazzei, Claudia Aiub, Israel Felzenszwalb, *Rio de Janeiro State University*

Some studies have correlated the mutagenic activity detected in the Salmonella/microsome assay with the levels of B[a]P and other nonsubstituted PAHs present in the samples, but recent reviews show that PAHs may not be the predominant mutagens in atmospheric pollution, and that nitro PAH, aromatic amines and aromatic ketones are potent mutagens. Nitro-PAHs are persistent environmental mutagens and can be found in airborne suspended particles from direct sources such as diesel and gasoline exhausts, or may be products of atmospheric reactions in the presence of NO2 and NO3 radicals. In the present work we compared PAH and Nitro-PAHs levels and mutagenicity using gas chromatography spectrometry and the Salmonella/microsome assay on organic extracts of PM2.5. The samples were collected in two periods: (I) July to October 2010 and (II) November 2010 to May 2011 at three sites in Rio de Janeiro – (1) low urban traffic at the University campus; (2) heavy urban traffic at Brasil Avenue and (3) Rebouças tunnel. For both periods, site 3 showed the highest concentrations of PAHs and nitro-PAHs. Period I showed the higher values of rev/m3. Mutagenic frameshift responses in the absence of metabolic activation were detected at all the sites in periods I and II. In the presence of metabolic activation this response was observed for all three sites in period I, but only for site 3 in period II. Nitroarenes and dinitroarenes were detected at all three sites in period I. In period II, the presence of nitroarenes was also detected at all sites, but dinitroarenes were only detected at sites 2 and 3. The information generated in this study shows that different levels of PAHs and nitroderivatives, influenced by seasonal variations in climatic conditions, probably contribute to the detected airborne mutagenicity.

6AC.1

A Smog Chamber-Flow Tube Study of the Direct Photolysis of Model Biogenic and Anthropogenic SOA. SANDRA BLAIR, Scott A. Epstein, Amanda MacMillan, Sergey Nizkorodov, *University of California, Irvine*

The physical properties and toxicity of “fresh” versus “aged” secondary organic aerosol (SOA) strongly depend on the type of aging. This paper focuses on SOA aging arising from the condensed-phase photolysis of particulate organic compounds. Previous studies of SOA aging have mainly relied on the photooxidation of SOA in smog chambers or in flow reactors. However, in these types of studies, it is challenging to isolate the effect of condensed-phase photolysis from gas-phase photochemical reactions followed by gas-to-particle partitioning. We designed and carried out experiments that produced SOA in a smog chamber, stripped the excess oxidants and gaseous organics with a denuder train, photolyzed the resulting particles in a quartz flow tube, and analyzed the SOA composition and mass concentration before and after direct photolysis of particulate organic compounds using various analytical techniques. The unique advantages of this method include the ability to exclude possible interfering factors caused by (1) oxidant recycling, (2) gas-phase photolysis of high-volatility organic compounds, and (3) dark aging. We will discuss the results for two model systems: alpha-pinene ozonolysis SOA and diesel photooxidation SOA prepared in the presence and absence of SO_2. Specifically, we will discuss the effect of UV photolysis on (1) particle mass concentration, (2) overall peroxide content, (3) chemical composition as measured by an aerosol mass spectrometer (AMS), (4) mass absorption coefficient, and (5) oxidative stress by particle suspensions as measured by a rapid kinetic bioassay demonstrating the inhibition of glutathione peroxidase 1 (GPx-1) by organic electrophilic pollutants. The health and climate implications of these measurements will be discussed.

6AC.2

A Real-Time Fast-Flow Tube Study of VOC and Particulate Emissions from Electronic, Reduced-Harm, Conventional, and Reference Cigarettes. SANDRA BLAIR, Scott A. Epstein, Sergey Nizkorodov, Rufus Edwards, Ralph J. Delfino, Michael Kleinman, Nosratola Vaziri, Norbert Staimer, *University of California, Irvine*

The tobacco industry has promoted “harm reduction cigarettes" as safer than conventional brands. This also includes electronic cigarettes which are currently not regulated by the FDA. One approach to evaluate the potential toxicity of electronic cigarettes and “reduced-harm” cigarettes is to compare their volatile organic compound (VOC) and particulate emissions to that of conventional and reference cigarettes. In particular, reactive organic electrophillic compounds such as unsaturated carbonyls and small particles may determine possible adverse health effects. Although conventional cigarettes have been well characterized, few studies have used comparative real-time analysis of cigarette puff composition. Previous online studies of cigarette smoke VOCs were limited to low time resolution measurements, complicated instrumentation, and/or availability. We designed and carried out experiments that puffed on a cigarette at a selected puff frequency, promptly diluted the emitted mainstream smoke in a fast-flow tube, and analyzed the VOC composition and particle number concentration in real-time. The mainstream smoke residence time in the fast-flow tube was on the order of a few seconds, allowing adequate time resolution for the various selected puff frequencies, as the analytical instruments each offered high time resolution (<=1s). A high resolution proton transfer reaction time-of-flight mass spectrometer (PTRMS) was used to analyze real-time cigarette VOC emissions and was able to resolve a highly electrophillic and toxic aldehyde, acrolein, from butenes, and determine the amount of acrolein and other carbonyls emitted per cigarette puff quantitatively. Several important factors in VOC and particle concentration will be discussed: (1) puff frequency, (2) "vaping" versus smoking, (3) puff number, (4) tar content, (5) absence or presence of a filter and filter type in reduced-harm cigarettes, and (6) traditional cigarette brands. Preliminary analysis indicates that electronic cigarettes are not free from acrolein emissions and have comparable particle concentration emissions to those of conventional cigarettes.

6AC.3

Measurements of Oxidized Organic Compounds during SOAS 2013 Using Nitrate Ion Chemical Ionization Coupled with High Resolution Time-of-Flight Mass Spectrometry. PAOLA MASSOLI, Harald Stark, Manjula Canagaratna, Heikki Junninen, Jani Hakala, Roy Lee III Mauldin, Mikael Ehn, Mikko Sipilä, Jordan Krechmer, Joel Kimmel, John Jayne, Jose-Luis Jimenez, Douglas Worsnop, *Aerodyne Research, Inc.*

We present ambient measurements of gaseous organic compounds by means of a High Resolution Time-of-Flight Chemical Ionization Mass Spectrometry (HR-ToF-CIMS) using nitrate ion (NO3-) chemistry. This technique allows to selectively detect low-volatility oxidized organic molecules (ELVOC) and sulfuric acid via clustering with NO3- and its high order clusters. The capability of making such measurements is important because both sulfuric acid and organic gas molecules have a recognized key role in new particle formation (NPF) processes and formation of secondary organic aerosols (SOA). The HR-ToF-CIMS was deployed during the Southern Oxidant and Aerosol Study (SOAS) at the forest supersite in Centreville, AL, from June 1 to July 15, 2013. The main goal of the SOAS campaign was to investigate the composition and sources of SOA in the Southeast US, where emissions are mainly represented by biogenic volatile organic compounds (BVOC) emissions occasionally mixing with anthropogenic emissions. During SOAS, the HR-ToF-CIMS detected a range of organic ions that based on previous literature could be identified as oxidation products of both isoprene and terpenes. The isoprene-related molecules showed a diurnal cycle with a day time peak, typically after 1500 local time, while the terpene products were higher at night (between 2000 and 0600 local time). Positive Matrix Factorization (PMF) analyses are applied to the dataset to extract additional information on the sources of the observed molecules and interpret the observations through the correlation with gas and particle external tracers. The sensitivity of the measurements to ambient RH is also explored. Finally, the ambient data are compared to laboratory measurements where oxidized organic vapors are produced using a Potential Aerosol Mass (PAM) flow reactor by the OH oxidation of biogenic gas-phase precursors (isoprene, a-pinene) over multiple days of equivalent atmospheric exposure.

6AC.4

Sources of Black Carbon 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, Nga Lee Ng, Lu Xu, Berk Knighton, Manvendra Dubey, Allison Aiken, Kyle Gorkowski, Shang Liu, Dominique Young, Dantong Liu, James Allan, *Aerodyne Research, Inc.*

We deployed a suite of instruments at a rural site approximately 65 km southeast of London in Detling, UK during January-February, 2012, as part of the Clean Air for London (CleafLo) campaign. Measurements included aerosol chemistry and optical properties, 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. Comparison with similar measurements in central London will also be presented.

6AC.5

Organosulfates from Pinene and Isoprene over the Pearl River Delta, South China. XIANG DING, Quanfu He, Xinming Wang, Jian Zhen Yu, Neil Donahue, *Guangzhou Institute of Geochemistry, CAS*

Biogenic organosulfates (OSs) are important markers of secondary organic aerosol (SOA) formation involving cross reactions of biogenic precursors (terpenoids) with anthropogenic pollutants. Till now, there is rare information about biogenic OSs in the air of highly polluted areas. In this study, fine particle samples were separately collected in daytime and nighttime from summer to winter 2010 at a site in the central of Pearl River Delta (PRD), South China. Pinene-derived nitrooxy-organosulfates (pNOSs) and isoprene-derived OSs (iOSs) were quantified using a liquid chromatograph (LC) tandem mass (MS/MS) coupled with negative electrospray ionization (ESI). The pNOSs with MW=295 exhibited higher levels in fall-winter than summer, probably owing to the elevated levels of NOx and sulfate in fall-winter. In contrast to observations elsewhere where higher levels occurred at nighttime, pNOSs levels in the PRD were higher during daytime in both seasons, indicating that the pNOS formation was driven by photochemistry over the PRD. This conclusion is supported by several lines of evidence: the specific pNOS which could be formed through both daytime photochemistry and nighttime NO_3 chemistry exhibited no day-night variation in abundance relative to other pNOS isomers; the production of the hydroxynitrate that is the key precursor for this specific pNOS was found to be significant through photochemistry but negligible through NO_3 chemistry based on the mechanisms in the Master Chemical Mechanism (MCM). For iOSs, 2-methyltetrol sulfate ester which could be formed from isoprene-derived epoxydiols (IEPOX) under low-NOx conditions showed low concentrations, largely due to the depression of IEPOX formation by the high NOx levels over the PRD.

6AC.6

Chemical Composition of Marine Emissions from Mediterranean Seawaters: Results from a Mesocosm Study. JORGE PEY, H. Langley DeWitt, Brice Temime-Roussel, Aurelie Même, Bruno Charriere, Richard Sempere, Anne Delmont, Sébastien Mas, David Parin, Clemence Rose, Allison Schwier, Badr Rmili, Karine Sellegri, Barbara D'Anna, Nicolas Marchand, *Aix-Marseille Université, CNRS, LCE FRE 3416*

Marine emissions are among the largest sources of secondary organic aerosols (SOA) globally. Whereas physical processes control the primary production of marine aerosols, biological activity is responsible for most of the organic components released from marine sources and potentially transformed into SOA when exposed to atmospheric oxidants. The Mediterranean atmosphere has been found to have high concentrations of SOA, especially in summer. The origin of these elevated concentrations of SOA is unclear but past measurements suggest that they are mainly from modern (non-fossil) sources.

In view of these recent findings, the gas- and particle-phase chemical fingerprint of marine emissions is desirable. As part of the Source of marine Aerosol particles in the Mediterranean atmosphere (SAM) project, a mesocosm study was conducted at the Oceanographic and Marine Station STARESO (Corsica) in May 2013. During these experiments, 3 mesocosms were deployed. To observe the effect of biological activity on volatile organic compounds (VOCs) and aerosol emissions, two of the mesocosms were enriched with different levels of nitrate and phosphate and one was left unchanged as a control. Physical and chemical properties of mesocosms and their atmospheres were followed during 20 days: aerosol size and concentration were measured by a SMPS; gas-phase composition of VOCs was determined by using PPR-ToF-MS; and aerosol chemical composition was obtained from HR-ToF-AMS. In parallel, incident light, water temperature, pH, conductivity, chemical and biological analyses, fluorescence of chlorophyll-a, and dissolved oxygen concentration were measured in the mesocosms.

Preliminary results suggest new particle formation processes linked to iodine chemistry. Aerosol composition inside the mesocosms was slightly enriched in organic aerosols, being oxygenated organic compounds the most important species in terms of mass concentration, but amine-related aerosol mass peaks varied the greatest in concentration between the mesoscosms. Enhanced VOCs occurred in the enriched mesocosms.

6AQ.1

Identifying Precursors and Aqueous Organic Aerosol Formation Pathways in the Humid, Photochemically-Active Southeastern US during the SOAS Campaign. NEHA SAREEN, Annmarie Carlton, Barbara Turpin, *Rutgers University*

Aqueous multiphase chemistry in the atmosphere can lead to rapid transformation of organic compounds, forming highly oxidized low volatility organic aerosol and, in some cases, light absorbing (brown) carbon. Because liquid water is globally abundant, this chemistry could substantially impact climate, air quality, health, and the environment. Gas-phase precursors released from biogenic and anthropogenic sources are oxidized and fragmented forming water-soluble gases that can undergo reactions in the aqueous phase (in clouds, fogs, and wet aerosols) leading to the formation of secondary organic aerosol (SOA_{AQ}). Recent studies have highlighted the role of certain precursors like glyoxal, methylglyoxal, glycolaldehyde, acetic acid, acetone, and epoxides in the formation of SOA_{AQ}. The goal of this work is to identify other precursors that are atmospherically important. In this study, ambient mixtures of water-soluble gases were scrubbed from the atmosphere at Brent, Alabama during the Southern Oxidant and Aerosol Study (SOAS). Four mist chambers in parallel collected ambient gases in a DI water medium at 20-25 L/min with a 4 hr collection time. Total organic carbon (TOC) values in daily composited samples were 64-180 micro-M. Aqueous OH radical oxidation experiments were conducted with these mixtures. Results from experiments conducted on two days showed precursors to be primarily odd ions and found in the positive mode by electrospray ionization mass spectrometry (ESI-MS), indicative of the presence of alcohols, aldehydes, organic peroxides, and epoxides. Targeted precursor masses were fragmented using MS/MS to gain structural insights (such as functional groups and O:C and H:C ratios) and identify possible compounds. Products were seen in the negative mode and included pyruvate and oxalate, confirmed using ion chromatography. The results from this study will be used to better understand the precursors and cloud chemistry of these atmospherically relevant mixtures.

6AQ.2

Particle Water and pH in the Southeastern US. HONGYU GUO, Lu Xu, Kate Cerully, Aikaterini Bougiatioti, Shannon Capps, Annmarie Carlton, Shanhu Lee, Nga Lee Ng, Michael Bergin, Athanasios Nenes, Rodney Weber, *Georgia Institute of Technology*

Particle pH is an important aerosol property that is difficult to directly measure and so often determined from thermodynamic calculations. pH can influence the solubility of metals, partitioning of acidic species, and the formation of secondary organic aerosols. An accurate measurement or prediction of particle water is needed to determine pH. As part of the Southern Oxidant and Aerosol Study (SOAS), Georgia Tech made detailed measurements at Centreville of particle organic and inorganic composition, aerosol hygroscopicity, and indirect measurements of particle liquid water content using nephelometers. Fine particle water was predicted by the sum of water associated with ions and organic species, the former water predicted by ISORROPIA using PILS-measured ions (ionic-water) and the latter water predicted from κorg (organic-water) determined from cloud condensation nuclei (CCN) activity. Predicted liquid water was in good agreement with measured liquid water determined from a measure of f(RH); ambient (RH and T) PM2.5 light scattering coefficient(σsp) and dry σsp. The sum up of ionic-water and organic-water agreed well with the measured water (regression slope of 0.96, intercept of 0.7µg/m3, R=0.86). Organic-water is found to be significant, accounting for 37% of total water based on a study average. At night organics accounted for 63% of total water. Using total predicted water, the study average fine particle pH was predicted at 0.98±0.61, and pH diurnal trends followed liquid water, with nighttime pH near 2 and during day near 0. ISORROPIA predictions were verified by agreement between predicted and measured ammonia. pH of the fine aerosol throughout the southeastern US was assessed based on measurements of inorganic compounds at various sites and during various seasons as part of the Southeastern Center for Aerosol Pollution and Epidemiology (SCAPE). pH generally ranged between 0 and 2. Winter pH was higher than summer, although water content was lower in winter.

6AQ.3

On the Link Between Hygroscopicity, Volatility, and Oxidation State of Ambient and Water-soluble Aerosol in the Southeastern United States. KATE CERULLY, Aikaterini Bougiatioti, Lu Xu, Hongyu Guo, James Hite, Nga Lee Ng, Rodney Weber, Athanasios Nenes, *TSI, Inc.*

The formation of secondary organic aerosol combined with the partitioning of semi-volatile organic components can impact numerous aerosol properties including cloud condensation nuclei (CCN) activity, hygroscopicity, and volatility. During the summer 2013 Southern Oxidant and Aerosol Study (SOAS) field campaign in rural Alabama, a suite of instruments including a CCN counter, thermodenuder (TD), and high resolution time-of-flight aerosol mass spectrometer (AMS) were used to measure CCN activity as well as aerosol volatility, hygroscopicity, composition, and oxidation state. Particles were either sampled directly from ambient or through a Particle-Into-Liquid-Sampler (PILS), allowing for the investigation of water-soluble aerosol components. Ambient aerosol exhibited size-dependent composition with larger particles being more hygroscopic. The hygroscopicity of thermally-denuded aerosol was similar between ambient and PILS-generated aerosol and showed limited dependence on volatilization at TD temperatures up to 100°C. The organic hygroscopicity appeared to decrease with increased heating, opposing the conventional view of the most volatile compounds being the least hygroscopic. No clear relationship was found between organic hygroscopicity and oyxgen to carbon ratio, while average carbon oxidation state increased with increased volatilization.

6AQ.4

Estimation of Organo-Sulfur in $PM_{2.5}$ via Isotope Dilution ICPMS and Ion Chromatography. ERIC EDGERTON, Karsten Baumann, Mike Fort, Stephanie Shaw, John Jansen, *Atmospheric Research & Analysis*

Production of secondary organic aerosol (SOA) involves a host of oxidation mechanisms for biogenic and anthropogenic VOCs and SVOCs. Some of these pathways may involve acid catalysis and produce a variety of sulfur-containing organic compounds in the condensed phase, such as isoprene epoxydiol sulfates. Information on total organic sulfur concentrations in $PM_{2.5}$ is therefore useful for constraining SOA production mechanisms in atmospheric models and for comparison with measurements based on direct analysis of individual organo-sulfur compounds. The purpose of this presentation is to describe an analytical technique for estimating total organo-sulfur in $PM_{2.5}$, and to present initial results of analyses for samples collected at several sites in the southeastern U.S.

Organo-sulfur is estimated as the difference between total-S and sulfate-S in gravimetrically prepared aqueous extracts of $PM_{2.5}$ from Teflon filters. Sulfate-S is analyzed via traditional ion chromatography (IC). Total-S is determined by isotope dilution dynamic reaction cell ICPMS. In this technique, sample extracts are spiked with a known mass of $^{33}SO_4$, and the three major isotopes of sulfur are quantified as $^{32}S^{16}O$ (48 amu), $^{33}S^{16}O$ (49 amu) and $^{34}S^{16}O$ (50 amu). Total-S mass in the sample is then calculated as:

$$\text{Total-S} = 1.048 * (^{32}S^{16}O) / (^{33}S^{16}O) * (IE_{49} / IE_{48}) * \text{Spike}_{33}$$

where, $(^{32}S^{16}O)$ and $(^{33}S^{16}O)$ are the ICPMS counts at 48 amu and 49 amu; IE_{48} and $IE_{49}$are the relative ion efficiencies for 48 amu and 49 amu; and Spike_{33} is the spike of $^{33}SO_4$ corrected for chemical and isotopic purity.

The IC and ICPMS are both calibrated with gravimetrically prepared NIST SRM 3181 (sulfate in water) and the ICPMS is further challenged with methanesulfonic acid and camphorsulfonic acid as model organo-sulfur compounds. Based on recoveries of external standards and model organo-S compounds, the extended uncertainty of total-S is 0.6%, and the extended uncertainty of the difference between total-S and sulfate-S is 0.9%.

Results from the Jefferson Street SEARCH site show mean organo-S of 42.5 +/- 15.6 ng/m^3 and 14.8 +/- 6.7 ng/m^3 during August 2012 and November 2012, respectively. These concentrations correspond to 6.4 +/- 3.3% and 4.9 +/- 2.1% of total-S during August and November, respectively. Day/night observations of organo-S during the SOAS campaign at Centreville, AL will also be presented and discussed.

6AQ.5

Constraints on the Parameters Dictating Organic Aerosol Volatility from Dual Thermodenuder Field Measurements in the Southeastern US.

PROVAT SAHA, Andrey Khlystov, Andrew Grieshop, *North Carolina State University*

The volatility of organic aerosols (OA) has emerged as a property of primary importance in understanding their source and atmospheric lifecycle. Parameters used to describe ambient OA volatility, such as the distribution of material among lumped components with varying effective saturation concentrations (C*; e.g. in the volatility basis set (VBS) approach) and the associated enthalpies of evaporation (ΔHvap), and evaporation coefficient (alpha) are highly uncertain. However, since OA evaporation is dictated by a large number of independent parameters (C*, ΔHvap, and alpha), it is difficult to constrain all of the volatility parameters with single-dimensional (e.g. thermodenuder temperature) perturbation to the initial equilibrium. Here, we discuss measurements of ambient OA volatility at two sites in the Southeastern US: (i) near Centreville, Alabama, at the main ground site of Southern Oxidant and Aerosol Study (SOAS), in June and July, 2013, and (ii) at the North Carolina State University (NCSU) main campus in October and November, 2013. In these studies, we simultaneously operated two thermodenuders (TDs): one stepping through various temperature settings (40-180 degC) at reasonably high residence time (RT; ~50 s) and another operating isothermally (at 60 or 90 degC), with varying residence time (~1 to 50 s). This dual TD approach provides more insight into OA evaporation kinetics and volatility parameters when coupled with an evaporation kinetics model. Approximately 50-65% OA mass evaporated at 100 degC with RT of 50 s, indicating that much of the OA is semi-volatile under atmospheric conditions; whereas about 10% of OA mass remained at 180 degC, indicating that extremely low volatile material consistently contributes to OA. An optimizing VBS-based mass-transfer model was used to invert observations and derive campaign-average volatility distributions and parameter values. Modeling results suggest that ΔHvap of OA was likely in the range of 100-120 KJ/mol and alpha in the range of 0.1 to 1. Results from these and future analyses enable the direct evaluation of emerging treatments of OA volatility in atmospheric models.

6AQ.6

Aqueous Sources of Secondary Organic Aerosol in the Southeast Atmosphere Study (SAS).

V. FAYE MCNEILL, Jason Surratt, Annmarie Carlton, Havala Pye, *Columbia University*

The reactive uptake of water-soluble volatile organic compounds (VOCs) by wet aerosols or cloud droplets, also known as aqueous SOA (aqSOA) formation, is likely an important source of aerosol organic material. Aqueous SOA formation is believed to be particularly important in the Southeastern United States, where aerosol sulfate concentrations, humidity, and volatile organic compound (VOC) concentrations tend to be high during photochemically active periods. Quantifying the relative contribution of aqSOA in the SE USA is one of the goals of the Southeast Atmosphere Study (SAS).

We will present the results of modeling studies examining cloudwater and aerosol water SOA formation pathways simultaneously in the context of SAS. The simulation outputs are compared to aqSOA tracer data which was collected at three ground sites, along with other observations of aerosol composition and abundance. aqSOA formation at ground sites is modeled using the detailed photochemical box model for aqueous aerosol formation, GAMMA (McNeill et al., ES&T 2012), taking data from SAS observations and CMAQ as inputs. The regional contribution of aqSOA to particle loadings will be evaluated using CMAQ with cloudwater glyoxal chemistry (Carlton et al. , ES&T 2008) coupled with simpleGAMMA (a reduced version of GAMMA), and CMAQ with the recent isoprene epoxide chemistry module of Pye et al. (ES&T 2013).

6BB.1

How Well Do Laboratory Studies Represent Microphysical Properties of Soot Emitted from Wildfires? RAJAN K. CHAKRABARTY, Nicholas Beres, Hans Moosmuller, Swarup China, Claudio Mazzoleni, Manvendra Dubey, Li Liu, Michael I Mishchenko, *Desert Research Institute*

Soot emitted from wildfires has been implicated in rapid global warming, accelerated melting of glaciers, changing monsoon patterns, and degradation of human health and the environment. It contributes to greater than threefold uncertainty in current estimates of climate forcing. This large uncertainty is primarily attributable to poor understanding of the microphysical properties of wildfire-emitted soot and their parameterizations in models and satellite retrieval algorithms. In recent years, researchers have made thorough efforts to characterize these properties for soot emitted from laboratory-scale combustion of wildland fuels (for e.g., the Fire Laboratory at Missoula Experiments (FLAME)) as a function of various process parameters such as fuel type, temperature and scale of flaming phase, environmental conditions driving the combustion process, and interrelationships of these parameters. These studies have been conducted under the assumption that they may closely mimic natural wildfires in their soot formation mechanism and emitted particle properties. Consequently, the current view holds that in flaming wildfires, soot is formed via the cluster–dilute aggregation mechanism and is emitted as aggregates with fractal dimension Df ~1.8 and mobility diameter Dm <= 1µm.

Here, we provide evidence of significant presence of a hitherto unrecognized form of soot– superaggregates (SAs)–in the outflow from two wildfires in Karnataka (India) and California (USA). SAs are porous, low-density aggregates of cluster-dilute aggregates with characteristic Df ~2.6 and Dm > 1µm that form via the cluster-dense aggregation mechanism in the flaming phase of wildfires. Their greater than one micrometer Dm render SAs undetectable using conventional soot aerosol-sizing instruments, such as the Scanning Mobility Particle Analyzer (SMPS). Using numerically-exact superposition T-Matrix optical modeling, we estimate SAs to contribute, per unit optical depth, up to 35% less atmospheric warming than freshly-emitted (Df ~1.8) aggregates, about 25% more warming than aged aggregates (1.8 <= Df <= 3.0), and ~90% more warming than spherical particles currently used in climate models.

6BB.2

Optical and Physical Properties of Biomass Burning Aerosols – Linking Laboratory and Field Measurements. ALLISON AIKEN, Manvendra Dubey, Shang Liu, Claudio Mazzoleni, Gavin McMeeking, Ezra Levin, Paul DeMott, Sonia Kreidenweis, Robert J. Yokelson, Allen Robinson, Neil Donahue, Christopher Cappa, Leah Williams, Nga Lee Ng, Douglas Worsnop, Timothy Onasch, *Los Alamos National Lab*

Aerosols from biomass burning (BB) sources, e.g. wildfires and wood burning for heating, contribute substantially to global emissions and climate. Black carbon (BC) from BB alone accounts for ~50% of global BC emissions, equating to ~0.6 W/m2 atmospheric warming. However, large uncertainties exist due to the complex morphology and mixing state of BB aerosol. Direct on-line rBC (single particle soot photometer; SP2) and optical properties of scattering and absorption (3-wavelength Photoacoustic Soot Spectrometer; PASS-3) are combined from laboratory and field measurements in order to improve climate predictions. First, we explore the relationships between combustion characteristics, e.g. gas-phase emissions, and aerosol optical and physical properties by parameterizing single scatter albedo (SSA) and rBC as a function of modified combustion efficiency (MCE). Then, we investigate the presence of a BC-coating enhancement in an area impacted by BB. Lastly, we quantify a potential rBC removal technique utilizing the SP2 for implementation similar to the widely-applied thermal denuder method (Huffman et al., 2009). During the Fire Lab At Missoula Experiments IV (FLAME-IV), single-source BB emissions have an inverse relationship between SSA and MCE. Parameterization and application to wildfire data indicate agreement within 5% (Liu et al., 2014). rBC coatings measured with the SP2 are used to calculate the ratio of total particle diameter to rBC core, which also has an inverse relationship with MCE. Increased organic carbon during smoldering (MCE's are <~0.9) supports this finding. Thickly-coated rBC that dominates BB emissions and rBC-inclusion particles (Sedlacek et al., 2012) are also compared from FLAME-IV and wildfires. A BC-coating enhancement of up to 50% was found during the ClearfLo campaign that occurred in winter with significant BB emissions from heating. A rBC removal method using the SP2 that can remove ≥90% of BC ≥100 nm dme is also evaluated for future climate applications.

6BB.3
Real-time Evolution of the Gas-phase Precursors for Secondary Organic Aerosol from Biomass Burning. Adam Ahern, Patrick Veres, Daniel S. Tkacik, Ellis Shipley Robinson, Rawad Saleh, Albert A. Presto, Allen Robinson, Robert J. Yokelson, Neil Donahue, RYAN SULLIVAN, *Carnegie Mellon University*

The chemical composition and evolution of biomass burning smoke is highly variable, both in the fresh near-fire emissions and in the aged plumes. Photochemical aging of the smoke plume can produce significant quantities of secondary organic aerosol (SOA) from the oxidation of gas-phase organic compounds. Field measurements, and simulated laboratory chamber experiments, have demonstrated a wide range of SOA enhancements in atmospherically aged smoke plumes. In some cases significant additional SOA mass is produced, while in others a net loss of organic aerosol mass occurred with aging. The chemical nature of the gaseous precursors and the mechanisms that determine the magnitude of SOA formation (or loss) remain largely unknown.

A unique dual smog chamber method was deployed at the Fourth Fire Laboratory at Missoula Experiments (FLAME-IV) to address this deficiency in our understanding of how biomass burning smoke evolves in the atmosphere, and its total contribution to aerosol loadings. Here we focus on the relationship between the variability and evolution of the gas-phase precursors and the resulting variability in SOA production or loss. Chamber aging experiments were conducted using a range of globally relevant biomass fuels, and different atmospheric aging conditions including exposure to UV blacklights, ozone, and nitrogen oxides. The two identical 7 m^3 Teflon chambers were simultaneously filled with diluted smoke from combustion using realistic, unconstrained burn profiles with varying contributions from flaming and smoldering-phase combustion. This dual chamber experiment (DUCE) method facilitated paired control/perturbed experiments with the same complex, realistic, but difficult to reproduce smoke emissions. The gas and particle emissions were measured in real-time and analyzed to establish possible correlations between reactant decay rates, volatile organic compound formation, and SOA formation. Two proton transfer reaction mass spectrometers measured the loss rates of less-oxidized gaseous SOA precursors and the formation of more oxidized products from atmospheric aging.

6BB.4
Fluoride Emissions from Biomass Burning. Thilina Jayarathne, Chelsea Stockwell, Robert J. Yokelson, Shunsuke Nakao, ELIZABETH STONE, *University of Iowa*

Fluoride is the 13th most abundant element on earth and widely dispersed throughout the lithosphere, hydrosphere, biosphere and atmosphere. Fluorides enter the atmosphere through soil dust, sea spray, geysers and volcanoes, as well as anthropogenic sources like brick manufacturing, aluminum smelting, fertilizer production and coal burning. Vegetation accumulates fluorides from the surrounding environment, which can be toxic to plants and animals that graze on them. In the study, we test the hypothesis that the burning of biomasses re-emits fluoride into the atmosphere. We analyzed water-soluble inorganic fluoride in 55 fine particulate (PM2.5) samples from biomass burning collected at the USDA Forest Service Fire Sciences Laboratory in Missoula, Montana during FLAME-IV laboratory study, using ion chromatography coupled with conductivity detection. Standard addition experiments and energy dispersive x-ray analysis were used to confirm the presence of fluoride in PM2.5 samples. Water-soluble fluoride was detected in samples from all conifers (n=11) and agricultural residues (n=15), but only 40% of the grasses and other perennial plants (n=13). Fluoride was not detected in remaining samples (n=16) collected from peat, shredded tires and cook-stove burns. A tight correlation (R2 > 0.95) between mass of PM2.5 and fluoride emitted from conifers and agricultural residues reflects a consistent fluoride mass fraction among similar fuels. Fluoride accounted for 0.06 – 0.15 % of PM2.5 emissions from conifers and 0.05 – 0.13 % of fluoride emitted by burning grasses and other perennial plants. Agricultural residues varied considerably, from 0.01 – 0.44 %, with maxima influenced by application of fluoride-containing fertilizers. PM2.5 emissions depended on burning conditions of fuel; hence fluoride emission factors were also influenced by combustion efficiency. These measurements help to explain prior ambient observations in which particulate fluoride in the atmosphere coincided with major biomass burning events and provide new insight to the global cycling of fluoride.

6BB.5

Smoke Marker Ratios from Controlled Laboratory Burns, Prescribed Burns, and Wildfires. AMY P. SULLIVAN, Sonia Kreidenweis, Bret Schichtel, Jeffrey Collett, *Colorado State University*

One of the main sources of organic carbon (OC) aerosols is biomass burning. Therefore, it is important to be able to determine the contribution of biomass burning to the total OC concentration. Smoke marker measurements provide one of the most common methods to make this determination. Key to using smoke markers for ambient aerosol source apportionment is knowledge of the smoke marker to OC concentration ratio at the source. There is still much uncertainty in these smoke marker ratios, especially for biomass burning emissions from prescribed burning and wildfires. Therefore, in this work, we aim to try to better understand the constraints and variability that should be placed on smoke marker ratios when trying to determine the contribution of smoke from prescribed burning and wildfires. Comparisons between source samples collected at the Fire Science Lab in Missoula, MT from the FLAME (Fire Science at Missoula Experiment) studies and samples collected from various prescribed burns and wildfires across the U.S. will be made. Smoke markers such as potassium and various carbohydrates (e.g., levoglucosan and galactosan) will be presented. Our results suggest that most smoke marker ratios depend more on the type of fuel involved in the burn than fire dynamics and that controlled laboratory burns can represent prescribed burns for a number of smoke marker ratios.

6BB.6

Impacts of Transboundary Peatland Burning Smoke on In Situ Acidity of Urban Aerosols. Shiguo Jia, Wei Hong Fan, Choon Nam Ong, Jeffrey Reid, LIYA YU, *National University of Singapore*

The smoke episode in June 2013 marks the highest aerosol burden in Singapore in the past decade, raising strong concerns about potential impacts on urban atmosphere and public health. Our study campaign conducted in 2012 and 2013 show that transboundary peatland burning smoke surged the local PM2.5 concentration, in average, by a factor of 4, with organic matter (>50% of PM2.5 concentration) dominating over sulfate as the most abundant compound class. This characterizes the peatland burning in Southeast Asia, degrading one of the major carbon sinks in the world.

Bulk PM2.5 in Singapore are strongly acidic (in situ pH=0.4) with the most acidic aerosols of 10–18 nm (in situ pH=-0.3). Interestingly, the transboundary smoke neutralized the urban PM2.5 by introducing more ammonium and increasing the average in situ pH to 1.4. As a worst case scenario for an adult with a tidal volume of 625 ml per breath, and a breathing rate of 12 times/min, 1-hour exposure to local emitted aerosols yielded a deposition of 4.0 micro-gram in the head, tracheobronchial, and alveolar regions together, with an average in situ pH of 0.6. Aerosols depositing in the tracheobronchial region are most acidic with an average in situ pH of 0.3. When the transboundary smoke was present, the total aerosol deposition after 1-hour exposure increased by 2.5 times; aerosols settling in the alveolar region exhibited the largest increment, changing from 1.2 to 4.2 micro-gram. The in situ acidity of depositing aerosols differs, depending on the amount of alkaline matter introduced by the transboundary smoke. During the smoky period in 2012, aerosols parking in the tracheobronchial region are most acidic (average in situ pH=-0.2) whereas during the smoke episode in 2013, the acidity of aerosols settling in all three regions is similar (average in situ pH=~1.0).

6EP.1

Airborne Measurements of Biogenic and Anthropogenic Secondary Organic Aerosol Formation in the Oil Sands Region of Alberta. JOHN LIGGIO, Katherine Hayden, Peter Liu, Amy Leithead, Samar Moussa, Jason O'Brien, Shao-Meng Li, *Environment Canada*

The Alberta oil sands (OS) region represents a strategic natural resource and is a key driver of economic development. Its rapid expansion has led to a need for a more comprehensive assessment of the associated potential cumulative environmental impacts. As part of the 2013 JOSM (Joint Canada-Alberta Implementation Plan on Oil Sands Monitoring) summer intensive field campaign, airborne measurements of various gaseous and particulate substances were made in the Athabasca oil sands region between August 13 and Sept 7, 2013. In particular, organic aerosol mass and composition measurements were performed with a High Resolution Time of flight Aerosol Mass Spectrometer (HR-ToF-AMS) supported by gaseous measurements of organic aerosol precursors with Proton Transfer Reaction (PTR) and Chemical Ionization (CI) mass spectrometers. The measurements data from selected flights were used to estimate the potential for local anthropogenic OS emissions to form secondary organic aerosol (SOA) downwind of precursor sources, and to investigate the importance of the surrounding biogenic emissions to the overall SOA burden in the region. The results of several flights conducted to investigate these transformations demonstrate that the SOA downwind of OS industrial sources is the product of a complex interaction between biogenic and anthropogenic precursors. Concurrent measurements of isoprene oxidation products (IEPOX) during transformation flights indicate that biogenic secondary organic aerosol (BSOA) contributes to the overall SOA formed in the region. The relative contribution of BSOA to the total primary OA and total SOA during a number of flights in the OS region will be described.

6EP.2

Winter Fine Particle Haze Episodes in the Bakken Oil and Gas Production Region. ASHLEY EVANOSKI-COLE, Anthony Prenni, Derek Day, Misha Schurman, Amy P. Sullivan, Yi Li, Barkley Sive, Yong Zhou, Jenny Hand, Kristi Gebhart, Bret Schichtel, Jeffrey Collett, *Colorado State University*

Oil and natural gas production in the Bakken formation region in North Dakota and Montana has rapidly increased in recent years due to the use of horizontal drilling and hydraulic fracturing. Though impacts of oil and gas drilling in other areas of the United States have been examined, the impacts on air quality in the rapidly developing Bakken formation region are relatively unknown. While fine particle concentrations are decreasing across much of the country in response to emission reductions of sulfur and nitrogen oxides, IMPROVE aerosol measurements reveal increased sulfate and nitrate concentrations in this region during winter. In order to better characterize winter air quality in the region, measurements of fine particle composition and precursor gases in the north unit of Theodore Roosevelt National Park and other nearby national park sites were conducted. In a pilot study, conducted February-April 2013, elevated concentrations of $PM_{2.5}$ ammonium nitrate and ammonium sulfate were observed. These high particle episodes were often in periods of stagnant wind conditions and were associated with higher concentrations of NO_x and NO_y. Excess ammonia remained in the gas phase in these episodes despite the formation of substantial ammonium nitrate. Elevated concentrations of SO_2 were also observed throughout the measurement period. A second, more comprehensive measurement campaign was conducted from November 2013 to March 2014 with higher time resolved gas and particle composition measurements (MARGA and HR-AMS) as well as VOC characterization. The characteristics, sources and transport patterns of these high particle episodes and gaseous precursors are examined to gain a better understanding of the impacts of oil and gas production activities on regional air quality.

6EP.3

Amines and Their Degradation Products from Post-Combustion Carbon Capture. STEPHANIE SHAW, Annette Rohr, Eladio Knipping, *Electric Power Research Institute*

Atmospheric amines have the potential to form aerosols through the formation of aminium salts or secondary organic aerosol. Moreover, researchers have highlighted a key role for amines in aerosol nucleation. The use of amine solvents for post-combustion carbon capture (PCCC) in power plants could lead to emissions of amines and amine degradation production products to the atmosphere. As a result, it is important to develop a clear understanding of the potential human and environmental impacts of those solvents. One critical need in order to better estimate and characterize emissions of the amine solvents and their degradation products is the need to standardize relevant stack sampling and analytical methods. Unfortunately, this issue is complicated by the varying chemical and physical properties of the several compound classes of interest, stage of method development, and difficulty of dealing with sampling constraints of power plant stacks. This led to the development of an international working group to collaboratively evaluate efficacy of methods that already have or could be applied in power plant flue gas, to improve characterization of sampling artifacts, to determine if standardized method performance metrics can be created, and to potentially design a method shoot-out test protocol. The goal is to summarize lessons learned and set the stage for future guidelines for more accurate determination of emissions of amines, related compounds, and their degradation products. Methods reviewed included both online (e.g. Fourier transform infrared spectroscopy) and offline (e.g. sorbent trapping and thermal desorbtion) analysis for both gas and particle phase compounds. An overview of the findings and recommendations will be summarized in this presentation.

6EP.4

Effects of Global Warming Mitigation Strategies in Major Energy Sectors on Primary and Secondary Aerosol. Michael MacKinnon, MARC CARRERAS-SOSPEDRA, Jack Brouwer, Donald Dabdub, *University of California, Irvine*

Future efforts to mitigate climate change will include transitions to alternative technologies and fuels seeking reductions in greenhouse gas (GHG) emissions from United States (US) energy sectors. In addition, displacement of conventional energy strategies will impact emissions of pollutant species directly influencing regional air quality (AQ) due to common generation processes and sources. Currently, sectors of paramount concern include transportation and power generation, which combined total over half of domestic GHG emissions and account for the bulk of emissions driving primary and secondary AQ concerns in many US regions, including ambient concentrations particulate matter.

The present study analyzes the potential reductions in particulate matter caused by an increased penetration of renewable sources of energy, novel technologies and cleaner fuels for transportation in three different regions of interest in the United States: California, Texas, and the Northeastern US (NEUS). The emission reductions are evaluated for the year 2055 with respect to a reference case projected using the Market Allocator (MARKAL) model. The emissions are based on the US Environmental Protection Agency’s National Emissions Inventory, and spatially and temporally resolved using the Sparse Matrix Operational Kernel Emissions (SMOKE) model. The effects of the emission changes on aerosol formation are evaluated using the Community Multiscale Air Quality (CMAQ) model.

Significant variation in energy profiles, demands, and constraints among study domains yields significant differences in regional air quality. For example, impacts on PM from power generation in California are modest compared to Texas and the NEUS, largely due to a relative lack of coal use. Current focus on light duty vehicle emission controls amplify impacts on PM from heavy duty vehicles, rail, and off-road sources in all study regions. Additionally, the industrial sector was shown to have comparable impacts to power generation and transportation on PM in all regions.

6EP.5

Detailed Characterization of Particulate Matter (PM) Emitted by Pre-commercial High-Efficiency Spark Ignition Direct Injection Gasoline Engine. ALLA ZELENYUK, Paul Reitz, Mark Stewart, Dan Imre, David Rothamer, David Foster, Mitchell Hageman, Axel Maier, Stephen Sakai, Michael Andrie, Roger Krieger, Kushal Narayanaswamy, Paul Najt, Arun Solomon, *Pacific Northwest National Laboratory*

Current engine development aims to reduce consumption of limited fuel resources and reduce carbon dioxide emissions by increasing fuel efficiency. While diesel engines achieve the highest fuel efficiency, they also generate the highest particulates mass, shown to be harmful to human health and the environment. Spark Ignition Direct Injection (SIDI) is a gasoline engine technology with potential to achieve very high fuel efficiency by operating more like diesel engines, blurring the lines that have traditionally existed between gasoline and diesel engines. At present, the studies providing detailed characterizations of particulate emission from these new engines are very sparse.

We present the results of a study, in which we characterized in detail the number concentration, size, composition, morphology, effective density, and mass of individual exhaust particles emitted by a single-cylinder SIDI test engine. These measurements were used to calculate particles' fractal dimension, average diameter of primary spherules, and number of spherules, void fraction, and dynamic shape factors as function of particle size.

We find that SIDI PM 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 diameter of primary spherules, while the larger primary spherules may be linked to wall/piston impingement. In addition, we find the SIDI PM to contain 40-60% organics that are tightly bound within the elemental carbon, making it impossible to remove them by thermo-denuder or in an evaporative chamber.

These results point to significant differences between the properties of PM produced by diesel engines and that generated by SIDI engine, requiring adaptation of existing after-treatment technologies used to reduce particulate emissions and their environmental impact.

6EP.6

Modeling Aerosol Release from Explosion-Induced Vessel Ruptures for Nuclear Fuel Reprocessing. FRED GELBARD, Alexander Brown, David L. Y. Louie, Chengcheng Feng, Nathan E. Bixler, *Sandia National Laboratories*

An accidental explosion in a chemical reprocessing vessel for spent nuclear fuel may not only rupture the vessel, but also form some radioactive aerosol from the solution in the vessel. For a safety analysis, there is a need for simulations and data to determine the aerosol particle size distribution as a function of the processing fluid properties, equipment dimensions, and explosive energy.

In this work, we model from basic principles the creation of aerosols from the initial explosion to release. We use a Lagrangian, three-dimensional, explicit, transient code to model the large deformations and short time scales of the structural response. The solid walls and equipment in the vessel are modeled with finite elements, allowing these elements to deform and separate, but they do not get atomized by the explosion. For short time-scales, the radionuclide solutions are modeled with Smoothed Particle Hydrodynamic (SPH) elements, which are coupled to the structural elements.

After the fluid has been ejected and liquid drops have separated, the system is then modeled with a finite element, fluid dynamics code that solves the Navier-Stokes equations for the flow induced by the explosion and the ejected drops. Aerodynamic drop break-up is modeled employing a Lagrangian transport framework coupled to the Eulerian gas phase solvers.

This physics-based approach provides a model of the explosion effects on the radionuclide solution, the rupture or failure of the processing vessel, the forced ejection of the radionuclide solution, and the break-up of the solution to form aerosols. The numerical approach is demonstrated with a simulation of an actual accident.

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6IM.1

Design and Testing of an Inhalable Particle Spectrometer. KIMBERLY ANDERSON, Mwangi Ndonga, David Leith, Jordan Rath, Azer Yalin, John Volckens, *Colorado State University*

Large particles (dp > 10 micrometers) exist in many atmospheres (e.g., workplaces, confined spaces, wind-blown dust). Although such particles can contribute up to 50% or more to the inhaled aerosol mass following exposure, very few instruments exist to count and size such particles in situ. Large inhalable particles deposit primarily in the oral and nasal cavities, with subsequent health effects targeting the upper respiratory system. Symptomatic health effects such as acute or chronic rhinitis, chronic pharyngitis, sinusitis, and nasal cancer occur in many industries, indicating the prevalence of exposure to these large inhalable particles. No commercially available instrument currently exists to count and size particle sizes between 30 and 100 micrometers. This presentation describes the development of a new instrument to characterize the size distribution and concentration of inhalable aerosols (from 10 to 100 micrometers in diameter) in near-real time. A virtual portable inhalable particle spectrometer (vPIPS) relies on the principles of virtual impaction and with vertical elutriation to separate large particles as a function of aerodynamic diameter. The instrument has a diameter of 118 mm and weighs 0.5 kg. A 785 nm 100 mW laser diode and Si photodiode detector provides real-time particle counts. The instrument sizes particles from 30 to 100 micrometers into 10 micrometer size bins. Experimental sampling efficiency was tested in a calm air chamber with particle sizes from 10 to 100 micrometers. The vPIPS was capable of size-selective sampling and showed good sampling efficiencies. Fluid flow and particle transport in the sampler was also evaluated using computational fluid dynamics modeling. Experimental sampling efficiencies showed good agreement with computational and analytical solutions.

6IM.2

A Small, Sensitive, Light-weight, and Disposable Aerosol Spectrometer for Balloon and UAV Applications. Ru-Shan Gao, HAGEN TELG, Timothy Bates, Richard McLaughlin, Laurel Watts, Steven Ciciora, James Johnson, Joshua P. Schwarz, Anne Perring, Andrew Rollins, Troy Thornberry, David Fahey, *NOAA/CIRES*

In-situ sampling with particle size spectrometers is an important method to provide detailed size spectra for atmospheric aerosol in the troposphere and stratosphere. The spectra are essential for understanding aerosol sources and aerosol chemical evolution and removal, and for aerosol remote sensing validation. These spectrometers are usually bulky, heavy, and expensive, thereby limiting their application to specific airborne platforms. Here we report a new type of small and light-weight optical aerosol particle size spectrometer that is sensitive enough (150 – 2500 nm diameter detection range) for many aerosol applications yet is inexpensive enough to be disposable. 3D printing is used for producing structural components for simplicity and low cost. Weighing less than 1 kg individually, we expect these spectrometers can be deployed successfully on small unmanned aircraft systems (UASs) and up to 25 km on weather balloons. Immediate applications include the study of Arctic haze using the Manta UAS, detection of the Asian Tropopause Aerosol Layer in the Asian monsoon system and SAGE III validation onboard weather balloons. Results from recent test flights onboard the Manta UAS will be presented.

6IM.3

High Speed Size Distribution Measurements of Aerosol Particles.

Michael Pikridas, Chongai Kuang, Steven Spielman, Susanne Hering, JIAN WANG, *Brookhaven National Laboratory*

A Fast Integrated Mobility Spectrometer (FIMS) was developed for rapid measurements of aerosol size distributions from 10 to 450 nm. The FIMS consists of a classifier, a condenser, and a detector (Kulkarni & Wang, 2006, J. Aerosol Sci.). Inside the classifier an electric field separates charged particles onto different flow lines, based on their electrical mobilities. The strength of the electrical field varies spatially by over three orders of magnitude, such that particles of a wide range of electrical mobilities can be simultaneously separated (Wang, 2009, J. Aerosol Sci.). The separated particles are then carried by a butanol-saturated sheath flow into the condenser, where a supersaturation of butanol is generated through electrical cooling and the classified particles grow into super-micrometer droplets. At the exit of the condenser, a laser sheet illuminates the grown droplets, and their images are captured by a CCD camera. The images provide both particle concentration and position, which directly relates to the particle electrical mobility. By simultaneously measuring particles of different sizes, the FIMS provides aerosol size spectra at a time resolution of 1 Hz, nearly 100 times faster than traditional SMPS. The sizing accuracy of the FIMS was characterized by measuring monodispersed aerosol classified by DMA over the size range of 10 to 450 nm. The results show that the FIMS measures the particle size accurately, and has a nearly 100% activation efficiency for particles as small as 10 nm.

Recent deployment onboard research aircraft demonstrated that the FIMS is capable of measuring aerosol size distribution spectrum in 1s, thereby offering a great advantage over SMPS in applications requiring high time resolution. In addition, FIMS could also improve the time resolution of other measurements relying on scanning mobility technique, such as aerosol hygroscopicity using Tandem DMAs. A system employing water-condensation technique is currently being developed.

6IM.4

A Liquid Nebulization / Differential Mobility Analysis / Transmission Electron Microscopy Approach to Evaluate Nanoparticles in Environmentally-Relevant Water Matrices.

BRIAN MADER, Mark Ellefson, Sue Wolf, *3M Company*

A liquid nebulization-differential mobility analysis method (LN/DMA) was used in conjunction with Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive Spectroscopy (EDS) for the evaluation of engineered nanoparticles (ENPs) in environmentally relevant aqueous matrices. The LN/DMA method was used to measure the size distribution and quantitative number concentration of ENPs in aqueous solutions; however the method alone cannot be used to directly determine the morphology and chemical composition of the ENPs. The LNS/DMA system was used in conjunction with the TSI 3089 Nanometer Aerosol Sampler; ENPs were aerosolized from aqueous media and deposited onto TEM grids for further evaluation of their morphology, size, and chemical composition using spectroscopic analysis techniques (TEM, STEM, EDS). To further evaluate the method, NIST-traceable reference materials were spiked into several aqueous matrices; aqueous media used in ecotoxicology testing, semiconductor grade ultra pure water, groundwater, and an industrial wastewater. For samples with significant signal to noise, the measured mean particle diameters of the reference materials were within the expected NIST-traceable size range for the materials. The method was also able to discern ENPs from other materials and non-volatile residues present in the native aqueous solutions. The optimum sampling parameters for the collection of ENPs onto TEM media by this method will also be discussed. Overall this method is particularly well suited for dose verification in ecotoxicology studies as well to support the studies of ENP behavior in aqueous matrices.

6IM.5

Development of a Miniature Plate Differential Mobility Analyzer (Mini-plate DMA). QIAOLING LIU, Da-Ren Chen, *Virginia Commonwealth University*

Recent epidemiologic studies have shown the good correlation between the morbidity/mortality of human being and the concentration of ambient particles, especially ultrafine particles. A cost-effective aerosol sizer in a small package is thus in great demand for conducting either spatial air quality monitoring or personal exposure studies. Differential mobility analyzers (DMAs) are powerful tools for characterizing ultrafine particles. The use of existed DMA systems is however limited in these applications because of their bulky size, heavy weight and high manufacture cost. A miniaturized, cost-effective mini-plate DMA has thus been developed in this work to address the above issues. The prototype mini- plate DMA is in its rectangular configuration, where aerosol and sheath flows travel between two parallel metal plates. A high DC voltage is applied on one of two plates and electrically ground on the other in order to establish an electrical field for particle classification. The overall particle classification length in the prototype DMA is 1 15/32". Two identical DMAs were manufactured and the tandem DMA (TDMA) technique was applied to calibrate the prototype performance. NaCl particles were used for this evaluation. The piecewise linear deconvolution scheme (Li et al., 2006) was then applied to obtain the true transfer function of mini-plate DMA at various particle sizes. The detail result of this study will be presented in this talk.

6IM.6

Initial Field Deployment of a Custom Multi-Channel Tandem Differential Mobility Analyzer (mc-TDMA). CHRISTOPHER OXFORD, Yang Wang, Steven Dhawan, David Hagan, Dhruv Mitroo, Pratim Biswas, Brent Williams, *Washington University in St. Louis*

A multi-channel Tandem Differential Mobility Analyzer (mc-TDMA) has been constructed for physical characterization of fine particles during field and laboratory studies. The mc-TDMA employs 2 long column DMAs (TSI, Model #3081), a condensational particle counter (TSI, Model #3776), and is fully automated to switch between a volatility channel, a hygroscopicity channel, a Scanning Mobility Particle Sizer (SMPS) channel, and an auxiliary channel. Here we present details on the instrument construction and operation as well as results from its first deployment to the Saint Louis Air Quality Regional Study (SLAQRS) in late summer 2013 where it sampled ambient particles as well as secondary aerosol downstream of a potential aerosol mass (PAM) oxidation chamber.

6PH.1

SPARTAN: An Emerging Global Aerosol Network.

GRAYDON SNIDER, Crystal Weagle, Randall Martin, Aaron van Donkelaar, Clement Akoshile, Paulo Artaxo, Jeff Brook, Brent Holben, Ralph Kahn, Nofel Lagrosas, Puji Lestari, Vanderlei J. Martins, Eduardo J. Quel, Yinon Rudich, Abdus Salam, S.N. Tripathi, Zhang Qiang, Michael Brauer, Aaron Cohen, Mark D. Gibson, Yang Liu, *Dalhousie University*

For many regions around the world ground-based observations of fine particulate matter (PM2.5) have insufficient spatial coverage to assess long-term health impacts. Although satellites offer a promising avenue to enhance spatial coverage, there are limitations and outstanding questions about the accuracy and precision with which ground-level aerosol mass concentrations can be inferred from satellite remote sensing. We have initiated a global network of ground-level monitoring stations designed to evaluate and enhance satellite remote sensing estimates in health effects research and risk assessment. This Surface PARTiculate mAtter Network (SPARTAN) is an emerging global federation of ground-level monitoring stations that provide hourly PM2.5 estimates in highly populated regions. Each station is collocated with an existing ground-based sun photometer to measure aerosol optical depth (AOD). SPARTAN filters are analyzed for total PM2.5 mass, black carbon, water-soluble ions and metals. A three-city pilot study has shown good agreement between SPARTAN air filters and the nephelometer. The network has now expanded to stations spread over four continents. Participating groups include those in Bangladesh, Brazil, Canada, China, India, Indonesia, Israel, Philippines, Nigeria, Vietnam, and the United States. This presentation will describe our recent aerosol and chemical speciation results and the implications for global PM2.5 concentrations.

6PH.2

Balancing Health and Climate Impacts of Aerosols in a Changing World using GEOS-Chem Adjoint Sensitivities.

FORREST LACEY, Daven Henze, *University of Colorado, Boulder*

Aerosol formation has significant effects on both health and climate. When looking at future emissions scenarios, such as the representative concentration pathways (RCPs) outlined in the IPCC AR5, it is important to identify control strategies for regions that will have an impact on both of these effects. The GEOS-Chem Adjoint model is used to calculate sensitivities of the formation of population weighted PM2.5 with respect to anthropogenic emissions of aerosols and aerosol precursors. This was done at a 2 by 2.5 degree latitude – longitude grid for both the 2000 world population and the projected 2050 world population. The adjoint model is also used to calculate the sensitivities of both global and regional surface temperature change with respect to anthropogenic emissions following the absolute regional temperature potential method at the same gridded resolution for both 2000 and 2050 following RCP 4.5 (Shindell et al. 2010).

Combining these sensitivities, we identify regions and countries that have the largest impact on both health and climate. This result is also used to explore the co-benefits of a large number of different emissions perturbations including the projected RCP scenarios and different UNEP control measures. The advantage of using these sensitivities is that the impacts of the different control strategies being explored can be calculated without additional model runs, whereas current techniques require additional model runs for each emissions scenario. These sensitivity results will aid policy makers by allowing them to quickly estimate the effects of different scenarios and determine the optimum allocation of resources and emissions reductions from both a regional and global perspective.

6PH.3

A Reduced-Complexity, Variable Grid Resolution Model for PM2.5 Transport and Transformation. CHRISTOPHER TESSUM, Jason Hill, Julian Marshall, *University of Minnesota*

Background: Air pollution modeling is usually done with either gaussian plume models (e.g., AERMOD, ISC) or with temporally explicit chemical transport models (e.g., CMAQ, CAMx, WRF/Chem). While both model types can be useful, the former neglects important physical and chemical processes, and the latter is commonly limited by computational costs.

Aims: To create a novel chemical transport model that includes the physical and chemical processes most important in determining $PM_{2.5}$ regulatory compliance and human exposure, that can simulate both intra-urban concentration gradients and long-range transport of pollution, and that can be run on a single desktop computer.

Methods: The model is based on a steady-state Eulerian framework with a population-based variable resolution computational grid. Meteorological and background chemical information is derived from the output of a 12-month, 12-km spatial resolution WRF/Chem simulation for the continental United States. The model includes mechanisms for advection, turbulent diffusion, pollutant removal by wet and dry deposition, and for partitioning between gas and particle phases for sulfur, nitrate, ammonia, and organic matter.

Results: We compare annual-average results of 12-month, continental U.S., 12-km spatial resolution WRF/Chem simulations for 12 emissions scenarios to predictions by our simplified model for the same emissions scenarios and spatial grid. For domain-average total $PM_{2.5}$ concentrations: R^2=0.97, mean fractional bias=-43%. For population-weighted total $PM_{2.5}$ concentrations: R^2=0.97, mean fractional bias=-2%. In general, agreement was better for primary $PM_{2.5}$ and particulate sulfate concentrations than for concentrations of other compounds. Each simplified model run takes ~30 processor hours, compared to ~120,000 processor hours for the comparable WRF/Chem simulation.

Conclusion: Our modeling approach can provide useful pollution simulations at several orders of magnitude less computational cost than comprehensive chemical transport models.

6PH.4

Linking Air Quality Health Impacts and Electricity Capacity Planning. PAUL KERL, Wenxian Zhang, Juan Moreno-Cruz, Athanasios Nenes, Matthew Realff, Armistead Russell, Joel Sokol, Valerie Thomas, *Georgia Institute of Technology*

Production of electricity from combustion sources generates sulfur dioxide and nitrogen oxide that transform in the atmosphere into other pollutants such as fine particulate matter and ozone. These air pollutants have a variety of negative consequences, such as premature mortality, asthma exacerbation, increased hospital admissions and decreased visibility. We create a mathematical formulation of a multi-decade least-cost electricity capacity planning model that newly links emission sensitivities from the Community Multi-scale Air Quality Model (CMAQ), to model air pollutant concentrations at a fine spatial and temporal resolution. This new capability allows us to use mixed integer linear programming to minimize a combined objective of monetized air quality health impacts and the cost of production of electricity. We examine planning for the state of Georgia within this linked framework.

6PH.5

Reducing Global Mortality from PM$_{2.5}$. JOSHUA APTE, Julian Marshall, *Lawrence Berkeley National Laboratory*

We investigate the regional distribution of potential health benefits of major worldwide improvements in ambient fine particulate matter (PM$_{2.5}$) concentrations. We develop high-resolution (10 km) global analyses of premature mortality attributable to ambient PM$_{2.5}$ ("PM mortality") using data from the 2010 Global Burden of Disease (GBD) assessment, including recently developed supra-linear integrated-exposure response (IER) functions (Burnett et al., 2014, EHP 1307049). We address two questions with this model that can illuminate discussions about mitigating this major health risk: (1) How is the global population and global incidence of PM mortality distributed as a function of region and ambient concentrations; (2) how do potential mortality benefits of achieving ambitious PM$_{2.5}$ targets vary among world regions?

The shape of the IER relationship yields surprising conclusions about the global distribution of PM mortality. While PM mortality rates are high in the most polluted parts of the world (especially China and India), a notably large burden of disease (~40% of global PM mortality) also exists for regions with more moderate PM$_{2.5}$ levels (<=25 micro-g/m^3) owing to the large populations that live in these areas (~63% of all humans). To achieve major (>50%) reductions in PM mortality in these regions (<=25 micro-g/m^3) would likely require attaining concentrations even cleaner than the WHO PM$_{2.5}$ air quality guideline (10 micro-g/m^3 annual average concentration). Globally, ~35% of total PM mortality would still remain if all regions above 10 micro-g/m^3 achieved this target. For the most polluted areas of the world (mean concentration ~90 micro-g/m^3; 8% of the population, 20% of all PM mortality), half of the PM mortality would remain even with a three-fold reduction in levels to ~30 micro-g/m^3. Substantially reducing the burden of disease from ambient PM$_{2.5}$ will require aggressive mitigation in nearly all regions of the world.

6PH.6

Development and Application of a Markov Chain Model for Predicting Influenza Risk and Control in an Office Environment. PARHAM AZIMI, Brent Stephens, *Illinois Institute of Technology*

Exposure to airborne pathogens such as influenza remains a significant threat to public health. However, influenza transmission and control in indoor environments remains poorly understood, as it is not clear which routes of transmission (fomite, inhalation, inspiration or direct spray) are dominant. The transmission risk associated with each route in indoor environments is a function of many variables, including, ventilation rates, the number of infector individuals and their cough and breath frequency, the concentration and distribution of pathogens in exhaled air, human activities, and infectious particles deposition, inactivation, transfer and removal rates. To improve our knowledge of predominate pathways of influenza transmission, we developed and applied a Markov chain model to estimate the intake dose of influenza viruses in the respiratory tract and mucous membrane of 24susceptible individuals in a 500 meter square hypothetical office environment assuming one infector and 8 hours exposure time. We explore the sensitivity of intake dose to each variable using existing ranges from the literature. In addition, this work develops a Monte-Carlo uncertainty analysis to predict the statistical distribution of some reported data and infection risk using a dose-respond model. The results show the direct spray is likely the dominant transmission pathway of influenza in the office. Therefore, human activity patterns and the number concentrations and distribution of infectious particles in exhaled breath and cough have the largest impact on influenza infection risk. The median infection risk was estimated to be ~11.5%, which interestingly, yielded an equivalent quanta generation rate in a transient Wells-Riley model of 125 per hour, which is generally in line with assumptions from the literature. Overall, the model can be used to further explore dominant pathways for influenza transmission in indoor environments under a variety of assumptions and to investigate the effectiveness of control strategies such as filtration, ventilation, and UVGI.

7AQ.1

Changes in Visibility and Local Radiative Forcing in the Southeast U.S. Linked to Decreased Aerosol Sulfate Mass. ALEXIS ATTWOOD, Rebecca Washenfelder, Weiwei Hu, Nick Wagner, Allison McComiskey, Pedro Campuzano-Jost, Douglas Day, Brett Palm, Suzane Simoes de Sa, Charles Brock, Eric Edgerton, Karsten Baumann, Jose-Luis Jimenez, Steven G. Brown, *CU CIRES- NOAA ESRL*

Sulfate aerosol is a major contributor to PM2.5 mass in the United States and impacts direct and indirect aerosol radiative forcing, visibility and health. The mass concentration of aerosol sulfate has decreased in the southeast U.S. by 3.9(±0.8)% yr-1 between 1992 – 2013, consistent with the 60% reduction in nationwide SO2 emissions from 1990 – 2010 following the Clean Air Act Amendment. During the Southeastern Oxidant and Aerosol Study (SOAS), which took place in the summer of 2013, we deployed a novel, broadband cavity enhanced spectrometer (BBCES) to measure relative humidity dependent aerosol extinction in the ultraviolet as a function of wavelength. The aerosol composition in this region is dominated by ammonium sulfate, which along with organics contributes 60 - 90% of surface PM2.5. Using submicron aerosol optical extinction and composition data, we determine a relationship between the enhancement in aerosol extinction at elevated relative humidity, γext, and the mass fraction of organics, which shows decreased water uptake and reduced optical extinction at lower sulfate and higher organic mass fraction. We calculate that the reduction in particle hygroscopicity has caused a -1.6(±0.3)% yr-1 change in aerosol optical extinction from 1998-2013 based on changes in chemical composition alone. This change in ambient extinction is separate and in addition to the change in extinction of -3.1(±0.8)% yr-1 that we calculate as a direct result of decreased aerosol mass over the same period. Direct measurements of visibility show an improvement between 1998 – 2013, which is consistent with these expectations. Radiative forcing calculations of the decreased aerosol extinction and resulting increased surface solar irradiance will also be presented.

7AQ.2

Cloud Condensation Nuclei, Cloud Droplet Number, and the Radiative Balance over the Southeastern United States: Measurement and Modeling Results from the NOAA SENEX Campaign. JACK LIN, Ricardo Morales Betancourt, Aikaterini Bougiatioti, Petros Vasilakos, Athanasios Nenes, Charles Brock, Nick Wagner, Daniel Lack, Daniel Law, Timothy Gordon, Mathews Richardson, Milos Markovic, Joshua P. Schwarz, Ann M. Middlebrook, Jin Liao, André Welti, Joost de Gouw, *Georgia Institute of Technology*

The southeastern United States is characterized by high biogenic and anthropogenic emissions and active photochemistry affecting aerosol production and CCN concentrations with important influences on the Earth’s radiative balance. In particular, the interactions between biogenic and anthropogenic emissions are not well characterized and may play an important role in explaining the anomalous cooling trend observed in the southeast United States over the latter half of the twentieth century.

Aerosol and CCN concentrations and aerosol size and composition data were collected aboard the NOAA WP-3D during the June-July 2013 NOAA SENEX mission, a part of the Southeast Atmosphere Study. We present measurements of CCN activity as well as calculations of cloud droplet number from a parameterization to assess associated radiative forcing for the southeastern United States. Cloud droplet number is calculated using data measured aboard the WP-3D as well as from the Community Atmosphere Model (CAM) and the Community Multi-scale Air Quality Model (CMAQ). Calculated droplet number sensitivities identify the parameters driving the difference between droplet number calculated from measurements and modeled aerosol parameters.

7AQ.3

Multivariate Analysis of Historical Trends in Condensed Phase Liquid Water in the Southeastern United States. THIEN KHOI NGUYEN, Annmarie Carlton, Shannon Capps, *Rutgers University*

Particle-phase liquid water is a ubiquitous component of atmospheric aerosols and influences a variety of critical atmospheric processes, including light scattering, the hydrological cycle, aqueous chemistry, and particulate matter (PM) formation. Previous studies indicate that there have been major improvements in air quality in the southeast United States over the past decade due to reductions in anthropogenic emissions such as sulfur dioxide and oxides of nitrogen. Yet despite the abundance and importance of aerosol water, it is not routinely measured, and mass concentrations are not well known. Here we use the thermodynamic model ISORROPIA (v2.1) to estimate aerosol water mass concentrations from 2000-2010 in urban and rural locations using speciated ion and meteorological data from sites that are a part of the Southeastern Aerosol Research and Characterization (SEARCH) network. These estimations are coupled with aerosol scattering data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) program and the Aerosol Robotic Network (AERONET) to better understand the historical trends of aerosol water in the southeastern United States in the context of improved air quality. Analysis in the region of the Southern Oxidant and Aerosol Study (SOAS) indicates decreases in aerosol water mass concentrations by 29%, 60%, and 67% over the last decade for June, July, and August, respectively. The observed trends are consistent with the hypothesis that decreases in aerosol water may explain recently noted reductions in organic mass concentrations despite no apparent decrease in biogenic volatile organic carbon precursor emissions. These results provide evidence for modulation of biogenically derived PM in the presence of anthropogenic perturbations.

7AQ.4

Vertical Profiles of Aerosol Extinction Over the Southeastern US during the Summer. NICK WAGNER, Charles Brock, Timothy Gordon, Daniel Lack, Mathews Richardson, Daniel Law, André Welti, Ann M. Middlebrook, Jin Liao, John Holloway, Jeff Peischl, Ilana Pollack, Thomas Ryerson, Martin Graus, Carsten Warneke, *NOAA Earth System Research Laboratory, Boulder, CO*

Recent studies have shown that during the summertime, aerosol loading in the southeastern United States measured in situ at surface is not enhanced as much as the AOD measured by satellites and AERONET. Regional modeling is able to reproduce the extinction at the surface, however not the AOD. An enhanced source of secondary organic aerosol above the surface layer has been proposed as a possible explanation for the discrepancy. During summer 2013, in situ measurements of aerosol extinction, hygroscopicity, and particle size distributions were collected from the NOAA WP-3 aircraft and the NASA DC-8 aircraft as part of the Southeast Atmosphere Study and SEAC4RS. We present an analysis of aerosol extinction profiles and compare these with ground-based measurements and previous studies. Measurements of aerosol composition and trace gases aboard the aircraft are used to determine if secondary organic aerosol production is enhanced above the surface.

7AQ.5

HSRL-2 Observations of Aerosol Variability and Mixing During Boundary Layer Evolution in Houston. SHARON P. BURTON, Amy Jo Scarino, Raymond R. Rogers, Chris Hostetler, Richard Ferrare, Timothy A. Berkoff, David B. Harper, Anthony L. Cook, Pablo Saide, *NASA Langley Research Center*

The NASA Langley airborne multi-wavelength High Spectral Resolution Lidar (HSRL-2) provides information on the vertical distribution of aerosol optical properties in the form of vertical “curtains” of aerosol extinction, backscatter and depolarization along the flight track. Deployed aboard the NASA Langley King Air on the DISCOVER-AQ field mission in Houston in September 2013, HSRL-2 flew a pattern that included 18 ground sites, repeated four times a day. These flights were coordinated with another aircraft making extensive in situ measurements. The horizontally and vertically resolved curtains of HSRL-2 backscatter and other measurements give an unparalleled view of the vertical, horizontal and temporal variability of aerosol and can provide a broader context for interpreting measurements from other instruments. The measurements of aerosol extinction, backscatter, and depolarization are also used to infer aerosol type (smoke, marine, urban, dust, etc.) and external mixing of aerosol of different types. During the DISCOVER-AQ Houston deployment, the four-day period between September 11 and September 14 was notable for a significant aerosol build-up and persistent smoke layers in the free troposphere. HSRL-2 generally observed significant horizontal and vertical variability in the morning with a relatively low boundary layer, a residual layer, and frequent upper layers of transported smoke. Each afternoon, the boundary layer grew and became more homogeneous and many of the upper layers became mixed with the boundary layer. Here we investigate the mixing and evolution of aerosols in the free troposphere and boundary layer over this period using the HSRL-2 vertically resolved measurements.

7AQ.6

Chemical Climatology of the Southeastern United States, 1999-2013. George Hidy, CHARLES BLANCHARD, Karsten Baumann, Eric Edgerton, Stephanie Shaw, Eladio Knipping, John Jansen, Shelley Tanenbaum, Justin Walters, Ivar Tombach, *Envair*

The southeastern United States has a unique climate representing subtropical-continental conditions, with a large biogenic contribution to organic compounds affecting air chemistry. The region has experienced major growth in population and industry resulting in increased air pollution since the 1950s, and followed by a decrease after the 1990s. Experiments, including the Southeastern Organic Aerosol Study (SOAS), took place in central Alabama in June-July, 2013 for detailed study oxidant photochemistry and aerosol formation at a process level. The majority of the experiments were located in rural Centreville, AL(CTR), one of eight sites of the Southeastern Aerosol Research and Characterization (SEARCH) program. The SEARCH has a major, long-term aerometric database representing both regional and local (urban-rural) conditions from the late 1990s to 2013. The data include meteorological parameters, and concentrations trace gases and particle mass and composition, that provide a unique view of chemical climatology, as well as short-term comparisons of late spring and summer averages and hourly variations in the region. The air chemistry is characterized by sulfur, reactive nitrogen and carbon emissions in a NOx sensitive photochemical environment and summer stagnation meteorology conducive to the presence of substantial aerosol concentrations. In 2013, the pollution levels at CTR and other SEARCH sites were the lowest since full measurements began in 1999. The dataset provides a perspective for the SOAS program in terms of long-term average chemistry (chemical climatology) in a changing atmosphere. Changes in gas and particle emissions between 1999 and 2013, mediated through meteorological processes, account for the decline in pollutant concentrations at the monitoring sites in the region. These results provide an opportunity to contrast the 2013 SOAS results with temporally and spatially variable conditions in support of the development of tests for the robustness of SOAS findings.

7AQ.7

Aerosol Optical Properties in the Ultraviolet Spectral Region during the Southern Oxidant and Aerosol Study.

REBECCA WASHENFELDER, Alexis Attwood, Charles Brock, Steven G. Brown, *University of Colorado and NOAA*

Optical properties of aerosols vary as a function of wavelength, but few measurements have reported the wavelength-dependence of aerosol extinction cross sections and complex refractive indices. In the case of brown-carbon, its wavelength-dependent absorption in the ultraviolet spectral region has been suggested as an important component of aerosol radiative forcing. During the Southern Oxidant and Aerosol Study in summer 2013, we deployed a new field instrument to measure aerosol optical extinction as a function of wavelength, using cavity enhanced spectroscopy with a broadband light source. The instrument consists of two broadband channels which span the 360-390 and 385-420 nm spectral regions using two light emitting diodes (LED) and a grating spectrometer with charge-coupled device (CCD) detector.

Biomass burning is thought to be one of the major sources of brown carbon aerosol, though direct ambient measurements of the optical properties of biomass burning aerosol, especially in the ultraviolet spectral region, remain sparse. Although the Southeast U.S. is typically less influenced by biomass burning during summer, there were three distinct biomass burning events measured during the SOAS 2013 field campaign. Here, we combine our wavelength resolved measurements of aerosol optical extinction with size distribution and composition data to better understand UV aerosol optical properties during these events. One of the key challenges is the separation of the aerosol absorbing and scattering components from a direct extinction measurement. Methods for separation of the real and imaginary parts of the refractive indices, and the challenges in doing so, will be discussed.

7BA.1

Development of a Novel Microscope Spectrofluorometer for Individual Bioparticle Characterization.

DONALD R. HUFFMAN, J. Alex Huffman, *University of Arizona and University of Denver*

Biological particles can contribute to many deleterious human health effects and may play roles in environmental processes such as the formation and evolution of mixed-phase clouds and precipitation. Fluorescence-based sensors have been increasingly employed in recent years for the discrimination of biological particles from ambient samples. However, most commercial particle fluorescence instruments provide fluorescence information in relatively few channels of wavelength dispersion and at a cost of $10k’s to $100k’s. A prototype microscope particle spectrofluorometer (MPSF; patent-pending) has been developed to inexpensively measure fluorescence emission spectra from many individual particles in a sample. Two versions have been built and initially tested. A bench-top version utilizes standard optical microscope components for light manipulation and an inexpensive point-and-shoot camera to detect and record images and spectra. A portable version prototype has been built utilizing a smartphone camera for image collection and on-board Wi-Fi components for transmission of images for analysis via cloud computer. While development and testing is still in its early stages, the smartphone version of the instrument offers the possibility to contribute uniquely to research, teaching, and amateur science communities.

7BA.2

Physico-chemical qualification and refinements of a new portable bio aerosols collector: BIODOSI. ROLAND SARDA-ESTEVE, Jean-Maxime Roux, *CEA*

As part of the overall security program for the fight against the spread of toxic biological agents (CBRN-E) the CEA (Center of Atomic Energy) has developed a portable collector based on electrostatic precipitation: BIODOSI. This new type of particle collector is lightweight (500g), silent (no pump) and can collect the particulate matter (PM) during more than 8 hours at a flow rate up to 7 LPM. The on board electronic can control and adjust all the collection parameters to maintain the collection efficiency at is optimum value. The first version BV1 (Sarda Esteve et al. AAAR, 2012; J.M Roux et al. ISPC-BWA 2013) was tested in real atmospherics condition at the super site ACTRIS, LSCE SIRTA-5, France in July 2013 to determine the capability of this new potable collector to capture low levels of fungal spores in the atmosphere. The collection efficiency (0.3 µm to 20 µm) was monitored on line. The samples were extracted in 10 ml of pure MilliQ water by sonication and the liquid extracts were compared to filter based traditional sampling methodology. All the liquid extracts were measured by Ion Chromatography (IC) for the major ions, IC-Pulsed Amperometric Detection (PAD) for the sugars and Liquid Chromatography Mass Spectrometry (LC-MS) for the specific analysis of Manitol and Arabitol (Sarda Esteve et al. AAAR, 2013). We report here the results of the physico-chemical characterization in real atmosphere for the first prototype BIODOSI Version 1 (BV1) and the refinements on the last prototype BV3 (Fig.1). The results obtained by measuring chemicals tracers of fungal spores as Manitol and Arabitol (Bauer et al 2008) show that this new portable collector can be used to identify bio aerosols events (Sarda Esteve and Roux, IOP, 2013).

This work was supported by the CBRN-E R&D research program from CEA.

7BA.3

International Inter-comparison of Laser/Light-induced Fluorescence (L/LIF) Methods for the Real-time Detection of Bioaerosols: BIODETECT 2014 Campaign at CEA/LSCE ACTRIS SUPERSITE (Saclay, France). Roland Sarda-Esteve, Martin Gallagher, J. ALEX HUFFMAN, Ulrich Poeschl, Hang Su, Denis Kiselev, Sampo Saari, John Sodeau, David O'Connor, Gavin McMeeking, Greg Kok, Michel Thibaudon, Dominique Baisnee, Jean Sciare, Olivier Favez, Jean-Maxime Roux, Marie-Helene Nadal, Christophe Bossuet, Laurent Olmedo, *CEA*

In the frame of the Bio Chemical Collectors (BCC) CBRN-E research project the French Atomic Energy Commission (CEA) organized an inter-comparison of laser/light-induced fluorescence (L/LIF) methods for the detection and quantification of bioaerosols. A comprehensive suite of commercially available (L/LIF) technologies, as well as a set of new prototypes, were operated during the intensive measurement campaign, BIODETECT 2014. This campaign took place at the CEA/LSCE ACTRIS SUPERSITE in suburban Paris, France in July – August 2014. During this period of the year, high concentrations of pollen and fungal spores are emitted into the air; these emissions have been shown to frequently coincide with pollution events. Accordingly, a key objective of BIODETECT 2014 was to understand how (L/LIF) techniques operate in an urban/suburban environment, specifically with respect to their ability to detect bioaerosols from amongst high concentrations of non-biological particles. Single-particle (L/LIF) techniques were compared with the method of collecting particles onto sticky tape for subsequent visual identification and analysis. Such methods have been utilized routinely by the National Network of Survey for Airborne contaminants (RNSA) to identify pollens and fungal spores. Direct comparisons between optical microscope studies and (L/LIF) techniques have only been performed recently and not alongside other detailed measurements. To study the potential interferences to bioaerosol detection a broad set of ancillary instrumentation was also deployed, and source apportionment tools were employed to identify aerosols sources.

This inter-comparison provided a robust evaluation of the ability of (L/LIF) systems to monitor pollen and fungal spores and has increased the knowledge for both bio-aerosol quantification and segregation in complex environments. The project also investigated the pertinence of shape factor or wavelength of excitation to distinguish the type of pollen that could generate allergies and other respiratory diseases.

This work is supported by the CBRN-E R&D research program from CEA/DAM.

7BA.4

Airborne Measurements of Bioaerosol Across the Southern U.S. ANNE PERRING, Darrel Baumgardner, Mark T. Hernandez, Joshua P. Schwarz, Ru-Shan Gao, Greg Kok, Gavin McMeeking, David Fahey, *CU CIRES- NOAA ESRL*

Airborne observations of fluorescent biological aerosol were made using a Wideband Integrated Bioaerosol Sensor (WIBS-4, Droplet Measurement Technologies, Boulder, CO) aboard the Cloud Lab blimp (a Skyship 600 airship) during a series of flights that took place in September and October of 2013. The project sampled a wide band of longitude across the southern U.S. as it traveled from Titusville, FL to Monterrey, CA and probed the atmosphere up to 1000m above the surface. The dataset is divided into geographic regions and average concentrations of fluorescent particles aloft are examined. Fluorescent particles represent a significant fraction of supermicron loadings aloft and particles detected by the WIBS are segregated into seven populations based on their fluorescent behavior. This allows for more specific analysis of the different contributors to fluorescent bioaerosols than has previously been reported. We observe distinct size distributions and geographic variations for the different fluorescent populations detected by the WIBS-4. These variations are discussed and potential attributions are posited based on a growing library of known biological materials. Auxiliary particle data from other DMT instruments aboard the airship are used to put the WIBS measurements in context and to examine possible interferences from non-biological fluorescent particles.

7BA.5

Analysis of Atmospheric Biological Particles with High-Resolution Microscopy Techniques. VERA SAMBUROVA, Alison Murray, Anna Gannet Hallar, Xufei Yang, Barbara Zielinska, *Desert Research Institute*

Atmospheric biological particles (bacteria, fungal spores, plant pollen, etc.) and their fragments are known to comprise a significant portion of the ambient particulate matter. They play an important role in atmospheric processes and can cause adverse health effects, leading to chronic respiratory diseases. For example, pollen and plant debris may trigger allergic reactions in people, while bacterial endotoxins induce inflammatory responses. Biological particles are released in very large quantities into the atmosphere and may be transported over long distances. Therefore, there is an urgent need for bioaerosol characterization and quantitative analysis. In the present study atmospheric biological particles were collected at a high-elevation site and characterized with electron and epifluorescence microscopy techniques.

Airborne biological species were sampled at the Storm Peak Laboratory (SPL) on Mt. Werner, Steamboat, CO (3210 m AMSL). First, the shape and morphology of the collected bioaerosols were examined with a high-resolution electron microscopy (EM). Hitachi TM 1000 microscope was applied to take EM images directly from the collected filter punches. The rest of the aerosol filter sections were used to enumerate the biological particles. For this purpose, the samples were flushed with a sterile water to release particles from the filters and then the eluent was filtered on to 0.2 micron black polycarbonate filters that have low fluorescent background. The filters were stained with fluorescent dyes (e.g. 4-6- diamidino-2-phenylindole, DAPI and acridine orange, AO) to mark macromolecules (DNA or protein) in microbial, spore, and pollen grains. Following mounting on microscope slides, the filters were examined under the epifluorescence microscope (1000X magnification) and cell fractions were enumerated. Microbial abundance was back-calculated to cells per cubic meter of air. The microscopy results were compared with the data obtained from the culture-based analysis (rRNA genes sequencing technique).

7BA.6

Development of a Passive Bioaerosol Sampler Using Piezoelectric Polymer. JENNIFER THERKORN, Jerry Scheinbeim, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Bioaerosol sampling typically requires pumps to pull air through sample media leading to increased costs, limited sampling durations, reduced deployability and structural damage to sampled microorganisms. Since bioaerosol particles carry electrical charge due to dispersion processes and metabolic activity, this research aims to develop the first passive bioaerosol sampler using a piezoelectric polymer (uniaxially oriented polyvinylidene fluoride, or PVDF) to electrostatically attract bioaerosol particles. PVDF is a ferroelectric polymer which has been polarized by application of an external electric field. Due to polymer polarization, one side is negatively charged and the other side positively charged. Particle collection efficiency of both sides of PVDF was compared to that of controls (PTFE filters) of the same size (47 mm diameter) when sampling non-neutralized fluorescent polystyrene latex (PSL) particles representing coarse environmental particles with biological content (2.9 and 5 micrometer) and Escherichia coli bacteria nebulized with 3-jet Collison Nebulizer into a settling chamber. PSL was analyzed using fluorometer and bacteria were stained and counted by microscope. For 5 micrometer PSL, the positive side of PVDF provided 19% increased collection while the negative side appeared to repel the net negative aerosol particles with 35% decreased collection ($p<0.001$). 2.9 micrometer PSL carried lower net charge compared to 5 micrometer PSL and both the positive and negative sides of the PVDF provided increased relative collection efficiencies over PTFE of 44% and 51% ($p<0.001$), respectively. For E. coli bioaerosol with a net negative charge, the positive side of PVDF provided >20% increased collection efficiency over PTFE. This is the first stage in sampler development and indicates that PVDF can be used to manipulate charged bioparticles. Future research will include sampling different bioaerosol species, testing vertically-oriented configurations to allow for simultaneous collection of positive and negative charged particles, sampling neutralized aerosol, and sampler validation.

7BA.7

Efficiency of Virus Collection with the Novel G-II Bioaerosol Collector. Jovan Pantelic, Michael Grantham, JING YAN, Fengjie Liu, Sheryl Ehrman, Donald Milton, *University of Maryland School of Public Health*

The use of an SKC biosampler (R)(SKC Inc, Eighty Four,PA) has been reported to maintain high infectivity of collected virus, but it does not meet our requirement for operating at high flow rates (≥ 130lpm). A new sampler, called the Gesundheit II (GII) was designed and built to be used to collect expiratory droplets samples from influenza infected subjects. In our study, we established the optimal G-II operating parameters and also characterized the biological collection efficiency and the maintenance of virus infectivity for four Influenza viruses by comparing GII with a commercially sampler, the SKC biosampler. We aerosolized four Influenza viruses (A/California/04/2009, A/Puerto Rico/08/1934, A/Udorn/1972 and B/Lee/1940) using a six-jet collision nebulizer and released in the G-II cone for 10 minutes. We picked these four viruses because of their different shape variance. The G-II was operated under optimized conditions with physical collection efficiency above 90%. 10 X PBS with 1% BSA was injected at the rate of 25 mL/h into the reservoir as a buffer. After 10 min aerosolization was stopped and condensate was collected from the reservoir. Experiments were repeated 3 times for each virus. The reservoir of the SKC biosampler was filled with 20ml of virus buffer (1X PBS with 0.1% BSA) prior to sampling. Samples were analyzed for infectivity using fluorescent focus assays and the total influenza virus particle number was determined using reverse transcriptase quantitative PCR. The GII collected 77%±0.06, 85%±0.27, 91%±0.15, and 117%±0.17 of the virus collected by the biosampler respectively. From the experiments results, the GII can sample several types of Influenza viruses and it can be efficiently used for collection of human expiratory droplets samples during the Influenza outbreaks.

7BB.1

Observations of Wildfire Smoke and Ozone at the Mt. Bachelor Observatory in Central Oregon.

DAN JAFFE, Nicole Wigder, Pao Baylon, Jon Hee, Qi Zhang, Shan Zhou, Sonya Collier, Lawrence Kleinman, Arthur J. Sedlacek, *University of Washington, Bothell, WA, USA*

Wildfires affect PM and O3 (ozone) across large areas of the Western US every summer. Over the past decade we have studied wildfire smoke using a variety of gas and aerosol observations at the Mt. Bachelor Observatory (MBO) in central Oregon, and combined these with satellite and aircraft data and models. In 2013, our usual observations were enhanced with Aerosol Mass Spectrometry and aircraft observations as part of the US Department of Energy (DOE) sponsored Biomass Burning Observation Project (BBOP). The overall pattern shows large fire-to-fire variability, which we are working to understand. From observations 12-48 hours downwind of wildfires at MBO, we find PM1 enhancement ratios of 0.06-0.42 micro-gram per cubic meter per ppbv of CO or 16-52 micro-grams per cubic meter per ppmv of CO2. The PM enhancement is strongly dependent on the modified combustion efficiency (MCE), with higher PM per unit of CO2 for more smoldering combustion. Comparing the single scattering albedo (SSA) measured at MBO vs. MCE to laboratory and near field fire emissions, we find that the single scattering is significantly higher 1-2 days downwind compared to recent emissions. This indicates important changes in the aerosol due to aging during transport. For the CO/O3 enhancement ratios we find values that can be negative up to a value of +0.51 ppbv per ppbv. In general we find that the CO/O3 enhancement ratio is higher at greater distances from the fire. NOx is an important factor in O3 production. The NOx/NOy ratio is a good indicator of positive O3 production. We also find that for many fires, NOx is rapidly sequestered in the form of PAN. This limits the near-field O3 production but likely increases it downwind.

7BB.2

Aerosol Chemistry and Processing at Mt. Bachelor Summit: Influences from Wildfire Plumes.

SHAN ZHOU, Sonya Collier, Jon Hee, Nicole Wigder, Dan Jaffe, Lawrence Kleinman, Arthur J. Sedlacek, Qi Zhang, *University of California, Davis*

In the summer of 2013, an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) was deployed continuously for 4 weeks at the Mt. Bachelor Observatory (MBO), located at the summit of Mt. Bachelor in Oregon (43.9794° N, 121.6885° W, 2,763 m a.s.l), to study the chemical characteristics and atmospheric processing of biomass burning (BB) aerosols, as part of the US Department of Energy (DOE) sponsored Biomass Burning Observation Project (BBOP). Our surface measurements were compared to simultaneous aircraft measurements. Observations at MBO indicated a dynamic variation in the chemical composition and physical properties of aerosols. Periods of low particulate matter (PM) loading (average = 2.9 micro-gram/m^3) showed highly oxidized organic aerosol (OA) with oxygen-to-carbon atomic ratios (O/C) reaching above 1, as well as containing an ammonium sulfate fraction of up to 50% of submicron aerosol mass. Contrasting periods of higher PM loading (up to 120 micro-gram/m^3) with markedly different characteristics have been frequently observed due to effects from injection of wildfire plumes into air masses transported to MBO. OA (> 90%) dominated aerosol composition during these BB periods, with elevated aerosol light scattering, elemental carbon, and gas-phase CO. OA from these plumes also showed an enhancement of the AMS BB tracer ion ($C_2H_4O_2^+$) at m/z = 60 and with O/C ratios ranging from 0.3 – 0.6. BB plumes showed variable Modified Combustion Efficiency (MCE) where the enhancement of aerosol light scattering and OA relative to CO_2 decreased with increasing MCE. An increase of PM enhancement relative to CO 1-2 days downwind of fire sources at MBO compared to observations near the source indicates secondary organic aerosol (SOA) formation. These analyses shed light on the overall impact of wildfires on regional air quality in the Pacific Northwest of the USA. Future analysis comparing ground site and aircraft measurements will be performed to investigate the importance of BB emissions as SOA precursors.

7BB.3

Aged Biomass Burning Size Distributions from BORTAS 2011. KIMIKO SAKAMOTO, James Allan, Hugh Coe, Jonathan Taylor, Thomas Duck, Jeffrey Pierce, *Colorado State University*

Biomass-burning aerosols contribute to aerosol radiative forcing on the climate system. The magnitude of this effect is partially determined by aerosol size distributions which are strong functions of source fire characteristics and in-plume microphysical processing. The uncertainties in biomass-burning emission number size-distributions in climate models lead to uncertainties in CCN concentrations and forcing estimates. The BORTAS-B measurement campaign collected data from boreal biomass-burning emissions over Eastern Canada in the summer of 2011 with the intention of adding to the body of observational datasets. We implement plume criteria to isolate the characteristic size-distribution of aged biomass-burning emissions (tilde 2 days) from fires in Northwestern Ontario. The composite size-distributions (Dpm = 232 nm, sigma = 1.7) are comparable to literature values of other aged plumes. The organic aerosol enhancement ratios (Delta OA/Delta CO) along the flight path show a strong, consistent correlations of (0.08-0.18) plusminus 0.01 across both flights that do not change with distance from the source, so no SOA production was detected within the aged plume. Finally, a Lagrangian microphysical model was used to determine an estimate of the freshly (tilde 1 hour) emitted size distribution and flux.

7BB.4

Lagrangian Photochemical Modeling of Aerosol Evolution in Biomass Burning Plumes. MATTHEW ALVARADO, Chantelle Lonsdale, Robert J. Yokelson, Sheryl K. Akagi, Emily Fischer, Katherine Travis, Jill Craven, Jonathan Taylor, Gavin McMeeking, Ian Burling, Shawn P. Urbanski, Cyle Wold, John Seinfeld, Hugh Coe, David R. Weise, *AER*

Biomass burning is a major source of atmospheric trace gases and particles that impact air quality at urban, regional, and global scales. Within minutes after emission, rapid, complex photochemistry within a smoke plume can cause large changes in the concentration, size distribution, composition, and optical properties of fine particles (PM2.5). Being able to understand and simulate this rapid evolution under a wide variety of conditions is thus a critical part of forecasting the impact of these fires on urban and regional air quality. The Aerosol Simulation Program (ASP) has been previously used within a Lagrangian parcel model to simulate the formation of secondary organic aerosol (SOA) and ozone within several African and North American plumes. In this work, we will present ASP simulations of the chemical evolution of a young biomass burning smoke plume sampled over California during the 2009 San Luis Obispo Biomass Burning campaign. We will discuss the sensitivity of the model simulations to uncertainties in the emissions, dilution rate, and gas- and particle-phase chemistry. We will then present our initial work in using the ASP model to develop a sub-grid scale parameterization of the near-source chemistry of biomass burning plumes for use in regional and global air quality models.

7BB.5

Investigation of Chemical and Physical Perturbations to Organic Aerosol Present in Biomass Burning Plumes over Prescribed Fires in South Carolina. ANDREW MAY, Taehyoung Lee, Gavin McMeeking, Sheryl K. Akagi, Amy P. Sullivan, Shawn P. Urbanski, Robert J. Yokelson, Sonia Kreidenweis, *Colorado State University*

Prescribed fires are a land-management practice that may lessen the severity of wildfires. However, as they are planned in advance, they provide an opportunity to perform well-coordinated research to characterize emissions and investigate plume evolution with atmospheric transport. During Fall 2011, we performed online measurements of gas- and particle-phase compounds in biomass burning plumes from prescribed fires during research flights over South Carolina. Here, we focus on the evolution of the organic aerosol (OA) in the plumes using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS). These experiments were performed in two phases. First, the emissions were characterized at the source to quantify OA emission factors and emission ratios. We then followed the plume downwind, sampling in a quasi-Lagrangian manner, in order to evaluate potential secondary OA (SOA) formation. During each fire, the plume was rapidly diluted via mixing with cleaner background air. From our AMS data interpretation, we infer that we have little evidence of SOA formation in our sampled plumes during 1-3 hours of atmospheric transport as we do not observe a substantial change in OA elemental ratios or the production of AMS mass fragments indicative of SOA. We attribute this lack of chemical change to the short timescales over which we were able to observe the plume. Furthermore, applying a predictive model to estimate the quantity of SOA produced within the plume over the timescales of our sampling suggests that SOA may contribute up to ~20% of the total OA mass within our plumes, and thus, may be masked by the remaining primary OA. Finally, emission ratios and emission factors decreased with increasing sample age, suggesting that dilution-driven evaporation of the OA was the dominant transformation pathway for the OA in the smoke plumes; this behavior can be modeled reasonably well using a recently-developed laboratory parameterization.

7BB.6

Observations on Aging of Biomass Burning Aerosols in Southern Africa. VILLE VAKKARI, Veli-Matti Kerminen, Johan Paul Beukes, Petri Tiitta, Pieter G. van Zyl, Miroslav Josipovic, Andrew D. Venter, Kerneels Jaars, Douglas Worsnop, Markku Kulmala, Lauri Laakso, *Finnish Meteorological Institute, Helsinki, Finland*

Aerosol particles originating from biomass burning contribute significantly to the atmospheric aerosol budget and thereby to both direct and indirect radiative forcing. A large number of studies have been carried out to characterize biomass burning aerosol in the immediate vicinity of fires, but less information is available on atmospheric aging of the emissions. In this study, combining remote sensing fire observations to ground-based long-term measurements of aerosol particle and trace gas properties at the Welgegund measurement station in South Africa (www.welgegund.org), we have been able to follow the time evolution of biomass burning plumes up to several hours in the atmosphere in both day and night time conditions.

Based on observations of 60 biomass burning plumes of variable age, we show that the climatically most important properties of biomass burning aerosols change rapidly and to a substantial degree during the first two to four hours of their atmospheric transport in most plumes. The changes in particle size distribution and chemical composition, driven by atmospheric oxidation and subsequent secondary aerosol formation, may reach a factor >10 increase in the cloud condensation nuclei concentration and a factor of 6 increase in the aerosol scattering coefficient.

7BB.7

Polluted vs Clean: Chronic Nitrogen Deposition Affects on Emissions from Burning of Forest Litter. Michael Giordano, David R. Weise, AKUA ASA-AWUKU, *University of California, Riverside*

Biomass burning is a large contributor of aerosols to the atmosphere. Aerosols from wildland fires can have a wide range of climatic impacts that are affected by combustion characteristics, fuel properties, and photochemical exposure. While the literature on biomass burning is continually expanding and exploring the impacts of these variables, one variable is heretofore understudied: the effects of chronic air pollution on biomass burning emissions. Here we explore the aerosol properties of forest litter collected from two sites along a nitrogen deposition gradient in the San Bernardino mountain range of southern California. Forest litter was burned at UC-Riverside's College of Engineering-Center for Environmental Research and Technology facility to determine aerosol characteristics such as hygroscopicity, volatility, composition, and particle number and volume concentrations. Cast conifer needles collected from the top-most layer of the forest floor comprised the fuel 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 to simulate day time conditions. A characterization of the aerosols and trace gases emitted was conducted over the span of the experiment. Results showed that while weighted emission factors for particle number were similar between the two fuels, there were significant differences between the aerosol volatilities (as measured by particle Volume Fraction Remaining, VFR) upon injection into the chamber (VFR > 0.2 at 100 C). This study demonstrates how chronic air pollution can affect emissions from wildland fires occurring in the wildland-urban interface.

7CA.1

Secondary Organic Aerosol Formation at an Urban Downwind Location in Long Island, New York. SHAN ZHOU, Sonya Collier, Jianzhong Xu, Fan Mei, Jian Wang, Yin-Nan Lee, Arthur J. Sedlacek, Stephen Springston, Qi Zhang, *University of California, Davis*

The US Department of Energy (DOE) sponsored Aerosol Life Cycle Intensive Operational Period field campaign took place at Brookhaven National Laboratory (BNL) at Long Island, New York, from July 1st to August 15, 2011. Here we present measurements from an Aerodyne High-Resolution Time-of-flight Aerosol Mass Spectrometer (HR-AMS), an Ionicon Proton Transfer Reaction Mass Spectrometer, and trace gas detectors to investigate the role of anthropogenic emissions on SOA formation at this urban downwind location. The average mass concentration of non-refractory submicron particles (NR-PM_1) was 15.3 (±8.9) micro-grams/m^3, higher than previously observed during summer at New York City (NYC), ~ 50 km to the west of BNL. Organics (64.8%) and sulfate (24.4%) were dominant PM components. Positive Matrix Factorization of the HR-AMS mass spectra indicates that organic aerosol (OA) at BNL was completely secondary in nature, and that there were three distinct secondary OA (SOA) types: (1) a highly oxidized and less-volatile oxygenated OA (LV-OOA; O/C = 0.79); (2) a less oxidized and semi-volatile oxygenated OA (SV-OOA; O/C = 0.41); and (3) a nitrogen-enriched OA (NOA) with an N/C ratio of 0.185. Volatility profiles of OA factors were determined using a thermodenuder upstream of the HR-AMS. SV-OOA accounted for 62% of the OA mass and showed a tight correlation with urban primary emission tracer species such as CO, BC, toluene, and benzene. These anthropogenic emission species all peaked between 7-8 a.m. local time (EDT) at BNL, ~ one-hour later than the peak of traffic emission species (e.g., hydrocarbon-like organic aerosol, CO, and BC) previously observed at NYC. This is an indication that SV-OOA was mainly associated with urban plumes transported from the populous NYC and New Jersey area to the west and southwest of Long Island. Back-trajectory analysis of the air mass source regions corroborates this conclusion. In this presentation, the physical-chemical characteristics and formation processes of SOA will be investigated.

7CA.2

Evidence of Ambient Aqueous SOA Formation in the Po Valley, Italy. AMY P. SULLIVAN, Natasha Hodas, Barbara Turpin, Kate Skog, Frank Keutsch, Stefano Decesari, M. Cristina Facchini, Jeffrey Collett, *Colorado State University*

Laboratory experiments suggest that water-soluble products from the gas-phase oxidation of volatile organic compounds can partition into atmospheric waters (i.e., fogs, clouds, and aerosol water) 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). There is evidence for ambient aqueous SOA in that smog chamber experiments form SOA that is less hygroscopic and oxygenated than atmospheric SOA and there appears to be a missing source of SOA based on the underestimation of model-predicted compared to measured SOA. However, few studies have attempted to observe ambient aqueous SOA. Therefore, a suite of measurements was made during the PEGASOS (Pan-European Gas-AeroSols-climate interaction Study) campaign conducted in June-July 2012 in the Po Valley, Italy to search for evidence of aqueous SOA. A key measurement for this analysis was water-soluble organic carbon (WSOC) as it is considered to be a good proxy for SOA. WSOC will be examined as a function of parameters known to play a role in aqueous SOA such as relative humidity (RH), liquid water content (LWC), and organic aerosol (OA) concentration. The conditions needed for aqueous SOA formation will be discussed. Our results suggest that, at this site, aqueous SOA appears to form in the dark. Elevated ammonia concentrations and the timing of its occurrence seem to play a large role in the formation of ambient aqueous SOA.

7CA.3

Examining New Pathways of Secondary Organic Aerosol Formation in a 3D Model: Role of Absorbed Water, Multi-generational Aging, Intermediate-Volatility Organics and Aqueous Chemistry. SHANTANU JATHAR, Christopher Cappa, V. Faye McNeill, Michael Kleeman, *University of California, Davis*

Numerous field campaigns have demonstrated the abundance of secondary organic aerosol (SOA) in urban, rural and remote environments. However, contemporary chemical transport models that include (a) semi-volatile SOA formation from gas-phase oxidation of volatile anthropogenic and biogenic precursors and (b) low-volatility SOA formation via condensed-phase chemistry are unable to predict the observed formation and properties of SOA. In this work, we examine the influence of absorbed water on the gas-particle partitioning of SOA and enhanced SOA formation from multi-generational aging, intermediate-volatility organics and aqueous processing of isoprene epoxide and glyoxal in a 3D air quality model. Simulations are performed for two domains, California and the Eastern United States, over representative summer episodes. SOA predictions from these new pathways are compared to those from traditional SOA pathways and to available measurements of SOA concentrations and properties. The ability of these new pathways to close the gap between predictions and measurements will then be discussed.

7CA.4

Modeling Regional Secondary Organic Aerosol from Isoprene in Southeast United States Using the Master Chemical Mechanism.

Jingyi Li, QI YING, *Texas A&M University*

In this study, the Community Multiscale Air Quality (CMAQ) model driven by the gas phase Master Chemical Mechanism (MCM) version 3.2 linked with a secondary organic aerosol (SOA) (CMAQ-MCM-SOA) was modified to include SOA formation from traditional and non-traditional pathways: (1) traditional equilibrium partitioning of semi-volatile products predicted by the gas phase MCM mechanism; (2) reactive uptake of isoprene epoxidiols (IEPOX) and methacrylic acid epoxide (MAE) formed under low and high NOx conditions, respectively; (3) equilibrium partitioning of dihydroxy-dihydroperoxides and methyl-tetrols and (4) reactive uptake of glyoxal and methylglyoxal. Oligomerization was modeled as a simple first-order decay process as used in the original CMAQ SOA mechanism. The acidity dependent reactive uptake coefficient of IEPOX was based on nonlinear fit of multiple lab experiments. The modified CMAQ-MCM-SOA mechanism in a box model setting was able to reproduce most of the reported SOA yields in the Caltech chamber experiments (Kroll et al. 2005, 2006) of isoprene under low and high NOx conditions. It was found that semi-volatile products alone could not explain the observed SOA under high NOx conditions and reactive surface uptake of MAE, glyoxal and methylglyoxal were necessary. The modified CMAQ-MCM-SOA model will be applied to study SOA formation in Southeast United States during a one-week long summer episode in August 2006 to determine the overall isoprene SOA and the importance of different pathways will be discussed.

7CA.5

Characterization of Organic Aerosol in Severe Haze Episodes Using FTIR during Fall 2013 in Beijing, China.

Xiaoying Li, Kathryn George, Caiqing Yan, MEI ZHENG, Ann Dillner, *Peking University*

Since January 2013, many cities in the North China Plain of China including Beijing have suffered severe fine particulate matter pollution episodes. During October 2013, PM2.5 in Beijing showed clear “sawtooth” pattern with PM2.5 concentration cycled through low to high every five days. About six sawtooth cycles were found during the study period. Previous studies indicated that organic aerosol (OA) played an important role in haze events. However, most organic aerosol studies are based on other techniques including aerosol mass spectrometry (AMS) or gas chromatography-mass spectrometry (GC/MS). To our best knowledge, this is the first study using Fourier-transform infrared transmission spectroscopy (FTIR) to characterize organic aerosol during haze episodes in China. PM2.5 samples were collected on 47 mm Teflon filter using the four-channel low-volume sampler, and then spectroscopic characterization provided information of organic functional groups (e.g. alkyl, hydroxyl, carbonyl, and aromatic groups). Preliminary analysis showed that carbonyl, carboxylic acid OH, saturated CH, unsaturated CH, and hydroxyl were present in the Beijing aerosol. All the investigated organic functional groups increased during haze events. Carbonyl and carboxylic acids account for a very small amount of the mass. However, it should be noted that concentration of aromatic CH in Beijing was much higher than that observed in samples in the U.S., where aromatic CH is rarely reported due to its low concentration. The high aromatic CH in the Beijing samples indicates the importance of anthropogenic sources in Beijing. More detailed information about chemical composition of these samples including major ions and detailed organic speciation as well as formation mechanisms of these episodes will be provided and discussed.

7CA.6

Instrument Intercomparison of Black Carbon Measurements and Correlations with Gas and Aerosol Composition during an Urban Field Study. MICHAEL WALKER, Brent Williams, Raul Martinez, Yaping Zhang, Dhruv Mitroo, David Hagan, Steven Dhawan, Li Du, Jay Turner, Hongyu Guo, Laura King, Rodney Weber, Lu Hu, Munkhbayar Baasandorj, Dylan Millet, Gavin McMeeking, *Washington University in St. Louis*

Efforts to quantify the global climate impacts and epidemiological effects of black carbon (BC) aerosols have historically been hampered by inconsistent measurements. A multitude of instruments exist that are capable of measuring BC mass concentrations, each doing so by different methods of detection. Recent attempts have been made to more accurately define BC in terms of what each instrument specifically measures (e.g., equivalent black carbon (EBC), refractory black carbon (rBC), elemental carbon (EC)). BC concentrations were measured by four instruments during a recent field campaign, the St. Louis Air Quality Regional Study (SLAQRS). More specifically, EBC was measured by an Aethalometer (Magee Scientific) and Multiangle Absorption Photometer (MAAP, Thermo Scientific), rBC by a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies), and EC with a semi-continuous OC-EC analyzer (Sunset Laboratory) during a ten day period in August 2013, allowing for an intercomparison of various measurement techniques. Observed differences will be discussed. Additionally, BC measurements have been correlated to measurements of volatile organic species measured by proton transfer reaction – mass spectrometry (PTR-MS), total organic aerosol mass and major inorganic aerosol species measured by a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and aerosol chemical speciation monitor (ACSM), and organic aerosol species measured by thermal desorption gas chromatography (TAG) and a volatility and polarity separator (VAPS). The suite of chemical information provided by these instruments is used along with meteorological data to help explain the observed variations in the BC measurements.

7CA.7

Black and Elemental Carbon in Two European Urban Areas – Temporal Trends, Site and Seasonal Similarities and Differences. Regina Hitzenberger, Jaroslav Schwarz, Isabella Aschauer, Richard Haindl, Wolfgang Ludwig, Robert Wagner, ANNA WONASCHUETZ, Gudrun Zecha, Petr Vodicka, Zdenek Wagner, Nadezda Zikova, Vladimir Zdimal, *University of Vienna*

Techniques for BC and EC analysis are compared in Prague (Czech Republic) and Vienna (Austria). In earlier studies (Vienna) seasonally different method conversion coefficients were obtained. Here we investigate conversion factors for the two cities and whether previous Vienna factors are still applicable under the changed source conditions.

Two back-to-back campaigns were performed in Prague and Vienna in summer 2012 and winter 2013 using several techniques (all sites: microaethalometer, MAAP, Sunset Laboratory instrument with NIOSH and EUSAAR II, integrating sphere for BC and brown carbon, BrC; Prague only: Sunset field instrument, multiwavelength Aethalometer). Number and mass size distributions of major ions, BC and BrC were also obtained.

Methods are well comparable at both sites regarding campaign averages. The BC content of the Vienna aerosol was 8% in summer and 3% in Winter, (values for Prague: 5% and 8%). Campaign averages were 0.9 µg/m³ (Vienna) and 0.7 µg/m³ (Prague) in summer and 2.8 µg/m³ and 1.9 µg/m³ in winter. BrC (biomass smoke) was found at both sites in winter, but only in Prague in summer. Some differences in conversion factors were found for the new and previous intercomparisons in Vienna.

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7NM.1

Collisional Growth Below 2 nm in Flame Aerosol Reactors.

JIAXI FANG, Yang Wang, Pai Liu, Pratim Biswas,
Washington University in St Louis

The ability to synthesize well controlled multicomponent nanoparticles during combustion synthesis is partially limited by a gap in fundamental knowledge during the initial stages of particle formation below 2 nm. Detailed mechanisms on particle formation and growth in flame aerosol reactors in the sub 2 nm size range is not well established partly due to previous measurement limitations in differential mobility analyzers (DMAs). Experimental evidence on the existence of stable clusters in flame aerosol reactors using high resolution DMAs has only recently been demonstrated [Wang et al., J. Aerosol Sci., 71:52-64]. We will extend this work by examining the detailed kinetics and pathways for particle inception by utilizing a tandem Differential Mobility Analyzer-Mass Spectrometer (DMA-MS) to measure cluster size distributions and their chemical composition for the synthesis of pristine and doped metal oxides. Results have indicated that monomers are rapidly consumed to form larger clusters while larger clusters continue to grow through collisional growth mechanisms. In addition, the synthesis of composite mixed oxides is explored to establish the effect of dopants on particle formation pathways. These results will provide new insight into the particle inception and growth mechanisms in flame aerosol reactors while further enabling combustion synthesis as a scalable method of advanced nanomaterials production.

7NM.2

Flame-driven Aerosol Synthesis of Multicomponent Metal and Non-Oxide Semiconductor Nanoparticles.

Di Qi, Singh Saurabh, Munish Sharma, MARK SWIHART, *University at Buffalo (SUNY)*

This presentation will describe our most recent efforts to synthesize metallic and semiconductor nanoparticles in the gas phase. Over the past few years, we have developed the high temperature reducing jet (HTRJ) process for aerosol synthesis of nanoparticles of hydrogen-reducible metals and semiconductors. It employs a fuel-rich hydrogen flame as the source of energy to decompose low-cost metal salt precursors and initiate nanoparticle formation. Aqueous precursor solutions are injected within a converging-diverging nozzle downstream of the flame. The high velocity gas flow atomizes the precursors, which then evaporate, decompose, and nucleate particles. Excess hydrogen ensures that the particles form in a reducing environment, so that metals or non-oxide semiconductors, rather than metal oxides, are formed. In most cases, the process fully converts precursors to products, which is particularly valuable for creating multi-component nanoparticles of controlled composition. Examples to be discussed will include copper-silver-tin mixtures and copper-nickel alloys, which are of interest for use in conductive inks for printable electronics, as well as copper chalcogenide-based semiconductor particles that are of interest for use in solar cells and other optoelectronic applications.

7NM.3

Kinetics of Sub 3 nm Titanium Dioxide Particle Formation in an Aerosol Reactor during the Thermal Decomposition of Titanium Isopropoxide (TTIP). YANG WANG, Pai Liu, Tandeep Chadha, Jiaxi Fang, Pratim Biswas, *Washington University in St Louis*

Measurements of particle size distributions using differential mobility analyzers (DMAs) can be utilized to study particle formation mechanisms. However, knowledge on the initial stages of particle formation has been missing because of the Brownian broadening effect in conventional DMAs, which limits the ability to measure sub 3 nm particles. Some studies have recently demonstrated the capability of a high resolution Half Mini DMA to measure sub 3 nm particles in a flame aerosol reactor. In this study, the Half Mini DMA was applied to investigate the particle formation mechanisms in a furnace aerosol reactor during the synthesis of titanium dioxide particles via thermal decomposition of titanium isopropoxide (TTIP).

Four different characteristic time scales: precursor reaction time, precursor residence time, particle coagulation time, and particle sintering time, were compared to examine particle inception and growth in the furnace aerosol reactor. At low synthesis temperatures (373 K ~ 673 K), a peak of TTIP precursor cluster with an approximate size of 1.8 nm was detected, along with scattered particles of smaller sizes, possibly generated from the fragmentation of TTIP molecules in the radioactive neutralizer. As synthesis temperatures increased to 723 K, the TTIP peak shape altered, due to the onset of the thermal decomposition reaction. In addition, a broader titanium dioxide particle size distribution following the TTIP peak appeared at higher synthesis temperatures, while the peak diameter further increased with temperature. Aerosol growth models will be used to simulate particle formation in the sub 3 nm range and compared with the experimental results.

7NM.4

Lanthanide Doped Silica Nanospheres – Surface Sampling in Deposition Studies. ERIN M. DURKE, Wesley Gordon, Amanda Jenkins, Jason Edmonds, *Edgewood Chemical Biological Center*

The overall objective of our research is to determine the degree of surface deposition resultant from the aerosolization of a dusty powder. Current methods for measuring the amount of deposited material require extraction of material from the surface, a process which involves manipulations that can disturb the settled material. In order to facilitate more reliable measurements of the amount of aerosol deposited, we have developed a model system of silica nanospheres, of known size and shape, with a lanthanide element incorporated into the spheres. The lanthanide we have chosen to work with is europium, an element whose fluorescence spectra is well characterized. Addition of the europium to the silica nanosphere allows fluorescence surface sampling to be performed after deposition, permitting measurement of the material without risk of disturbance or dislodging due to movement during traditional surface sampling techniques. Preliminary measurements of the 200 nm doped spheres have shown the fluorescence intensity to be linear (R = 0.9998) over 0.1 µM to 100 µM concentrations of the doped spheres in IPA. Results have also indicated that detection of the spheres is more sensitive for surface sample, than in solution.

7NM.5

Near-road Modeling and Measurement of Cerium-containing Aerosol Generated by Nanoparticle Diesel Fuel Additive Use.

BRETT GANTT, Shamia Hoque, Robert Willis, Kathleen Fahey, Juana Delgado-Saborit, Roy M. Harrison, Garnet Erdakos, Prakash Bhave, K. Max Zhang, Kasey Kovalcik, Havala Pye, *U.S. EPA*

Cerium oxide (ceria) nanoparticles (n-Ce) are used as a fuel-borne catalyst in diesel engines to reduce particulate emissions, yet the environmental and human health impacts of the ceria-doped diesel exhaust aerosols are not well understood. To bridge the gap between emission measurements and ambient impacts, size-resolved measurements of ambient aerosol composition and mass concentration have been performed in Newcastle-upon-Tyne, United Kingdom, where an n-Ce additive has been in continuous use in a bus fleet since 2005. These observations show that the cerium aerosol fraction thought to be of non-crustal origin and associated with the use of n-Ce has a mass size distribution peaking at 200 nm in aerodynamic diameter and a mass concentration of ~0.3 ng per cubic meter. The diurnal cycle of the observed cerium aerosol concentrations suggests that n-Ce use in Newcastle buses is a significant source of cerium at the measurement site. Simulations with a near-roadway multi-component sectional aerosol dynamic model predict that the use of n-Ce additives changes the size distribution of emitted aerosols such that the number concentration of nuclei mode aerosols (< 50 nm in diameter) increases but the total mass concentration decreases. In the atmosphere, dilution and deposition leave < 25% of the emitted aerosol number concentration remaining 300 meters downwind from the roadway. The near-road model predicts a downwind cerium aerosol mass size distribution peaking at 150 nm in aerodynamic diameter, a value similar to that measured for non-crustal cerium in Newcastle. The diameter at the peak of the cerium aerosol mass size distribution is predicted to increase by 35 nm in the ambient atmosphere (300 meters downwind from the roadway) due to condensation of organic gases onto the cerium-containing aerosols.

7NM.6

A Liquid Nebulization / Differential Mobility Analysis (LN/DMA) Based Method for the Quantification of Nanomaterials in Environmentally-Relevant Water Matrices.

BRIAN MADER, Mark Ellefson, Sue Wolf, *3M Company*

A liquid nebulization-differential mobility analysis (LN/DMA) methodology was evaluated for the measurement of the size distribution and quantitative number concentration of engineered nanoparticles (ENPs) in environmentally relevant aqueous matrices. The analysis time is eight minutes per analysis and requires little routine sample preparation and less than 8 mL of sample. For the ENPs studied, the method was capable of rapid, non-invasive, direct analysis of ENPs in many types of aqueous media. Twelve NIST traceable reference materials consisting of polystyrene latex, SiO2, gold, and silver and having diameters from 18 nm to 200 nm were used in the evaluation. The reference materials were spiked into six aqueous matrices; algae and daphnia growth media used in ecotoxicology testing as well as semiconductor grade ultra pure water, groundwater-sourced drinking water, water used in manufacturing activities and an industrial wastewater. The mean measured particle diameters of the reference materials were within the expected NIST-traceable size range for the materials. Matrix matched calibration curves were prepared to determine the individual response factors of each reference material. The response factors were used to quantify the levels of the reference materials spiked into each aqueous matrix. For samples with appropriate signal to noise, and with the exception of one data point, recoveries were within the range of 70 to 130%. This method is particularly well suited for dose verification in ecotoxicology studies as well to support the studies of ENM behavior in other aqueous matrices.

7NM.7

Aminated Reduced Graphene Oxide-Titanium Dioxide Nanocomposites (AGOTi) for Carbon Dioxide Capture and Photoreduction. YAO NIE, Wei-Ning Wang, Yi Jiang, John Fortner, Pratim Biswas, *Washington University in St. Louis*

Carbon dioxide (CO2) capture and utilization is a promising technology to potentially address global climate change. The photocatalytic conversion of CO2 into hydrocarbon fuels has attracted abundant research attention in recent years (Wang et al., 2012). However, so far there have been few reports about CO2 capture using the same material as CO2 conversion. In this work, aminated reduced graphene oxide-TiO2 (AGOTi) nanocomposites, synthesized using a one-step furnace aerosol reactor method, were demonstrated to effectively capture and photo-reduce CO2. In the method, ethylenediamine (EDA) solution was added to the TiO2 and GO precursor to functionalize the GO surface with amino groups. To achieve the desired nanocomposites, the TiO2/GO ratio, the EDA/GO ratio and the furnace temperature were all optimized. Our CO2 capture results showed that there was no obvious capture for pure GOTi; while after being functionalized with amino groups, a high adsorption of CO2 was observed. This provided direct evidence that surface functionalization of graphene oxide with amino groups could greatly enhance the capture of CO2. When the temperature increased above 473 K, both capture and photoreduction performance decreased significantly, which indicated that synthesis temperature could determine the abundance of functional groups on the AGOTi nanocomposite surface, thus affecting the overall performance. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), flourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy were performed to evaluate the size, morphology, and surface chemistry of AGOTi material. Based on the characterization results, the mechanisms of CO2 adsorption and photoreduction on AGOTi will be discussed in this work.

References

Wang W.N. et al., (2012), JACS, 134, 11276-11281.

7NP.1

Effect of Chemical Structure on the Rapid Formation of Extremely Low Volatility Organic Compounds from BVOC Oxidation. MIKKO SIPILÄ, Tuija Jokinen, Torsten Berndt, Mikael Ehn, Heikki Junninen, Pauli Paasonen, Stefanie Richters, Frank Stratmann, Hartmut Herrmann, Douglas Worsnop, Markku Kulmala, Veli-Matti Kerminen, *University of Helsinki*

Oxidation products of terpenes and isoprene have a major influence on the global secondary organic aerosol burden, and atmospheric nanoparticle and cloud condensation nuclei (CCN) production. Here we draw special attention to the formation of highly oxidized, extremely low volatility organic compounds (ELVOC), from ozonolysis and OH radical oxidation of series of biogenic volatile organic compounds (BVOC) including terpenes and isoprene. We show that ELVOC from these precursors can be formed promptly after the initial attack of an oxidant via formation of RO2 radical and successive intramolecular hydrogen shifts followed by a rapid reaction with oxygen (O2). We demonstrate how the structure of the VOC and the initial oxidation reaction affects the formation of ELVOC. Investigated BVOC include compounds with endocyclic double bond (such as alpha-pinene and limonene), exocyclic double bond (e.g. beta-pinene) and acyclic compounds (e.g. myrcene or isoprene). Formation of ELVOC can result in CCN formation, while the formation of higher volatility oxidation products could potentially even inhibit CCN production. This feature would be due to the preferential partitioning of higher-volatility species into larger, already CCN-sized particles which increases condensation and coagulation sinks. These results advance understanding of observations in environments with different biogenic emission patterns and oxidation conditions. The results also provide new guidance for developing large-scale modeling frameworks that simulate current or future biosphere-atmosphere-climate interactions.

7NP.3

Chemical Mechanisms Behind the Isoprene Suppression of Biogenic New Particle Formation. SHANHU LEE, Yi You, Janek Uin, Alex Guenther, Joost de Gouw, William Brune, Paul Wennberg, Alex Teng, Tran Nguyen, Jason St. Clair, John Crounse, Pawel Misztal, Gabriel Isaacman, Allen H. Goldstein, Karsten Baumann, Eric Edgerton, *Kent State University*

Secondary aerosol formation in forests is a significant source of atmospheric aerosol particles. We have investigated the process of new particle formation in a mixed deciduous forest under anthropogenic influences, during the Southern Oxidant and Aerosol Study (SOAS) in the summer of 2013 in the state of Alabama. Particle size distributions down to approximately 1 nm and concentrations of various gas-phase nucleation precursors such as sulfuric acid, ammonia/amines, isoprene, monoterpenes, and various oxidation products of biogenic VOCs were measured. There was a complete absence of new particle formation during the six weeks of the campaign in June and July. Frequent sub-2 nm cluster formation with peak concentrations in the 10000 particles per cubic centimeter range occurred and they were strongly correlated to sulfuric acid/sulfur dioxide concentrations. However, no subsequent growth of these clusters to larger sizes was observed. Additionally, the measured sub-2 nm cluster concentrations showed a strong difference between day and night (2 to 3 orders of magnitude lower at night), in contrast to the previous reports from the Finnish boreal forest which showed a constant particle pool in the sub-2 nm size range. Several factors, such as high temperatures and high condensation sink can partially explain the lack of the cluster growth, but the conditions should have been favorable for new particle formation on some of the campaign days. Previous chamber experiments, field observations and the comparison of relevant atmospheric conditions from this and other measurement sites (a Michigan deciduous forest and Amazon rain forests), consistently point to high isoprene emissions as the likely reason for the lack of new particle formation in the mixed forest. From these observations, we propose several chemical mechanisms behind the isoprene suppression of biogenic new particle formation.

7NP.4

Atmospheric Nanoparticle Growth, Particle Phase Reactions and Particle Phase State. TAINA YLI-JUUTI, Ilona Riipinen, Ulrich Poeschl, Manabu Shiraiwa, *Max Planck Institute for Chemistry*

For nanoparticles formed in the atmosphere from the trace gases, growth to larger sizes is the key to survival and to having climatic effects. By now it is known that organic vapors play a crucial role in the atmospheric nanoparticle growth in many environments, however not all of these organic compounds are identified yet. Also, several open questions still remain on the role of particle phase reactions and mass transport limitations in the nanoparticle growth. In this study we combine the approaches from two recently developed models that are used for describing particle growth and particle phase processes in order to gain a more complete picture of the roles of different particle phase processes in nanoparticle growth. MABNAG (Model for acid-base chemistry in nanoparticle growth) couples thermodynamics of acid-base chemistry from E-AIM (Extended Aerosol Inorganics Model) with a traditional dynamic condensation model and takes in to account the non-ideal mixture effects for equilibrium vapor pressures. KM-GAP (Kinetic multi-layer model for gas-particle interactions in aerosols and clouds) on the other hand uses kinetic approach for the condensation and explicitly resolves mass transport and chemical reactions at the surface and within the particle bulk. By merging these two models, MABNAG and KM-GAP, we compare and discuss the influence of particle phase salt formation and oligomerization, particle phase mass transport limitations, and condensation of low-volatile gas phase oxidation products on atmospheric nanoparticle growth.

7NP.5

Observation of Water Vapor Uptake by Dimethylamine-Sulfuric Acid Cluster Ions in the Sub 2 nm Size Range via Ion Mobility Spectrometry-Mass Spectrometry. Jikku Thomas, Siqin He, Joseph DePalma, Carlos Larriba-Andaluz, Murray Johnston, CHRISTOPHER HOGAN JR., *University of Minnesota*

A number recent studies suggest that the combination of amines and sulfuric acid in the vapor phase lead to the formation of stable clusters, and hence can lead to new particle formation in the atmosphere. Using high resolution ion mobility spectrometry-mass spectrometry, we have determined the mobilities of singly charged ions of the type $(H^+)(DMA)_x(H2SO4)_y$ (DMA = dimethylamine; H2SO4 = sulfuric acid), where x ranges from 4 to 8 and y ranges from x-1 to x+5, and further examined water uptake by these clusters near atmospheric pressure and room temperature, at relative humidities ranging from 0 to 25%. For measurements we generated ions via positive electrosprays of dimethylamine-sulfuric acid solutions, and electrostatically directed ions into a parallel-plate differential mobility analyzer, operated with a resolution near 50. Water vapor uptake was monitored by humidifying the sheath flow of the differential mobility analyzer. Measurements clearly show that for a given number of dimethylamine molecules in a cluster, the extent of water vapor uptake increases with increasing number of sulfuric acid molecules, with a maximum 10% shift in cluster ion inverse mobility apparent at the highest examined relative humidities. Selected cluster structures, predicted via density functional theory calculations, were used in gas model scattering calculations to compare measured mobilities to predictions. Further, classical theories of heterogeneous uptake have been compared to measurements. Overall, we show that even at modest relative humidities $(H^+)(DMA)_x(H2SO4)_y$ clusters clearly uptake several molecules, which needs to be considered in models of cluster growth and new particle formation.

7NP.6

Particle Formation from Methanesulfonic Acid and Ammonia/Amines via Laboratory Experiments, Ab Initio Calculations, and Modeling Studies. HAIHAN CHEN, Mychel E. Varner, Andrew Martinez, Veronique Perraud, Micheal, J. Ezell, Kristine Arquero, Jeremy Horne, Benny Gerber, Donald Dabdub, Barbara J. Finlayson-Pitts, *University of California, Irvine*

New particle formation is frequently observed in the tropospheric boundary layer. It accounts for up to half of global cloud condensation nuclei. Therefore, understanding new particle formation from gaseous precursors is critical in reducing the current uncertainties associated with climate-aerosol interaction. While sulfuric acid reacting with ammonia/amines has been well established as the main nucleating pathway, recent field and laboratory studies suggest that other gas precursors may contribute. These additional precursors include methanesulfonic acid from the oxidation of organosulfur compounds that are generated from biological processes over oceans as well as agricultural and domestic activities. In this study, laboratory experiments are performed in a borosilicate glass flow reactor to investigate particle formation from methanesulfonic acid and ammonia/amines. The relative effectiveness of particle formation from ammonia, methylamine, dimethylamine, and trimethylamine with methanesulfonic acid and the dependence on precursor concentrations and relative humidity are reported. In parallel, quantum chemical calculations are performed to provide insights on initial clusters and processes leading to particle formation. Calculations show that the observed effects of gas precursors and relative humidity on particle formation are related to the structures and stabilities of initial clusters. The nucleating pathway is further implemented in a three dimensional airshed model in the South Coast Air Basin of California to evaluate emissions of methanesulfonic acid and ammonia/amines and their contributions to particle formation.

7NP.7

New Particle Formation in the Volatility Basis Set. NEIL DONAHUE, Wayne Chuang, Ismael Kenneth Ortega Colomer, *Carnegie Mellon University*

Oxidized organic compounds can be involved in all portions of new particle formation and growth, and there is compelling evidence that many particle formation events in the atmosphere involve oxidized organics. We have added new findings regarding production of extremely low volatility organic compounds (ELVOCS) from gas-phse oxidation of organic compounds as well as calculations of the stability of small complexes to parameterized new-particle formation and growth within the framework of the volatility basis set (VBS). Here we shall present simulations of formation and growth events both for ambient (boreal forest) and lab (the CLOUD experiment at CERN) conditions.

8AC.1

Chlorine-initiated SOA Formation from Biogenic VOCs.

CHRISTOPHER LIM, Kelsey Boulanger, Jesse Kroll, *MIT*

Chlorine-initiated oxidation of volatile organic compounds (VOCs) can compete with VOC oxidation by the hydroxyl radical under certain tropospheric conditions, and likely contributes to the formation of secondary organic aerosol (SOA). However, previous laboratory studies of SOA from chlorine-initiated oxidation of VOCs are limited, particularly with regards to the chemical composition of the aerosol. In this work we examine the formation of SOA from Cl atoms plus two biogenic VOCs, alpha-pinene and isoprene, with the aim of determining SOA composition and identifying chemical markers of Cl-initiated chemistry. Experiments were carried out in an environmental chamber, with chlorine radicals generated from the UV photolysis of molecular chlorine. On-line characterization with an Aerodyne High Resolution Time of Flight Aerosol Mass Spectrometer (AMS) is used to provide information on chemical composition, such as O/C, H/C, Cl/C and major product ions; however, analysis is complicated by the absence of major chlorinated organic peaks and the formation of refractory species, such as tin (IV) chloride, in the AMS mass spectra. In addition to AMS measurements, FTIR is used to detect carbon-chlorine bonds from filter samples taken during chamber experiments.

8AC.2

Products Formed during the Heterogeneous Oxidation of Polycyclic Aromatic Hydrocarbons in an Atmospheric Chamber.

KLARA ONDRUSOVA, Richard E. Cochran, Haewoo Jeong, Alena Kubatova, *University of North Dakota*

Polycyclic aromatic hydrocarbons (PAHs) have long been of great interest due to their known toxicity to human health and indirect impact on our climate. After emitted into the atmosphere through various primary emission sources, PAHs can be oxidized to less volatile derivatives. Such oxidation pathways can occur in both the gas phase and gas-particle (heterogeneous) phase. While significant work has been devoted to determining the mechanisms behind the gas-phase oxidation of PAHs, our current understanding of their oxidation in the heterogeneous phase is limited. In this work PAHs are oxidized in a 10 m3 atmospheric chamber under atmospherically relevant conditions. Focus was given to identifying the wide range of products formed as well as determining the kinetic formation rates of the various products. Initial experiments were performed using model particle substrates, ammonium sulfate and silica particles, to compare kinetic formation rates against those obtained under gas-phase conditions. Experiments were then done using diesel-exhaust PM emitted from an idling diesel engine. PM samples were collected onto quartz filters for off-line analysis by gas chromatography-mass spectrometry (GC-MS). Additionally PM sample were collected onto a newly developed quartz tube sampler for off-line analysis by thermal desorption/pyrolysis-gas chromatography/mass spectrometry (TD/Py-GC/MS). This latter PM sampling method allowed for the investigation of high molecular weight (low volatility) and oligomeric species not easily detected with GC-MS. PM concentrations and size distributions were continuously monitored throughout the experiments using an online scanning mobility particle sizer (SMPS).

8AC.3

Molecular Composition and Photochemical Aging of Alpha-Pinene SOA and Alpha-Humulene SOA Generated Under Nocturnal and Diurnal Conditions. DIAN ROMONOSKY, Sergey Nizkorodov, Julia Laskin, Alexander Laskin, *University of California, Irvine*

Secondary organic aerosol (SOA) formation readily occurs in reactions of biogenic volatile organic compounds (BVOC) with ozone (nighttime and daytime), OH/NO_x (daytime), and NO_3 radicals (nighttime). Each of the BVOC oxidation pathways may be expected to produce a uniquely different set of SOA compounds, with different physical properties. The main goal of this study was to explore the effect of each of these three oxidation conditions on the molecular composition and photochemistry of SOA prepared from common BVOC. A typical monoterpene (alpha-pinene) and sesquiterpene (alpha-humulene) were chosen to model SOA formation in a smog chamber via: (1) BVOC + O_3, (2) BVOC + NO_3, and (3) BVOC + OH + NO_x + hv. In selected experiments, ammonia was added to the chamber after SOA formation to investigate its effect on SOA composition. The resulting SOA was collected on an inert substrate, extracted in water, and photolyzed in an aqueous solution in order to model the photochemical cloud-processing of SOA. The extent of change in the molecular level composition of SOA over 4 hours of photolysis was assessed with high-resolution mass spectrometry (HR-MS). The data were collected in spring of 2014, and will be fully analyzed in time for the AAAR meeting. However, the preliminary analysis revealed significant differences in the molecular composition between monoterpene and sesquiterpene SOA formed by the different oxidation pathways. The composition further evolved during photolysis. This study highlights the importance of aqueous photochemistry in the aging of biogenic SOA.

8AC.4

Characterization of Organic Precursors and Products during Aqueous Hydroxyl Radical Oxidation of Po Valley, Italy and Fresno, CA Fog Water. Jeffrey R. Kirkland, Yong Lim, Lynn Mazzoleni, Jeffrey Collett, Stefano Decesari, M. Cristina Facchini, Amy P. Sullivan, Frank Keutsch, BARBARA TURPIN, *Rutgers University*

Aqueous chemistry in clouds, fogs and aerosols is known to alter properties of aerosols and budgets of gases. However, this chemistry remains only partially understood. Laboratory studies with simplified systems have been used to refine our understanding of aqueous processing and further our understanding of aqueous chemical mechanisms. However, few studies have explored aqueous chemistry in the complex mixtures found in atmospheric waters. Such studies will aid the identification of potentially important precursors to aqueous processing and organic aerosol formation.

In this work, fogwater samples collected in Fresno, CA and Po Valley, Italy (winter 2006; 2011-2012) were oxidized with hydroxyl radicals. Hydroxyl radicals were generated in situ by photolysis of hydrogen peroxide at a rate of 0.2 - 0.4 M/s. Experimental samples were analyzed by ion chromatography, electrospray ionization (ESI) mass spectrometry (MS), ultra-high resolution Fourier transform ion cyclotron resonance MS, and MS-MS to characterize precursors and products. Control experiments were also conducted. Oxalate and pyruvate were among the products in all experiments conducted with OH, but not in control experiments (with UV or hydrogen peroxide). Several reactive species were identified in the ESI positive mode. Based on mass fragments, several precursors of OH oxidation were identified.

8AC.5

Secondary Organic Aerosol from Gas Phase Methylsiloxane Oxidation: Products and Reaction Mechanisms. YUE WU, Murray Johnston, *University of Delaware*

Cyclic volatile methylsiloxanes (cVMS), such as octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5), are widely used in consumer products and easily released into the atmosphere owing to their high vapor pressures. Field measurements suggest that ambient nanoparticles contain significant amounts of silicon, and one hypothesis is that cVMS react in the atmosphere to form secondary organic aerosol (SOA) containing silicon. In this work, SOA from cVMS oxidation is characterized by advanced mass spectrometry techniques to elucidate the particle phase products and reaction mechanisms.

During the experiment, the gas vapor of D_5 was created by passing clean, dry air over the D_5 liquid. This air flow was introduced into a photoreaction chamber (PC) along with an additional flow of ozone that had been bubbled through the deionized water. UV radiation in the PC produced OH from ozone and water, which then reacted with gaseous D_5. Particulate matter in the air flow exiting the PC was collected for 20-24 h onto a Teflon coated, glass fiber filter for analysis. The filter was extracted for analysis by direct infusion ESI-MS and thermal decomposition EI-MS. ESI-MS shows the appearance of many ions between 337 and 471 m/z (corresponding to modified D_5 monomers), 707 and 857 m/z (corresponding to modified D_5 dimers), 1169 and 1213 m/z (corresponding to modified D_5 trimers). Each region shows evidence of both functionalization and fragmentation of the D_5 precursor. EI-MS confirms two major building blocks of oligomers are D5 and D_4TOH, an OH substituted product of D_5. Follow up experiments are being performed with high resolution ESI-MS/MS to determine accurate molecular formulas and confirm structural information. The results will be presented for SOA produced from D_5 and other precursors, such as octamethylcyclotetrasiloxane (D_4), hexamethylcyclotrisiloxane (D_3).

8AC.6

Effect of Ambient Primary Organic Aerosols on Secondary Organic Aerosol Formation. JIANHUAI YE, Bruce Urch, Greg J. Evans, Arthur Chan, *University of Toronto*

Secondary organic aerosol (SOA) is known to pose serious health effects and plays a significant role in global climate change. Current atmospheric models assume that all organic species, including both primary organic aerosol (POA) and SOA form a well-mixed liquid phase and oxidation products partition into POA similarly as into SOA. Under this assumption, gas/particle partitioning equilibria for different SOA systems are parameterized in laboratory experiments (Odum model, volatility basis set etc.) with SOA-only organic phases.

Recently, Song et al. (Geophys. Res. Lett., 2007) demonstrated that SOA yield of alpha-pinene ozonolysis was not enhanced by introducing dioctyl phthalate and lubricating oil (POA surrogates) as expected, which indicated the overestimation of the results from the “Odum model”. Similarly, Asa-Awuku et al. (Geophys. Res. Lett., 2009), showed that different POA compositions may result in distinct phase partitioning behaviours. In both cases, the POA were laboratory-generated.

In this work, we examine the validity of “single phase” assumption by studying the interactions between ambient POA and SOA from the ozonolysis of alpha-pinene. The study is conducted adjacent to a major roadway in Toronto, Canada. Ambient POA is introduced into a custom-made quartz reactor (10.2 cm I.D. × 120 cm L.) together with alpha-pinene and oxidized with ozone. Aerodyne Aerosol Chemical Speciation Monitor (ACSM) will be used to determine the chemical compositions of POA. Aerosol size distributions and number concentrations are measured using a Scanning Mobility Particle Sizer (SMPS). Alpha-pinene concentrations are monitored using GC-FID.

In this study, we compare the experimental SOA yields of alpha-pinene ozonolysis in the presence of ambient POA to those predicted from the “Odum model”. In addition, POA/SOA phase partitioning behaviours are investigated with varying POA compositions during the day. Finally, the role of humidity in POA/SOA phase partitioning is also examined.

8AC.7

Spectroscopy of Cloud-Processed Aerosols: Glyoxal Oligomers. SARAH D. BROOKS, Elena Avzianova, *Texas A&M University*

Quantifying the formation of secondary organic aerosol products in evaporating cloud droplets is a challenge, since reactions occurring in a water-restricted environment do not necessarily proceed by the same mechanisms as those which occur when water is readily available. Raman microscopy and Attenuated Total Reflectance Fourier Tranform Infrared Spectroscopy were utilized to facilitate investigations of equilibria between various hydrated and oligomeric forms of glyoxal in aqueous glyoxal solution droplets. The assignment of spectra is obtained through density functional quantum chemical calculations of vibrational wavenumbers, Raman activities, and infrared intensities. Several forms of glyoxal derivatives with similar functional groups, e.g., hydroxyl and dioxolane rings, are found to be present. The absence of a Raman spectral peak corresponding to the vibrational carbonyl stretch provides evidence that both carbonyl groups of a glyoxal molecule become hydrated in solutions of a broad concentration range. The presence of bands corresponding to deformation vibrations of the dioxolane ring indicates that dihydrated glyoxal oligomers are formed in glyoxal solutions with concentrations of 1 M and higher. Under typical ambient temperature and humidity conditions, concentrated glyoxal solution droplets undergo evaporation with incomplete water loss. Our results suggest that formation of crystalline glyoxal trimer dihydrate from concentrated solutions droplets is hindered by the high viscosity of the amorphous trimer and requires dry conditions that could rarely be achieved in the atmosphere. Hence, in the atmosphere particles containing these organic compounds may be present in an amorphous state under a broad range of conditions.

8AC.8

A Study of the Aqueous Phase Processing of Organic Aerosols through Compound Specific Stable Isotope Analysis. DENISE NAPOLITANO, Pierre Herckes, *Arizona State University*

Secondary organic aerosols (SOAs) are formed in the atmosphere through oxidative and photochemical reactions of primary organic aerosols (POAs) or volatile organic compounds (VOCs). While gas-phase SOA formation from VOCs has been well-studied and documented, aqueous-phase SOA formation remains a poorly understood process, likely causing substantial errors in the estimation of organic aerosol concentrations in atmospheric models. Field studies of SOA formation involving all three phases of aerosol particulate matter (PM), gas phase VOCs, and aqueous phase organic substances have not been conducted, but it would be greatly beneficial to isolate and track compounds in the atmosphere through all phases as these reactions proceed. Both an understanding of how SOAs form in the aqueous phase, as well as whether the SOA precursors originated from POAs or VOCs, can be addressed through studying the stable carbon isotopic composition of organic atmospheric species. Analyses of aerosol particulate matter (PM) and fog collected from various regions of North America for total carbon isotopic composition by isotope ratio mass spectrometry (IRMS) clearly reveal processes that involve isotope effects when fog is present. Performing compound-specific isotope analysis (CSIA) using a gas chromatography-combustion-IRMS (GC-C-IRMS) system on various types of atmospheric species as fog forms and evaporates will aid in identifying the processes that lead to isotope fractionation and show how these processes affect the carbon isotopic composition of SOAs formed in the aqueous phase (aqSOA). This information will allow us to determine the precursors of specific aqSOA and if the precursors originated as PM or VOCs. These analyses will provide novel analytical results to add to the community's knowledge of aqueous SOA processing and demonstrate the effects that these reactions have on model estimates of the organic aerosol budget.

8AC.9

Optical Properties of Water Soluble Organic Carbon (WSOC) in Atmospheric Aerosols and Fog Waters. JINWEI ZHANG, David Hanigan, Paul Westerhoff, Pierre Herckes, *Arizona State University*

Water soluble organic carbon (WSOC) is an important part of atmospheric aerosol particles. Despite its abundance, little is known on its optical properties, in particular the absorptivity and how it related to the chemistry and structure of WSOC. Possible transformations by aqueous phase processing are also poorly understood.

Here we present measurements of WSOC absorptivity in the UV-Vis range of a variety of atmospheric aerosols and fog/cloud waters representative of urban, remote and rural areas and collected during different seasons. UV-vis absorptivity by WSOC in aerosols was significantly larger than that in fog waters. When the specific absorptivity (normalized by organic carbon content) was considered, the absorptivity varied only over a small range for any given location. We will also discuss the impact of inorganic species, humidity and pH on WSOC absorptivity and the resulting impact on atmospheric aqueous photochemistry through screening effects.

8AC.10

Surface-specific Chemical Reactions for Atmospheric Surfactants Observed Directly with Synchrotron-based XPS. NONNE PRISLE, Gunnar Öhrwall, Josephina Werner, Olle Björneholm, *University of Helsinki, Helsinki, Finland*

Atmospheric organic aerosols from a wide range of environments often comprise surface active compounds, i.e. molecules that concentrate in the surfaces of aqueous solutions. A major class of atmospheric surfactants is the fatty acids and their carboxylate anions. We have investigated aqueous solutions of such straight-chain carboxylic acid sodium salts with carbon numbers from 1-10, mixed with different inorganic salts commonly found in atmospheric aerosols. These solutions are considered representative model systems for aqueous aerosols found in the atmosphere, e.g. marine aerosols with concentrations relevant for CCN activation. Aqueous solution surfaces were probed directly using synchrotron-based X-ray photoelectron spectroscopy (XPS) on a liquid jet. XPS is a highly surface sensitive and chemically selective technique and thus ideal for probing the chemical environment of surfactants adsorbed at the air-water interface. XPS measurements were performed at the Swedish national synchrotron facility MAX IV Laboratory, Lund University.

We verify by direct observation that carboxylate anions are significantly partitioned to the aqueous surface, confirming significant surface activity as expected from their influence on bulk aqueous surface tension. Specifically in mixtures with weakly acidic ammonium ions, we find that surface-adsorbed carboxylates are protonated to a degree that is orders of magnitude greater than expected from solution bulk properties. We have investigated the variation of this enhanced protonation with surfactant concentration, organic-inorganic mixing ratio, and pH, in order to establish the underlying mechanism. The observed changes in chemical composition of the aqueous surfaces occur without corresponding changes in solution bulk properties and may influence chemical reactivity and physical properties of the surface. Surface specific composition and properties are particularly important for heterogeneous atmospheric processes occurring on the very large surfaces of sub-micron aerosols.

8AC.11

Identification and Characterization of Visible Absorption Components in Methylglyoxal-Ammonium Sulfate Mixtures. W. SEAN MCGIVERN, Thomas C. Allison, James Radney, Christopher Zangmeister, *National Institute of Standards and Technology*

Methylglyoxal (MG) is formed in large quantities from the atmospheric oxidation of numerous volatile organic compounds, particularly aromatic species. MG in aqueous solution shows only a small visible absorption and thus absorbs little incoming solar radiation as a droplet. However, reaction of MG and ammonium salts is known to cause the visible absorption to increase markedly, leading to the conversion of a near-colorless droplet to a partial absorber. Chromatographic analysis of the products from the reaction of MG and ammonium sulfate has revealed that, although the overall composition is complex, most of the visible absorption is caused by a small number of compounds. Fraction collection of the eluate from an HPLC analysis of the reaction mixture revealed only a single "brown" fraction that showed any visible absorption. MS-MS analysis of this absorbing fraction demonstrates that the visibly absorbing products primarily consist of imino compounds of aldol-like condensation reactions. The presence of the nitrogen in the pi-conjugated system of the imino-substituted products redshifts the ultraviolet absorption spectrum relative to the pure aldol condensate such that visible absorption can occur in the the long-wavelength tail. Density functional theory has been used to calculate how the presence of the imino and carbonyl moieties on these product molecules affects the near-UV absorption spectra and individual pKa values.

8AC.12

Gas-phase Oxidation of Naphthalene, Acenaphthylene and Acenaphthene Initiated by the Nitrate Radical: Mechanistic Study and SOA Formation. MATTHIEU RIVA, Manuela Cirtog, Emilie Perraudin, Bénédicte Picquet-Varrault, Eric Villenave, *EPOC, Université Bordeaux, France*

The aerosol organic fraction constitutes a significant part of urban particulate matter and may play a major role in all air pollution processes. In the atmosphere, the main origin of organic aerosol may often arise from secondary sources. It is well-known that volatile organic compounds (VOCs) such as monoterpenes or monoaromatics are involved in the formation of secondary organic aerosols (SOA). However, the total mass of SOA measured on several sampling sites cannot be explained by the simple presence of such VOCs. Recent studies indicate that PAHs such as naphthalene, acenaphthene and acenaphthylene could be one of the "missing" sources of SOA, particularly in urban areas. NO3 radical is known to be the main oxidant of VOCs during night time. Different studies have demonstrated the large reactivity of nitrate radicals with volatile organic compounds, especially with unsaturated species. Such high reactivity of NO3 with some VOCs may lead to significant impact in the formation of SOA.

Reactions of naphthalene, acenaphthene and acenaphthylene with nitrate radicals were carried out in the CSA chamber, at room temperature and atmospheric pressure. Gas-phase products were followed in real time using both a proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS) and FTIR. A SMPS was used to measure the aerosol concentration, the size distribution and to quantify aerosol formation yields.

This work presents the first exploration of the impact of nitrate radicals on SOA arising from PAH oxidation. Kinetics measurements were also performed in order to determine the reaction rate constants of the three PAHs and the impact of NO2. Based on the gas-phase identified products, new insights on chemical mechanisms are proposed.

8AC.13

Chemical Characterization of Gas- and Aerosol-Phase Products from Isoprene Ozonolysis in Presence of Acidic Aerosol: Re-examination of Secondary Organic Aerosol Formation. Matthieu Riva, SRI HAPSARI BUDISULISTIORINI, Tashana Detwiler, Zhenfa Zhang, Avram Gold, Jason Surratt, *University of North Carolina at Chapel Hill, Chapel Hill, NC*

Atmospheric aerosols are critical in many environmental processes and can adversely affect the global climate and human health. It is now recognized that the largest mass fraction (20–90%) of atmospheric fine particles (PM2.5) is generally organic, and is mostly dominated by secondary organic aerosol (SOA) formed from the oxidation of volatile organic compounds (VOCs). Isoprene is the most abundant non-methane hydrocarbon emitted into the Earth's atmosphere and is derived from terrestrial vegetation. Prior studies have demonstrated the formation of SOA arising from its photooxidation. Most of these studies have been focused on the hydroxyl radical (OH)-initiated oxidation of isoprene and have demonstrated that certain highly oxidized compounds, such as isoprene-derived epoxides, enhance the formation of SOA by heterogeneous reactions. Isoprene ozonolysis is less documented and only partial mechanisms are currently proposed. Recently, one study demonstrated the presence of oligomer products in the particle phase but the mechanism to explain the formation of these compounds remains unclear. Moreover, the explanation of the SOA formation from nucleation arising from isoprene ozonolysis remains unknown.

Therefore, in this work we explored SOA formation from isoprene ozonolysis. Experiments were conducted in an indoor smog chamber facility at room temperature. Gas phase characterization was performed using high-resolution time-of-flight chemical ionization mass spectrometry (HRToF-CIMS) equipped with acetate reagent ions. SOA chemical characterization was investigated using ultra performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-Q-ToFMS) and gas chromatography interfaced with electron ionization mass spectrometry (GC/EI-MS) with prior trimethylsilylation. Impact of environmental conditions (OH radicals, aerosol acidity, seed particle composition) on SOA formation arising from isoprene ozonolysis have been investigated and new insights on the chemical mechanism are proposed.

8AQ.2

Investigating Chemical Reaction Pathways in the SE US Using Comprehensive Gas Chromatography. KELLEY C. BARSANTI, Melissa J. Roskamp, Wentai Luo, Lindsay E. Hatch, James F. Pankow, *Portland State University*

Laboratory studies of secondary organic aerosol (SOA) formation have shown that the product distribution and SOA yields from anthropogenic and biogenic precursors vary significantly with the identity of the initial oxidant (e.g., OH/O_3 vs. NO_3), and other conditions such as NO_x level (more specifically HO_2/NO/NO_2 ratios) and particle acidity. Thus it is known that anthropogenic emissions can have a significant influence on biogenic SOA formation; less clear are: 1) the degree to which these laboratory-observed effects are typically manifested under ambient conditions; and 2) how such processes might be best constrained in predictive models. In this work we performed a detailed analysis of two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC/TOFMS) data from the PINOT NOIR campaign (Particle Investigations at a Northern Ozarks Tower: NOx, Oxidant, Isoprene Research), centered in the Southeastern US. Utilizing GC×GC/TOFMS values for concentrations of volatile and semivolatile organic compounds (S/VOCs) together with data for trace gases and meteorology, we sought to identify and quantify important organic aerosol precursors and reaction products indicative of anthropogenically vs. biogenically influenced SOA formation mechanisms. The results have provided inputs to a suite of organic aerosol models of varying complexity for predicting the limits of SOA formation under a range of atmospherically relevant conditions. This research supports the goals of the Southeast Atmosphere Study (SAS), namely: 1) improved identification and quantification of dominant SOA precursors in the Southeastern US, and 2) further understanding of organic aerosol sources and the interplay between biogenic and anthropogenic emissions.

8AQ.3

Representativeness of Aggregate Vertical Profiles and Influencing Factors from NASA DISCOVER-AQ.

MICHAEL SHOOK, Gao Chen, James Crawford, Bruce Anderson, Andreas Beyersdorf, Richard Moore, Amy Jo Scarino, Kenneth Thornhill, Edward Winstead, Luke Ziemba, *SSAI*

The vertical distribution of aerosols is a critical factor in the assessment of surface air quality as well as direct radiative forcing. However, both the vertical and horizontal distribution of aerosol loading within the boundary layer and lower free troposphere can be highly variable, even within regional spatial scales and diurnal time scales. This variability can be due to a number of factors, including source emissions, boundary layer structure and mixing state, and meteorology. The NASA DISCOVER-AQ field campaign's three deployments thus far (Baltimore-DC, summer 2011; California San Joaquin Valley, January 2013; and Houston, summer 2013) have generated approximately 600 vertical profiles, which provide a unique opportunity to evaluate this variability. Using these datasets, this study will assess the representativeness of aggregate vertical profiles of aerosol loading and properties, along with trace gases and other constituents. This will be achieved by comparing individual profiles to aggregate profiles. In addition, factors influencing the degree of representativeness (such as local meteorology, boundary layer properties, and emissions sources) will be investigated.

8AQ.4

Minimizing Cloud Shattering Effects: Comparing Aerosol Measurements Made during the 2013 SEAC4RS Campaign Behind Two Types of Airborne Sampling Inlets.

KENNETH THORNHILL, Michael Shook, Luke Ziemba, Bruce Anderson, Andreas Beyersdorf, Gao Chen, Edward Winstead, Richard Moore, *SSAI*

In the summer of 2013 the Study of Emissions and atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys (SEAC4RS) field campaign was conducted primarily over the Southeast United States. Among its goals was to characterize the aerosols associated in and around clouds throughout the troposphere. As part of the campaign the NASA DC-8 was instrumented with an extensive suite of aerosol and gas-phase in-situ sensors. This study will look at comparing the responses of two aerosol inlets that were used during the SEAC4RS 1) the Clarke Solid Diffuser Inlet and 2) Clarkson's High Cross-flow Aerosol Sampler (Hi-CAS). Typically in-cloud environments have presented a problem for aerosol measurements due to artifacts created from cloud shattering. As a result in-cloud data is often filtered out of archived datasets. An interstitial inlet such as the Clarkson Hi-CAS shows promise in minimizing cloud-shattering effects allowing for representative data to be collected within clouds. This study will use a suite of aerosol size distributions, condensation particle counters, and optical measurements to compare the response of the two inlets in clear air and in both ice and liquid cloud regimes from data collected during the SEAC4RS campaign.

8AQ.5

Southern Oxidant and Aerosol Study (SOAS); A Modelling Perspective. PETROS VASILAKOS, Yongtao Hu, Jack Lin, Lu Xu, Nga Lee Ng, Armistead Russell, Athanasios Nenes, *Georgia Institute of Technology*

The impact of bio-produced aerosols on climate, as well as air quality, innately carry large uncertainties, given our incomplete understanding of the mechanisms that lead to their production. The recent SOAS campaign was focused on addressing the fundamental questions that arise from these uncertainties, such as what are the impacts of anthropogenic activities to biogenic secondary organic aerosol (SOA) production.

To complement the SOAS study, we simulated the dynamics of primary and secondary pollutants during the SOAS campaign using the Community Multi-scale Air Quality (CMAQ) model, driven by forecasted meteorology from the Weather Research and Forecasting (WRF) model. Biogenic emissions and land use will be provided from the Biogenic Emissions Inventory System version 3 (BEIS3). Both ground and aloft measurements are used for comparison.

Preliminary, 36-km resolution, ground level results and statistical analysis indicate that CMAQ is able to effectively capture, both quantitatively and qualitatively, the evolution of most SOA species, coming from gas phase monoterpene, sesqueterpene and isoprene oxidation.

By carrying out additional sensitivity and statistical analyses using our CMAQ results and measurements, we assess the link between SOA and factors leading to their formation, in order to elucidate some of the uncertainties linked to SOA formation.

8BA.1

Characterization of a Rotating Drum System for Bioaerosol Studies in Biocontainment. MICHAEL SCHUIT, Shanna Ratnesar-Shumate, Jamie Kline, John Yeager, Kristin Bower, Paul Dabisch, *NBACC*

Knowledge of the impact of environmental conditions on the persistence of bioaerosols is critical for public health modeling, the results of which can be utilized to estimate the spread of disease and ultimately inform preparedness and response efforts to emerging agents. While rotating drums for the study of the persistence of bioaerosols have been used for many years, the scope of many previous studies has been limited by the inability to control test conditions or by the biosafety level of the laboratory. The objective of this study was to characterize a novel small rotating drum aerosol chamber capable of controlling temperature, relative humidity, and simulated solar radiation levels in a laboratory operating at Biosafety Level 4. The chamber’s ability to achieve and maintain environmental settings over extended time intervals was tested, and the simulated solar light spectrum and intensity variation were mapped. Additionally, tests were conducted using polystyrene latex (PSL) microspheres to determine the physical decay rate as a function of particle size within the chamber at different rotation rates, and the results were compared with published models from the literature. The data demonstrate that the test system was able to tightly maintain all combinations of environmental parameters tested. A gradient in solar intensity (~15%) over the length of the drum was observed, which may lead to a variation in exposure levels of particles within the chamber. Tests with PSL microspheres showed a marked particle size dependent improvement in retention times when the drum was rotating, although the results did not agree with published models. Regardless, the system was able to maintain particle concentrations of sizes up to 6 micro-meter aerodynamic diameter for periods of time sufficient to measure the inactivation of microorganisms, which will facilitate future work examining the impact of environmental factors on the persistence of microorganisms in aerosols.

8BA.2

Preferential Aerosolization of Different Strains of a Swine Pathogen: Streptococcus Suis. LÉA GAUTHIER-LEVESQUE, Laetitia Bonifait, Phillipa Perrott, Nathalie Turgeon, Marc Veillette, Caroline Duchaine, *Université Laval, Canada*

Bioaerosols are airborne biological particles present in different environments, composed of plant and animal material. The biological diversity of swine barn air is well known, often composed of entire microorganisms such as Lactobacillus, Clostridium, Mycobacterium, Pasteurella and Streptococcus. The microbial concentration in the air may reach 10^9 bacteria per m^3 of air. Many pathogens are part of airborne bioaerosol community in these establishments. The goal of this study is to understand the behaviour in bioaerosols of Streptococcus suis, a swine pathogen causing meningitis, septicemia, endocarditis, pneumonia and also a zoonosis agent implicated in three human epidemics in China. There are 35 serotypes of S. suis based on the immunogenic reaction of their capsule. Serotype 2 is the most often isolated in case of swine and human diseases. Our hypothesis is that certain serotypes could be preferentially aerosolized and thus, more likely to be inhaled and reach the airways. To verify this hypothesis, a stainless steel aerosol chamber with multiple sampling ports has been designed and built. To mimic natural aerosolization processes, bubbling has been used to nebulize the S. suis suspensions. S. suis bioaerosols have been recovered on polycarbonate filters (0.4 micro-meter). qPCR and PMA-qPCR technologies were used to distinguish intact from damaged cells in the samples and thus, the resistance of serotypes to aerosolization processes. During aerosolization, serotype 2 was preferentially aerosolized compared to serotype 5 and its ratio was enriched in the air when compared to the nebulizing solution. Also, the serotype 2 membrane was less damaged than the serotype 5 after the aerosolization. The preferential aerosolization phenomenon is not explained yet but the capsular composition could allow an easiest aerosolization and a protection against the stresses induced thus conserving its infectious state.

8BA.4

Emissions and Dispersion Bioaerosol in Four Sites During Spring-Summer at Tijuana, Mexico. LILIA HURTADO, Guillermo Rodriguez, Miguel Zavala, Penelope Quintana, Luisa Molina, Bertha Landeros, Mirna Brito, *Universidad Autonoma de Baja California, Tijuana, Mexico*

In every field of activity in which the organic material is handled, emissions of dust, gases, odors and bioaerosols are present, has become a major public concern because of the possible effects on the health of workers and local residents. Pathogenic airborne microorganisms may also have public health consequences.

The bioarosols emission measurement were carried out at four sites considered as possible sources of bioaerosols, that during the spring-summer in a treatment plant wastewater, landfill, livestock management and suburban Tijuana river. Air samples were taken with the air sampler M Air T (Millipore), at different distance from the center of activity at each site. Cultivation methods based on the viable count of mesophilic bacteria, total and fecal coliforms, enterococci and other pathogenic bacteria. During sampling, temperature, solar radiation, relative humidity and wind speed were measured. Higer concentration of microorganisms in the wastewater and river Tijuana a maximum of 2.4×10^6 and 4.3×10^6 CFU/m^3 respectively were observed. The highest dispersion of airborne microorganisms to 10 meters in all sampling sites. A gradual decrease of bioaerosols dispersion as advanced in the distance to 100 meters with an average of 54.3% reduction of total and fecal coliforms, 47% enterococci, 31% decrease in other organisms. This study concludes that these sites are generating of bioaerosols and weather conditions are an important factor for dispersing to nearby towns, although these concentrations gradually decrease, are still present and may represent a health problem.

8BA.5

Investigation of Bioaerosol Sampling Efficiency with the Steam Jet-Aerosol Collector. Wei-Ting Chen, Andrey Khlystov, Huey-Jen Su, Nai-Tzu Chen, Wei-Yen Tu, MING-YENG LIN, *National Cheng Kung University*

Viral aerosol is characterized by its small size and can result in adverse health effects. Some viral aerosol such as Influenza virus can pose serious threat to human health. However, sampling viral aerosol is difficult due to its small size. One effective method for sampling sub-micron aerosol is through aerosol condensation growth. The Steam Jet Aerosol Collector (SJAC) uses the condensation growth method for particle collection, and was applied to viral aerosol sampling for the first time. Another advantage of the SJAC is the ability to collect aerosol in aqueous samples, which enable real time detection of biological agents. MS2 bacteriophage was used as the test aerosol and we searched for the SJAC's optimum operation parameter settings. We will report how different solvent vapor and temperatures affect the viability, condensation growth, and collection efficiency of MS2 bacteriophage when using the SJAC. The experimental result can facilitate our understating of how different solvents affects the condensation growth of viral aerosol and improve our understanding of infectious viral aerosol.

8BA.6

In Vitro Aerosolized Antigen Dosimetry Lung Models. AYESHA MAHMOOD, John Dye, *US Army Medical Research Institute for Infectious Disease*

The dynamics of aerosol deposition in the human airway is associated with the localized and systemic physiological responses. The quantitative measurement of droplet deposition for in vitro modeling of aerosol exposure is important to our understanding of human exposure to chemical and biological agents. Inhaled aerosols are of particular interest for the pharmaceutical evaluation and for better understanding of disease pathogenesis, with and without environmental irritant exposure. The overall objective of this work is to define simplified methods to quantify antigen weight and droplet size, to design biomimetic tissue models. To this end, the Lung Mucosal Tissue Equivalent module (MTE) was cultured with either upper (nasal) or lower (alveolar) respiratory track epithelial cells, to mimic the local respiratory environment. These tissue models exhibit distinctive transepithelial electrical resistance and permeability to inert FITC-dextran molecules. This work builds on the barrier function understanding of our lung MTE tissue models and utilizes the VitroCell system for controlled aerosol generation in vitro. The real-time quantitative measure of aerosol droplet deposition dynamics show that the aerosolized delivery can be controlled with droplet size range of 2.5-6um. Larger droplets of 4.5-6um were applied to the nasal MTE. Relatively smaller, 2.5-4um, droplets were applied to the alveolar MTE. The weight and size of the droplet deposition on the MTE was quantified with known concentrations of FITC-Dextran. The results demonstrate distinct differences between the size and weight of the droplets designed to mimic the upper and lower airway physiology. There was a range of cloud deposition profiles with each molecular weight of antigen. This variation is dependent on cloud settling profiles and somewhat anticipated in a dynamic delivery system. Compared to the nasal model, there was a higher degree of variance with the alveolar airway droplet deposition. The results confirm biomimetic inefficiency of aerosolized mode of delivery and define controllable parameters for future studies.

8BA.7

Evaluation of a Low-cost Micro-Channel Aerosol Collector for Bioaerosols in a Pilot Study. IGOR NOVOSSELOV, *Enertechnix Inc*

Bio-aerosol detection and identification is vital for assessment and control of airborne pathogens, allergens and toxins. Assays capable of accurate identification and quantification of these agents generally rely on a sample collected from the environment, but most current collectors provide very limited time resolution and relatively dilute samples. A low-cost micro-Channel Collector (μCC) which offers fine temporal and spatial resolution as well as high collection efficiency and delivers highly concentrated samples in very small liquid volumes has been developed and tested. The design and optimization of this μCC has been guided by computational fluid dynamics (CFD) modeling. Collection efficiency tests of the sampler have been performed in a well-mixed aerosol chamber using aerosolized fluorescent microspheres in the 0.5 μm to 6μm diameter range. Samples were collected in the μCC and eluted into a 100 microliter liquid aliquots. Culture analysis was used for biological aerosols and bulk fluorescence measurements were used for inert spheres to determine the performance of the collector. Typical efficiencies of the collector are above 50 % for 0.5 μm particles and 90% for particles larger than 1 μm. The experimental results agree with the CFD modeling, showing that concentration and capture efficiency of polystyrene spheres are a function of their aerodynamic diameters. Biological environmental samples including aeroallergens and endotoxin were collected and analyzed in the pilot study. The collected biological samples correlate well with the subjects activity type and level for indoor and outdoor environments.

8BA.8

Viral and Bacterial Microbiome of Air in a Daycare Center. AARON PRUSSIN II, Kyle Bibby, Linsey Marr, *Virginia Tech*

Viruses are known to cause a wide array of diseases in humans, animals, and plants. The study of viral bioaerosol community structure has remained largely unexplored. Recent developments in viral metagenomics provide a great opportunity for improving knowledge about viral communities and disease transmission. However, there remain significant challenges related to the study of viral bioaerosols, compared to viruses in other environments such as water, humans, and soil.

Previous research has examined the bacterial and fungal microbiomes in many indoor environments, such as homes, workplaces, retail stores, schools, and hospitals; however published studies on the viral microbiome in indoor air have been limited. One hotbed of combined microbiological and human activity is daycare centers, which are likely to harbor numerous and diverse microbes in the indoor environment, thanks in part to the activities of young children who have not yet gained the ability or willingness to control their bodily fluids. Children that attend daycare centers are at two to four times greater risk of developing infectious diseases and get sicker than children cared for at home. We provide a perspective on the importance of studying viral bioaerosols, the challenges of studying community structure, and preliminary results of the viral and bacterial microbiome of indoor air in a daycare center. Initial results demonstrate the high-relative abundance of Propionibacteria phages in air and the dominance of transport of viral community structure.

8BA.9

Fluorophore-Tagged Reagents for Aerosol Experiments.

CYNTHIA J. KAESER, Elizabeth K. Wheeler, Joanne J. Osburn, A. Daniel Jones, George R. Farquar, *Lawrence Livermore National Laboratory*

Fluorophore-tagged particles have been developed to expand the suite of human-safe bioaerosol simulants to include simulants for fluorescence biodetector testing. Combining the FDA-approved saccharide food additives used as the bulk material in the R&D100 award-winning DNA-tagged biosimulant DNATrax with naturally fluorescing amino acids and vitamins, the modified tags make this simulant suitable for fluorescent-based biodetector network evaluation and aerosol transport studies while being biodegradable and safe for human exposure.

Many currently available biodetectors take advantage of the natural fluorescence of aromatic amino acids and use a combination of ultraviolet laser induced fluorescence (UVLIF) with light scattering size determination to identify bioaerosol threats and unknown aerosols with similar characteristics. When testing biodetectors, the biosimulant used must maintain the typical size range of bioaerosol threats (1 to 10 micro-meter) and have fluorescent labeling adequate for detection. Typical biosimulants used for this purpose are spore surrogates for Bacillus anthracis or fluorescent-labeled synthetic polymer beads. While anthrax spore surrogates including B. atrophaeus (formerly B. globigii) and B. subtillis provide the complex fluorescence spectrum associated with biological threat agents and synthetic beads provide spectral customization, both have limited use in high traffic areas due to safety concerns. Prepared from food-grade saccharides safe for human exposure as the bulk material, these particles are demonstrated to have the desired morphology and tunable fluorescence.

To achieve the tunable emission spectra, several fluorophores were combined in various amounts according to simple algorithms. The resulting combinations shift the wavelengths of the major peaks observed when using a 266 nm excitation wavelength. The fluorescent intensity of each particle was also tunable by adjusting the amount of the fluorophore tags added while keeping the ratio of fluorophores constant. This presentation will discuss the utilized particle production and fluorescent characterization methodologies.

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8BA.10

Generation and Characterization of Large Particle Aerosols Using the Center Flow Tangential Aerosol Generator for Nonhuman Primate Aerosol Models.

KYLE BOHANNON, Matthew Lackemeyer, Jens Kuhn, Jiro Wada, Lisa Hensley, Peter Jahrling, Reed Johnson, *NIAID*

Aerosol droplets of saliva and other respiratory secretions ranging from .05-500 micro-meter can be generated from coughing, sneezing, talking, and exhalation. These droplets can vary in particle size and have the potential to carry infectious viruses and bacteria. To improve public health preparedness and medical countermeasure development for airborne microorganisms, a well characterized animal model is required to develop prophylaxis and therapeutics. Generally, non-human primates (NHPs) are the desired animal model of choice for studying the infectivity of inhaled infectious agents. Very few NHP studies have examined the correlation of bioaerosol particle size and infectivity using particles ranging from 1 to 20 micro-meter. In general, aerosol generation of small particles (<3 micro-meter) penetrate deep within the alveolar region, whereas aerosolization of large particles (7-10 micro-meter) move within the nasopharyngeal region, depositing within the nose, mouth, pharynx, and larynx. Particles that are intermediate in size (3-6 micro-meter) will deposit within the tracheobronchial region. Controlling the particle size and evaluating the site of infection will further refine the NHP models and thus facilitate countermeasure development. The purpose of this research is to provide a simple, viable method to generate and deliver large particle aerosols using the Center Flow Tangential Aerosol Generator (CenTAG, CH Technologies Inc., USA). The CenTAG is a large particle aerosol generator that can produce aerosol particles ranging from 5-14 micro-meter in size. Testing different regional deposition patterns in a NHP respiratory tract can improve experiments in determining an infectious dose that mimics human disease in a NHP aerosol model.

8BA.11

Non-Human Primate Model Development Using Large Particle Aerosolized Cowpox Virus.

MATTHEW LACKEMEYER, Kyle Bohannon, Amy Papaneri, Gary Sparks, Reed Johnson, Peter Jahrling, *NIAID*

Zoonotic orthopoxvirus infections continue to be a threat to public health in numerous countries. For instance, cowpox and monkeypox viruses are endemic in Europe and Africa, respectively, where they have caused repeated human infections, sometimes with grave consequences. In addition, orthopoxviruses are considered possible starting materials for the construction of biological weapons. To improve public-health preparedness and medical countermeasure development, well characterized nonhuman primate models need to be established for human orthopoxvirus infections. Aerosolization represents the most natural route of infection for orthopoxviruses and would also be the most likely route of infection during an intentional biological attack. For countermeasure licensure, the US Food and Drug Administration (FDA) asks for drug evaluation in animal models that mimic the natural course of the targeted disease, including infection route. Aerosol particle size and respiratory tract deposition play a key role in disease course, presentation, and time to death. In general, aerosol generation of small particles (<3 micro-meters) penetrate deep within the alveolar region, whereas aerosolization of large particles (7-11 micro-meters) move within the nasopharyngeal region, depositing within the nose, mouth, pharynx, and larynx. Particles that are intermediate in size (3-6 micro-meters) will deposit within the tracheobronchial region. Controlling the particle size and evaluating the site of infection will further refine the development of aerosol nonhuman primate models for orthopoxvirus infections and thus facilitate medical countermeasure development. We previously established a small-particle cowpox virus aerosol exposure model, which unfortunately did not mimic human disease. Here we present the results of a similar study in rhesus monkeys challenged with four distinct large particle aerosols.

8BA.12

Quantum Cascade Laser Cavity Ring Down Spectroscopy: New Method for the Characterization and Detection of Aerosols.

Erin M. Durke, ANGELA M. BUONAUGURIO, Jason Edmonds, *Edgewood Chemical Biological Center*

Aerosolized chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) are potential threats for the warfighter, resulting in the need for aerosol identification and detection for further developments in protection and mitigation. One of the most reliable techniques for the identification of trace gas species is absorption spectroscopy. Cavity ring down spectroscopy (CRDS) is a highly sensitive and selective absorption method with the ability to detect trace levels of chemical species. Its advantage is based on the extremely long effective path length, providing precise detection of the rate of decay of light from a high finesse optical cavity to directly measure the absorption of the trace gas. The mid-wave (MWIR) and long-wave (LWIR) infrared regions are of particular interest due to the characteristic rotovibrational absorption bands exhibited in these regions for identification of a species. Quantum cascade lasers (QCLs) have the capability of emitting both infrared wavelength regions, of 3-8 µm and 8-15 µm, respectively. During the first year of this multi year effort, we have developed a new method for the characterization of aerosols by combining the highly powerful spectroscopic method of cavity ring down spectroscopy and the ability to detect in the IR fingerprint region using quantum cascade lasers for identification. This novel technique results in in situ investigations of chemical aerosols. The development of this method and preliminary data on accepted test vapors and simulants, leading up to aerosols of chemical warfare agents, are presented.

8BA.13

Simultaneous Real-time Fluorescence and Microscopy Measurements of Bioaerosols during the BIODETECT 2014 Campaign in Paris Area. DOMINIQUE BAISNEE, Michel Thibaudon, Raphaelle Baumier, Gavin McMeeking, Greg Kok, David O'Connor, John Sodeau, J. Alex Huffman, Walfried Lassar, Kyle Pierce, Martin Gallagher, Ian Crawford, Georges Salines, Roland Sarda-Esteve, *CEA*

During the BIODETECT 2014 intensive campaign which was conducted at CEA/LSCE SUPERSITE (suburban) and LHVP Paris (urban), simultaneous measurements of particulate matter below 10 micron in size (PM10) were made using real-time fluorescence and microscopy-based methods. One of the objectives of the BIODETECT 2014 intensive campaign at these two sites was to evaluate the ability of a Wide Band Integrated Bioaerosol Sensor (WIBS) to detect bioaerosol events in suburban/urban sites impacted frequently by pollution events. The microscopic identification of bioaerosols was done by the National Network of Survey for Airborne contaminants (RNSA) to identify pollens and fungal spores. This network has more than 25 years of experience in the fast detection and identification of the species present in the atmosphere using a pollen/fungal spores trap. The multiple WIBS instruments used here were inter-compared and calibrated at CEA. We present here the experimental strategy that we used to constrain the WIBS fluorescence measurements and the preliminary results obtained from the one month experiment. One important result is that the WIBS can track bioaerosols events including pollen and fungal spores even when air masses are heavily impacted by traffic emissions.

More work is needed to do a source apportionment of fluorescent contributors and to define which co-located measurements are needed to constrain the LIF method for the improved detection of bioaerosols.

This work is supported by the CBRN-E R&D research program from CEA/DAM

8BA.14

BIODETECT 2014 Campaign in Paris Area: Overview of the Experimental Strategy and Preliminary Results. ROLAND SARDA-ESTEVE, J. Alex Huffman, Martin Gallagher, Michel Thibaudon, Dominique Baisnee, Raphaelle Baumier, Gavin McMeeking, Greg Kok, John Sodeau, David O'Connor, Ian Crawford, Michael Flynn, Sampo Saari, Ulrich Poeschl, Olivier Favez, Tanguy Amodeo, Jean Sciare, Nicolas Bonnaire, Walfried Lassar, Kyle Pierce, Cédric Chou, Allan Bertram, Georges Salines, Jean-Maxime Roux, et al., *CEA*

During summer 2014 (June to August) the BIODETECT 2014 campaign took place at two sites in the region of Paris, France: CEA/Saclay (suburban) and Paris/ LHVP (urban). A set of innovative fluorescence instruments have been deployed to compare their ability to detect and characterize in real time the bioaerosol present in urban and suburban atmospheres. All on line fluorescence instruments were calibrated with the same, fresh sets fluorescent polystyrene latex (PSL) spheres at the start, middle, and end of the campaign for quality control. To understand atmospheric and biological processes involved in the fluorescent particulate matter observed, microscopic identification and collection onto species-specific agar gelwas performed every 30 minutes during several periods of the campaign. Analysis of chemicals tracers (e.g. arabitol, mannitol) was performed by a novel real-time technique to track specific fungal spores events by coupling a Particle Into Liquid Samples (PILS) to a triple quad mass spectrometer (ABSCIEX). The sampling sites were often impacted by anthropogenic sources and pollution events from Paris. To constrain the data set a full range of instruments commonly used in atmospheric science were used. PM1 mass in each of several common chemical fractions (e.g. sulfate, nitrate, organics, chloride) was provided via ACSM. Also recorded was: size distribution of particle number between 10 nm to 20 µm (TSI, SMPS and APS), total aerosol mass (TEOM-FDMS), combustion tracers (Aethalolmeter AE33), and traces gases measurements like VOC (PTRMS) NOx and Ozone (Teledyne). Ice nuclei (IN) studies have been performed to identify size-resolved concentrations of IN.

We present here our preliminary results on the inter-comparison methods to detect bioaerosols in the atmosphere.

This work is supported by the CBRN-E R&D research program from CEA/DAM.

8BA.15

BIODETECT 2014: Ambient Observations by a Comprehensive Suite of Light-induced Fluorescence Techniques during Summer Near Paris, France.

WALFRIED LASSAR, Roland Sarda-Esteve, Kyle Pierce, Martin Gallagher, Ian Crawford, John Sodeau, David O'Connor, Gavin McMeeking, Greg Kok, Ulrich Poeschl, Jean Sciare, Dominique Baisnee, Sampo Saari, J. Alex Huffman, *University of Denver, CO*

A comprehensive international measurement campaign (BIODETECT 2014) was performed on institute roofs at two contrasting sites near Paris, France. This work was supported by the CBRN-E R&D research program from CEA/DAM. Site one was at the CEA/LSCE SUPERSITE on the plateau of Saclay (20 km south-west of central Paris) and the second site was Le laboratoire d'hygiène de la Ville de Paris (LHVP) in the heart of urban Paris. Measurements took place during late June through early August 2014. The central goal of this campaign was to determine the degree to which existing Light-Induced Fluorescence (LIF) technologies can detect bioaerosols within a complex urban environment. The focus of this poster will be an overview of measurements by LIF instruments, primarily WIBS (Wideband Integrated Bioaerosol Sensor) and UV-APS (ultraviolet aerodynamic particle sizer), with respect to observations of diurnal patterns, changes with respect to fluctuating meteorological conditions and influence from urban Paris. Single particles analyzed by the WIBS can be categorized based on the relative fluorescence intensity present in each of the three fluorescence channels, and cluster analysis can further compartmentalize observed particles to reduce data complexity. Preliminary findings will be presented. Novel experiments with UV-APS allowed for investigation of the role the instrument detector gain plays in the determination of particle fluorescence. The gain on the photomultiplier tube (PMT) was systematically ramped, and resultant fluorescent particle numbers were compared with WIBS and other LIF instruments. This alteration of the PMT gain of the UV-APS was an attempt to answer the technical question about whether the higher gain would enhance the ability of the instrument to see weakly fluorescent particles, or simply increase noise.

8BA.16

A Global Overview of Measurements of Fluorescent Biological Particles Using Ultraviolet Aerodynamic Particle Sizer (UVAPS) and Wideband Integrated Bioaerosol Sensor (WIBS).

KYLE PIERCE, Niall Robinson, Ian Crawford, Martin Gallagher, David Healy, David O'Connor, John Sodeau, Miia Hiltunin, Markku Kulmala, Warren Stanley, Paul Kaye, Carolyn J. Schumacher, Paulo Artaxo, Meinrat O Andreae, J. Alex Huffman, *University of Denver*

Biogenic and biological aerosols are ubiquitous in the Earth's atmosphere, influencing atmospheric chemistry and physics, the biosphere, climate, and public health. Systematic global measurements of airborne bioaerosols have been relatively rare, however, contributing significant uncertainty to our understanding of their properties and effects. The recent development of instruments capable of detecting biological aerosols in real-time have enabled detailed ambient observations.

The ultraviolet aerodynamic particle sizer (UV-APS) and wideband integrated bioaerosol sensor (WIBS) were deployed at a variety of measurement sites on five continents over the last decade to observe trends in fluorescent biological aerosol particles (FBAP) in a host of different environments. Most studies showed exhibited average peaks at ~3 micro-meter in size and diurnally in the early morning, with an average mass concentration on the order of 1 microgram m^3 . This continuity suggests that the number concentration of bioparticles over vegetated regions may be dominated by fungal spores or agglomerated bacteria within a relatively narrow size range. A analysis of these global measurements and trends will be shown.

8BA.17

Seasonal and Spatial Variation of Bioaerosols in Midwestern United States. CHATHURIKA RATHANYAKE, Nervana Metwali, Zach Baker, Peter Thorne, Patrick O'Shaughnessy, Thilina Jayarathne, Pam Kostle, Elizabeth Stone, *University of Iowa*

This study examines the temporal and spatial variation of bioaerosols using six sites in Iowa. Coarse particulate matter (PM_{10}) samples were collected at three urban sites (Davenport, Waterloo and Council Bluffs) and three background sites (State parks of Lake Sugema, Backbone and Viking Lake) during January, April, July and October in 2012. Samples were analyzed for chemical and biological tracers of fungal spores, pollens, bacteria, and animal detritus. Fungal spore tracers (arabitol, mannitol and fungal glucans) were highest in July, elevated in April, October and lowest in January. Significant correlation was observed between mannitol and arabitol ($p<0.001$, $r=0.8$) and a moderate correlation observed for mannitol and fungal glucans ($p<0.001$, $r=0.4$) during spring summer and autumn, indicating similar sources. Fungal glucan levels were significantly higher at urban sites compared to background sites ($p<0.001$) as determined by a paired t-test. Bacterial endotoxins peaked in October (0.5 ± 0.3 EU m-3), averaged 0.3 and 0.2 EU m-3 at urban and rural sites, respectively, and had a significant urban excess ($p=0.001$). Monthly average total protein concentrations ranged 0.9 – 3.8 µg m-3 (measured against bovine serum albumin standards) peaked in July and also had an urban excess ($p<0.001$). Our spatial analysis revealed urban enhancements of bioaerosols in Iowa, which are expected to be related to increased human activities that create bioaerosols in urban areas. The observed seasonal variation of fungal spore tracers and proteins is attributed to the greater extent of vegetation during summer and autumn, while peak endotoxin levels are attributed to agricultural dusts released during the harvesting season.

8BA.18

Evaluation of the WIBS-4A for Biodefense-Related Applications. ELIZABETH CORSON, Jonathan Eshbaugh, David Drewry, *Johns Hopkins University Applied Physics Laboratory*

The Ultraviolet Aerodynamic Particle Sizer (UVAPS, TSI Inc.) has been utilized by the bioaerosol defense community for many years. The UVAPS measures single particle aerodynamic size, concentration, and fluorescence at 355 nm, parameters which are especially useful for the study of bioaerosols. In recent years, alternative bioaerosol measurement instruments have become available, including the Wideband Integrated Bioaerosol Sensor (WIBS-4A, Droplet Measurement Technologies Inc.), which has been used extensively for environmental research. The WIBS-4A provides measurements of particle size, particle aspect ratio, and fluorescence at two excitation wavelengths, 280 nm and 370 nm. The additional fluorescence measurement could aid in better discrimination of biological and non-biological particles. To better understand the utility of the WIBS-4A, various substances of interest, including Bacillus thuringiensis spores, vegetative bacteria, fluorophores, and environmental background, were aerosolized in the laboratory and measured with both the UVAPS and the WIBS-4A. Additionally, measurements of a vegetative bacteria aerosol exposed to ozone, relative humidity, and UV light, conditions known to change the fluorescence signature, were made with both instruments. Particle size, concentration, and fluorescence measurements from both instruments were compared and contrasted to explore the benefits as well as the limitations of the WIBS-4A in the context of defense-oriented applications. Due to differences in system design between the UVAPS and the WIBS-4A, the data they produce need to be interpreted differently, and methods for data interpretation are explored. With additional data channels as well as a compact form factor, the WIBS-4A has the potential to offer valuable insight into bioaerosols of interest to the defense community.

8BA.19

Leveraging Real Time Fluorescence Pattern Recognition of Airborne Biological Particles a National Reconnaissance and Database of Water Damaged Buildings.

Darrel Baumgardner, Kevin McCabe, Greg Kok, Gary Granger, Matthew Coghill, MARK T. HERNANDEZ, *University of Colorado Boulder*

Storm and flood damage to the US domestic building stock has significantly increased because of flood zone construction practices, as well as changing climate patterns. The USGS estimates that in the years between 1934 and 2001 the costs of storm associated damage to US buildings followed an increasing trend from less than $ 0.5B to more than $ 3B/yr when normalized to 1995 US Dollars. The incidence of human disease has been reported to increase markedly following residential flooding as well and adverse environmental risks have been associated with occupation of damp and water damaged buildings. Indoor (bio)aerosol exposures have not been extensively documented other than culture-based techniques in this context. 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. In this context, a new generation of commercial UV-LIF instruments has demonstrated the utility of particle fluorescence in a multitude of field trials; however, 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 germane to public health in large cohort of flood damaged buildings across the US.

Distinct patterns of airborne fluorescent particle signatures were disaggregated by room, and resolved from more than 2000 observations inside water damaged buildings. These observations were log-normally distributed, with clear distinctions between room type in commercial and residential environments. When calibrated to chamber studies of a library of the most commonly occurring airborne fungi, optical spectra associated with bioaerosols can be compiled into useful databases and distributions, which may be leveraged—in real time—to denote significant deviations from indoor air norms.

8BB.1

Contribution of Biomass Burning to the Total Organic Aerosol in the Eastern Mediterranean.

AIKATERINI BOUGIATIOTI, Iasonas Stavroulas, Evangelia Kostenidou, Francesco Canonaco, Spyros Pandis, Athanasios Nenes, Nikolaos Mihalopoulos, *Georgia Institute of Technology*

The contribution of biomass burning to the total organic aerosol was studied at the remote background site of Finokalia, Crete for a period of 16 months (June 2012 to December 2013). The study is based on measurements performed using an Aerosol Chemical Speciation Monitor (ACSM) and the resulting organic components identified by Positive Matrix Factorization (PMF) analysis of the organic mass spectra. Different factors and subsequently different sources are identified depending on the season, each factor having varying contribution to the total organic aerosol (OA). Based on PMF analysis, long-range transport of biomass burning from Southeastern Europe and countries surrounding the Black Sea influences the site during two periods (April-May and July-September). The contribution of the fresh BBOA factor during these periods is on average 17.1±2.2% to the total OA. A distinct regional source of olive tree branches burning, which is a common agricultural waste management practice in the Mediterranean area after the annual pruning of olive trees, is also identified from November to February (not included in the aforementioned BBOA). The main difference between the mass spectrum of the olive tree branches burning and other published biomass burning spectra is the almost equal intensities of m/z 43 and 44 and the lower intensity of m/z 60. The olive tree branches burning factor may contribute up to 48% to the total identified OA during wintertime. This source can be regarded as an important during this season in the Mediterranean area, as the olive tree branches burning mainly takes place when there is no rainfall or high wind speeds, which could scavenge the produced particulate matter.

8BB.2

Assessment of Alternatives to Indoor Stove Use on the Navajo Nation. WYATT CHAMPION, Barbara Klein, Perry Charley, Avery Denny, James McKenzie, Kathleen Stewart, Paul A. Solomon, Lupita Montoya, *University of Colorado Boulder*

The combustion of wood and coal indoors is prevalent in the Navajo Nation, due largely to the low cost and availability of these fuels. The pollutants produced from the combustion of these solids fuels, principally fine particulate matter (PM2.5), have been associated with negative health effects in humans including asthma exacerbation, chronic obstructive pulmonary disease (COPD), and increased mortality. Through the identification and implementation of heating alternatives for the Navajo Nation, pollutants emitted indoors (and their subsequent transport outdoors) can be decreased, potentially improving the respiratory and circulatory health of residents. Some of the alternatives identified include integration of active and passive solar technologies, the use of gas stoves for heating, and the repair and insulation of exiting solid-fuel stoves. Cultural acceptance, economic considerations, and other limitations were assessed for each of the alternatives, and recommendations were made for future heating interventions. The characterization of emissions from the combustion of the solid fuels used in the Navajo Nation has been proposed as well, using an Aprovecho Portable Emissions Monitoring System (PEMS) and standardized protocols. The emissions of particulate matter (PM), carbon monoxide (CO) and elemental constituents from wood and coal combustion are being characterized and their potential health effects evaluated. Energy access in Native Nations is complex, but an appreciation of cultural and economic limitations can be useful for assessing the effectiveness of proposed energy alternatives.

8BB.3

Photochemical Processing of Secondary Organic Aerosol Precursors in Biomass Burning Smoke Measured by Comprehensive Two-Dimensional Gas Chromatography. LINDSAY E. HATCH, Wentai Luo, James F. Pankow, Daniel S. Tkacik, Adam Ahern, Rawad Saleh, Ellis Shipley Robinson, Allen Robinson, Ryan Sullivan, Neil Donahue, Robert J. Yokelson, Anton Rusanen, Ditte Mogensen, Sampo Smolander, Michael Boy, Kelley C. Barsanti, *Portland State University*

Biomass burning (BB) is the second largest source of volatile organic compounds (VOCs) worldwide; such VOCs may undergo photochemical processing leading to secondary organic aerosol (SOA) formation. Previous studies have demonstrated wide variability in the extent of SOA production in aged BB plumes, likely due to differences in SOA precursors and burn/plume conditions. In this work, we are coupling detailed laboratory measurements and process-level modeling to probe the key variables impacting BB SOA formation. As part of the fourth Fire Lab at Missoula Experiment (FLAME-4) in 2012, smog chamber experiments were conducted on fresh BB smoke from a variety of vegetative fuels. In these experiments, comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GCxGC/TOFMS) was applied for the first time to characterize the identities and reactivities of BB VOCs. Our highly speciated measurements of gas-phase species using GCxGC/TOFMS, in conjunction with co-located real-time gas- and particle-phase instrumentation, can better assess the role of specific isomers (e.g., monoterpenes) and non-conventional precursors in leading to SOA formation in BB plumes. Further advancements can be achieved by coupling these measurements with process-level modeling. Thus, we are applying a detailed aerosol box model, which includes a near explicit description of gas-phase chemistry (using the Master Chemical Mechanism) and iterative gas-particle partitioning, to further investigate the critical reaction pathways and atmospheric conditions that influence BB SOA production. Here we present a synthesis of measurement and modeling results for the aging of black spruce smoke.

8BB.4

Climatic Implications of Peat Fire Emissions. Adam Watts, Rajan K. Chakrabarty, Vera Samburova, HANS MOOSMULLER, *Desert Research Institute*

Globally, organic soils and peats may store as much as 600 Gt of terrestrial carbon, representing 20 – 30% of the planet's terrestrial organic carbon mass. This is approximately the same carbon mass as that contained in Earth's atmosphere, despite peatlands occupying only 3% of its surface. Effects of fires in these ecosystems are of global concern due to their potential for enormous carbon release to the atmosphere. The implications for contributions of peat fires to the global carbon cycle and radiative forcing scenarios are significant. The mostly smoldering combustion of peats consumes carbon that may have accumulated over a period of hundreds to thousands of years. In comparison, combustion of aboveground biomass fuels releases carbon that has accumulated much more recently, generally over a period of years or decades.

Here, we focus on laboratory characterization of emissions from smoldering combustion of peat soils from three locations representing the various biomes in which these soils occur (boreal, subtropical, and tropical). Small amounts of soil (<200 g) are being burned in the DRI biomass burning facility. Carbon dioxide and monoxide and aerosol mass emissions are being quantified. Radiative properties of aerosol emissions are characterized with a multi-wavelength photoacoustic spectrometer and nephelometer [Moosmüller et al., 2009]. Particle concentration and size are being measured using an electrical low-pressure impactor (ELPI). Subsamples of particulate matter (PM) collected on filters will be used for chemical analysis and morphological examination using electron microscopy [Chakrabarty et al., 2006]. Radiative forcing of peat burning emissions will be estimated using simple analytical equations.

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8BB.5

Hygroscopicity and Cloud Condensation Nucleation Activity of Fresh Biomass Burning Aerosol: Black Carbon Mixing States. SHUNSUKE NAKAO, Ezra Levin, Gavin McMeeking, Christian Carrico, Thilina Jayarathne, Elizabeth Stone, Sonia Kreidenweis, *Colorado State University*

Biomass burning is an important source of atmospheric black carbon (BC). The atmospheric lifetime of BC depends on its ability to act as cloud condensation nuclei (CCN), which is governed by the hygroscopic coatings and particle size. Due to the strong dependence of CCN activities on biomass fuel types, it is essential to investigate the wide range of fuel types in well-controlled systems. During the fourth Fire Laboratory at Missoula Experiments (FLAME 4) study, we examined the single hygroscopicity parameter kappa of biomass burning aerosol emitted by the open combustion of 17 different biomass fuels. In addition to the conventional hygroscopic growth measurements and size-resolved CCN measurements, we determined the hygroscopicity of particles with and without BC-core individually by applying the recently developed combination of the Hygroscopicity Tandem Differential Mobility Analyzer – Single Particle Soot Photometer (HTDMA-SP2) (McMeeking et al., ACP, 2011), in which particles were first separated by the HTDMA based on the hygroscopicity and then the hygroscopic growth factors of particles with and without the refractory BC component were determined based on laser induced incandescence and light scattering. Kappa varied from 0.02 (weakly hygroscopic) to 0.6 (highly hygroscopic) depending of biomass fuel types, in agreement with previous studies. Kappa acquired by the HTDMA and the size-resolved CCN measurement agreed reasonably. HTDMA-SP2 measurements suggested varied extents of particle heterogeneity; overall, most BC-containing particles were inferred to be thickly coated with organics and inorganics, based on the similar kappa values of BC-containing particles and non BC-containing particles. This study suggests that the majority of BC particles emitted during the biomass burning experiments of this study was CCN active at the point of emission.

8BB.6

Characterization of Emissions from the Combustion of Solid Fuels Used in the Navajo Nation and Others relevant to Developing Communities. Charles James, Sandra Garcia-Fine, Barbara Ward, WYATT CHAMPION, Lupita Montoya, *University of Colorado Boulder*

The combustion of solid fuels for heating and cooking contributes to elevated concentrations of indoor particulate matter (PM) in many developing communities, where young children, women, and the elderly usually have the highest exposure to these emissions. High indoor PM has been shown to cause acute and chronic respiratory and cardiovascular disease, among others. Biomass, wood charcoal, and sometimes, coal, are often the most accessible fuels in developing communities. This experimental study characterized the emissions from combustion on fuels used in the Navajo Nation and others relevant to other developing areas. The fuels tested from the Navajo Nation included Black Mesa anthracite coal, Juniper, and Piñon pine. The combustion efficiency and emissions from these fuels were compared to Kingsford charcoal briquettes, wood charcoal, and a charcoal briquette made from pyrolyzed human waste, developed at the University of Colorado. The later is a proposed biofuel for developing communities underserved by sanitation infrastructure. Standardized Water Boiling Tests and emissions monitoring from an Aprovecho Portable Emissions Measurement System, a TSI DusTrak®, and filter sampling for gravimetric, elemental, and carbon analyses were used.

8CA.1

Measured Optical Absorption and Scattering Coefficients of Agglomerates of Coal Fly Ash and Powdered Activated Carbon. TIAN XIA, Akosua Miller, Herek Clack, *University of Michigan*

The most mature technology for controlling mercury emissions from coal combustion is the injection into the flue gas of powdered activated carbon (PAC) adsorbents having chemically treated surfaces designed to rapidly oxidize and adsorb mercury. However, carbonaceous particles are known to have low electrical resistivity which contributes to less efficient capture during electrostatic precipitation, the most widely used method of particulate control for coal-fired power plants worldwide. Our previous analyses provided estimates of likely PAC emissions resulting from the use of PAC injection as a mercury emissions control technique, and their potential climate forcing impact. The present work supports the continued examination of the potential climate forcing effects of fugitive powdered mercury sorbents by measuring optical absorption and scattering coefficients of fly ash and mixed fly ash-PAC aerosols as a function of PAC concentration. The aerosols are elutriated from a partially fluidized bed and sampled and characterized using a novel photoacoustic extinctiometer. SEM imagery of the collected aerosols provides additional insight into the agglomeration state of the mixed aerosols. These results provide the optical property data base needed to evaluate the climate forcing impact of fugitive PAC and establish allowable PAC collection efficiencies and emission rates for coal-fired power plants in the future.

8CA.2

Predicting Ambient Aerosol Thermal Optical Reflectance OC, EC and TC Measurements from Infrared Spectra.

ANN DILLNER, Satoshi Takahama, *University of California, Davis*

Organic aerosol functional group composition in aerosol samples has been measured using infrared spectroscopy (Ruthenburg et al., 2014, Takahama et al., 2013). One method for calibrating infrared spectra for functional group measurement is partial least squares regression (PLSR), a multivariate technique that relates spectral absorbances to the moles of functional groups on standards (Ruthenburg et al., 2014, Reff et al. 2007). The objective of this work is to demonstrate the feasibility of using infrared spectra of aerosol samples and PLSR to predict thermal optical reflectance (TOR) OC, EC and TC measurements of aerosols. Parallel quartz filter samples used for TOR analysis and PTFE filter samples used for infrared analysis from select sites in the IMPROVE network are used in the demonstration. A subset of samples is used to develop the calibration and the remaining samples are used to evaluate the calibration. Various scenarios for selecting the calibration and test sets are evaluated along with comparing two different PLS algorithms (PLS1 and PLS2) and using raw or baseline corrected spectra. The agreement between predicted and observed OC and EC compares well to the agreement between collocated samples analyzed by TOR.

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8CA.3

Uncertainties in Global Aerosol and Climate Forcings from Biofuel Emissions.

JOHN KODROS, Catherine Scott, Salvatore Farina, Jeffrey Pierce, *Colorado State University*

Prevalent use of biofuel as a source of energy for domestic tasks has created concerns for air quality and climate. Successful interventions of improved combustion devices decreases emitted particle concentrations and improves air quality. The net effect of changing emission scenarios on climate remains uncertain. Combustion of wood, agricultural waste, and dung emits black (BC) and organic carbon (OC). BC and OC can alter climate through absorption and scattering (direct effect), altering cloud properties (indirect effect), and altering the temperature profile (semi-direct effect). Recent studies have focused on the positive direct effect from black carbon absorption. Black carbon can also have a cooling effect when activated as a cloud condensation nuclei. The net forcing from BC and OC is dependent on emission mass, size distribution and chemical mixing state. To test the sensitivity of particle number and aerosol radiative forcing to these uncertainties we run a sensitivity study using GEOS-Chem-TOMAS. With the current emission dataset we find biofuel emissions contribute close to 25% of global BC and OC mass. In heavy source regions biofuel contributes more than half of total BC and OC mass. Altering the size distribution leads to changes in particle number of around 10% in source regions. The sensitivity of aerosol number from uncertainties in size are on the same order of removing biofuel emissions. The aerosol indirect effect is dependent on particle number which in turn is dependent on emitted size distribution. Thus, while it is clear combustion improvements will lead to improvements to health, the net result on climate remains uncertain.

8CA.4

Laboratory Evaluation of Black Carbon Aerosol Deposition to Snow. Larry Hermanson, JOSHUA P. SCHWARZ, Anne Perring, Milos Markovic, David Fahey, *NOAA/CIRES*

Black carbon deposition to and in snow has been identified as a significant forcer of climate with the potential to change snow melt timing and extent with implications for water availability. In ambient measurements, there have been conflicting results about the fate of BC in the snow; some suggest that it can be concentrated at the top of the snow pack, increasing its effectiveness as a light absorber, while other suggest that the BC can be removed from the snow pack with melt. To address these questions, we have conducted measurements of laboratory black carbon aerosol deposition to snow, and eventual removal in melting, under controlled laboratory conditions. Deposition rates as a function of depth in the snow were assessed with a single particle soot photometer (SP2), for both bare and coated BC particles, and coatings of differing water activity. Here we present the early results of these tests.

8CA.5

Primary and Secondary Organic Aerosol during Severe Haze Episodes in January 2013 in Beijing, China. CAIQING YAN, Mei Zheng, Xiaoying Li, Huaiyu Fu, Xiang Ding, Quanfu He, Xinming Wang, *Peking University*

During January 2013, a significant large area in North China Plain experienced several severe hazes including Beijing, the capital city of China. The haze resulted in very poor visibility and it was clearly associated with high PM2.5 mass concentration. The hourly PM2.5 mass concentration measured by Tapered Element Oscillating Microbalance (TEOM) during these episodes was as high as 828µg/m3, and offline 24-h average PM2.5 mass concentration also showed the highest value as 500µg/m3. Characteristics and sources of organic aerosol during these high PM2.5 pollution episodes were discussed. Offline filter samples were analyzed for organic carbon (OC), elemental carbon (EC) by the Sunset ECOC analyzer and various individual organic compounds including some important tracers for carbonaceous aerosol by gas chromatography-mass spectrometry (GC-MS). OC, one of the most important major components in PM2.5, varied from 4 to 80µg/m3. OC concentration increased during haze episode days but its relative importance in PM2.5 decreased (a lower percentage). OC/EC ratio ranged from 2.7 to 10.9, which showed higher influence by secondary organic aerosol during haze periods. The result agreed well with the estimate of secondary organic aerosol from the organic tracer-based method. The contributions of various sources to primary and secondary organic aerosol during our study period were estimated. Sources of primary OA (e.g. dust, biomass burning, coal combustion, vehicular emission etc.) were quantified by the chemical mass balance (CMB) model. Sources of secondary organic aerosols were estimated based on the tracer method with SOA from different VOCs precursors (e.g. isoprene, α-pinene, ß-caryophyllene, and toluene). Our findings indicate that these haze periods were associated with high relative humidity, and inorganic ions such as sulfate, nitrate and ammonium increased significantly and became more important in PM2.5. During these haze events, organic aerosol was dominated by secondary organic aerosol while in clean days, primary organic aerosol was more important in OA, providing supportive evidence that secondary components played a very important role in haze episodes.

8CA.8

Evaluation of Black Carbon and Carbon Monoxide Levels at Low Traffic Sites in Tijuana-Tecate, Mexico Air Basin.

Jesus Guerrero-García, Guillermo Rodríguez-Ventura, JAVIER EMMANUEL CASTILLO-QUIÑONES, Lilia Hurtado, Penelope Quintana, Miguel Zavala, Luisa Molina, *Universidad Autónoma de Baja California*

Recent studies in CalMex 2010 shown that black carbon (BC) is an important pollutant associated to PM2.5 and CO emission in Tijuana air basin. State Report of Air Emissions, for Tijuana-Playas de Rosarito region, estimates emissions of PM2.5 and CO are 76,873.7 and 5,936.9 tons/year respectively. This study aimed to compare BC levels in low traffic urban air of Tijuana-Tecate region, to investigate the distribution of BC and CO to provide scientific information needed in mapping out, an appropriate air quality management. Measuring was carried out by an aethalometer at one low traffic site in Tijuana and one in Tecate, Mexico during two periods between January and February 2013. Meteorological and CO concentrations data were provided from the Monitoring Stations of the Secretary of Environmental Protection of Baja California (SPABC). In general, BC and CO average hourly concentration in Tijuana site was 1.07 µg/m3 and 1.52 ppm appeared to be higher than Tecate site with 0.32 µg/m3 and 0.56 ppm respectively.

Time series for BC and CO shown high Spearman correlations for Tijuana site ($r_s = 0.84$, $p<0.05$) and ΔBC/ΔCO = 1.03 µg m-3 ppm-1, and for Tecate site ($r_s = 0.64$, $p<0.05$) and ΔBC/ΔCO = 0.61 µg m-3 ppm-1. Prevalent wind direction in this study suggests BC and CO transport from Tijuana to south Tecate municipality. BC diurnal concentration showed a similar behavior like other urban areas with higher levels in weekdays than weekends, except in Tecate site.

8CA.9

Global Modeling of SOA: The Use of Different Mechanisms for Aqueous Phase Formation.

GUANGXING LIN, Joyce Penner, Sanford Sillman, Akinori Ito, *University of Michigan*

There is growing interest in the formation of secondary organic aerosol (SOA) through condensed aqueous phase reactions. In this study, we use a global model (IMPACT) to investigate the potential formation of SOA in the aqueous phase. We compare results from several multiphase process schemes with detailed aqueous phase reactions to schemes that use a first order gas-to-particle formation rate based on uptake coefficients. The predicted net global SOA production rate in cloud water ranges from 13.1 Tg/yr to 46.8 Tg/yr while that in aerosol water ranges from -0.4 Tg/yr to 12.6 Tg/yr. The predicted global burden of SOA formed in the aqueous phase ranges from 0.09 Tg to 0.51 Tg. A sensitivity test to investigate two representations of cloud water content from two global models shows that increasing cloud water by an average factor of 2.7 can increase the net SOA production rate in cloud by a factor of 4 at low altitudes (below approximately 900 hPa). We also investigated the importance of including dissolved iron chemistry in cloud water aqueous reactions. Adding these reactions increases the formation rate of aqueous phase OH by a factor of 2.6 and decreases the amount of global aqueous SOA formed by 31%. None of the mechanisms discussed here is able to provide a best fit for all observations. Rather, the use of an uptake coefficient method for aerosol water and a multi-phase scheme for cloud water provides the best fit in the Northern Hemisphere and the use of multiphase process scheme for aerosol and cloud water provides the best fit in the tropics. The model with iron chemistry under predicts oxalate measurements in all regions.

8CA.10

Mass and Energy-Based Emission Factors and Gas-Particle Partitioning of Intermediate-Volatility and Semi-Volatile Organic Compounds from Laboratory Combustion of Boreal and Sub-Tropical Peat. LAXMI NARASIMHA YATAVELLI, L.-W. Antony Chen, Joseph Knue, Vera Samburova, Madhu Gyawali, Adam Watts, Rajan K. Chakrabarty, Hans Moosmuller, Xiaoliang Wang, Barbara Zielinska, Judith Chow, John Watson, Anna Tsibart, *Desert Research Institute, Reno*

Peatlands contain up to a third of the Earth's terrestrial soil carbon, approximately equal to the mass of carbon in the atmosphere. Combustion of peatlands is believed to be a large source of gas and particulate matter (PM) emissions. The influence of climate change on fire frequency and intensity, and thus emissions, in peatlands is not fully understood. Warming and anthropogenic land-use changes may accelerate fire regimes in these ecosystems. To better characterize peat combustion emissions and evaluate their impacts on the atmosphere, series of burns were conducted in an 8 m3 combustion chamber at the Desert Research Institute, Reno, NV. Peats from Alaska and Florida (USA) and Siberia (Russia) were burned at two different fuel moisture levels. Real-time measurements included CO2, CO, NOx (NO and NO2), and SO2 concentrations, PM size-distributions, PM and black carbon mass concentrations, and aerosol light-absorption and scattering coefficients. In addition, Teflon-membrane, quartz-fiber, and Teflon-impregnated glass fiber (TIGF) filters followed by XAD-4 cartridges were collected for detailed chemical analysis. To estimate mass- and energy-based emission factors, change in fuel mass and infrared energy emissions were continuously monitored during each burn.

Here, we will present mass and energy-based emission factors of inorganic gases, PM2.5 (aerodynamic diameter <2.5 μm) and black carbon mass concentrations, organic and elemental carbon, and a large number of intermediate-volatility (300<c*<c*

8CA.11

Molecular Characterization of Optically Active Organo-Nitrogen Species in Organic Aerosol. CHRIS STANGL, Murray Johnston, *University of Delaware*

Nitrogen-containing organics are thought to be a major contributor to the light-absorbing components of aged secondary organic aerosol (SOA). The formation of these "brown carbon" species is initiated via evaporation of water following uptake of volatile organic compounds by seed droplets containing dissolved inorganic salts. The loss of water creates a supersaturated environment where aqueous-phase reactions can occur, resulting in the formation of photoactive compounds e.g secondary imines (Schiff bases) from carbonyls and ammonia. These organo-nitrogen species are capable of absorbing incident solar radiation, thereby contributing to radiative forcing. Extensive studies have been carried out with glyoxal (C2H2O2), a potential brown carbon precursor that has been shown to form light-absorbing species following reaction with ammonium salts. Initial experiments were performed in which bulk solutions of ammonium sulfate and glyoxal were atomized into droplets, which were passed through a diffusion dryer initiating solvent evaporation. The resulting particles were collected onto a filter, extracted into solution and analyzed by UV-visible absorption spectroscopy and high-resolution electrospray ionization mass spectrometry. UV-VIS analysis of the extracted particulate matter showed large absorbance peaks at 220 nm and 280 nm, with a tail extending into the visible region. ESI-MS analysis of the extracted particulate matter indicated the presence of imidazole, a previously identified brown carbon contributor, along with its derivatives. Current work involves characterization of absorbing species produced via other atmospherically relevant SOA precursors, including monoterpenes (alpha pinene, limonene) as well as other small molecules such as methyl glyoxal. Concurrent measurements of absorption and molecular composition will be achieved by LC-UV-MSMS with high mass resolving power.

8CA.12

Absorption Enhancement of Monodisperse Cook Stove Soot Coated with alpha-Pinene SOA: Measurements and Modeling. Georges Saliba, Adam Ahern, Rawad Saleh, James Liacos, Eric Lipsky, Ryan Sullivan, Allen Robinson, R. SUBRAMANIAN, *Carnegie Mellon University*

Direct radiative forcing by black carbon (BC)-containing aerosols (BCA) is affected by the relative fraction of non-BC material and the particle morphology – collectively referred to as “mixing state”. Bond and Bergstrom (2006) predict a range of absorption enhancements depending on the shell/core diameter ratio of a BC particle coated with non-BC material. Recent field work by Cappa et al. (2012) suggests a lack of absorption enhancement in ambient aerosol, in contrast to laboratory experiments using flame-generated BC and dioctyl sebacate. We conducted BC mixing experiments using more atmospherically-relevant flaming cook stove soot and a targeted examination of the core/shell space, using mobility size-selected soot and coating it with alpha-pinene secondary organic aerosol (SOA), generated in a 2 m^3 Teflon chamber after injection and characterization of the nascent soot. A suite of instruments, including two photoacoustic extinctiometers (PAX-405, PAX-532), an SMPS, a soot particle aerosol mass spectrometer (SP-AMS), and a single-particle soot photometer (SP2) were used to characterize three nascent core diameters (100, 130, and 150 BC nm mass-equivalent diameter) and SMPS-based shell/core diameter ratios from 1.3 to 2.5. Preliminary Mie modeling is in line with experimentally-determined absorption enhancement, within experimental and modeling uncertainties. The leading edge only (LEO) optimization technique is used to determine the coating thickness of BCA. Preliminary results indicate the maximum shell/core diameter ratio based on the SP2 as 1.7-1.8, smaller than the SMPS-determined 2.3-2.5. The poster will explore these differences further.

8CA.13

Emissions from Burning Incense and Dung: Two Unregulated Sources of Brown Carbon in Asia. LAXMI NARASIMHA YATAVELLI, Rajan K. Chakrabarty, Joseph Knue, Madhu Gyawali, Guenter Engling, Hans Moosmuller, David Rhode, L.-W. Antony Chen, Xiaoliang Wang, Judith Chow, John Watson, *Desert Research Institute, Reno*

Emissions from residential cooking fires and cultural burning are unregulated and can be a large source of gases and carbonaceous particles in Asia. Incense and dung burning is wide spread in South and East Asia but there is limited information on emission factors of intermediate and semi-volatile organic compounds. These, primarily indoor, sources also pose significant health risks due to human exposure to toxic gases such as carbon monoxide (CO), oxides of nitrogen (NOx = NO + NO2) and particulate matter (PM) in high concentrations. There are very few systematic studies on estimating the regional impacts of incense and dung burning on air quality and climate. We will present inorganic and organic emissions from laboratory combustion of incense from India and dung from Tibetan Yak and Sheep. Burns were conducted in a 8 m3 combustion chamber at the Desert Research Institute, Reno, NV. A mixture of five different kinds of incense sticks was burned to simulate cultural burning in religious places. Dung burning was tested with two different stove types: a three-stone setup and a small, commercially available metal stove. Real-time measurements included CO2, CO, NO, NO2, and SO2 concentrations, PM size-distributions, PM and black carbon mass concentrations, and aerosol light-absorption and scattering coefficients. In addition, Teflon-membrane, quartz-fiber, and Teflon-impregnated glass fiber (TIGF) filters followed by XAD-4 cartridges were collected for detailed chemical analysis. Emissions of volatile, intermediate volatility, and semi-volatile organics (VOC, IVOC, and SVOC) will be presented in gas and particle-phases. Emission factors for chromophoric functional groups will be discussed along with inorganic gases, PM1, PM2.5, elements, and organic and elemental carbon fractions.

8CO.1

Measured and Modeled Biodiesel Exhaust from Diesel Vehicles: A MOVES2010b Evaluation. JIM DUNSHEE, Britt Holmén, *University of Vermont*

The EPA's MOtor Vehicle Emissions Simulator (MOVES) utilizes second-by-second modal (i.e., acceleration, deceleration, idle, and cruise) vehicle activity patterns to estimate mobile source emissions rates. MOVES estimates emissions rates on the basis of vehicle operating modes (OpModes), which are defined by vehicle specific power (VSP) and vehicle speed. OpMode specific emissions rates in the MOVES relational database are based on statistical and physical relationships between available data from existing emissions research on a wide range of vehicle types and ages operating on different fuels. Certain real-world conditions are not currently well-represented in the MOVES database. This is a growing issue as new vehicle technologies and emissions regulations continue to develop. In particular, MOVES estimated emissions from modern light-duty vehicles fueled by biodiesel blends are presently based on very limited data sources and assume overly simplistic relationships between operational variables and emissions rates.

This work compares the accuracy of MOVES2010b emissions rates by OpMode for a passenger car run on various blends of biodiesel to real-time emissions data (gas and particle phase) collected from a 1.9L Volkswagen diesel engine coupled to an eddy current dynamometer. The engine was run on a transient drive-cycle, developed from on-road data, and fueled by waste cooking oil based biodiesel blends (B0, B10, B20, B50, and B100). Lab collected data of tailpipe emissions rates were binned based on scaled tractive power (STP) to allow for comparison to MOVES VSP-based OpMode emissions rates. Results from this work demonstrate the need to implement new modal emissions data and adjustment factors into the MOVES framework in order to more accurately quantify light-duty biodiesel blend PM emissions. Future work will examine developing an algorithm to convert MOVES PM2.5 emissions estimates to PN emissions rates based on the relationship between PM2.5 (filter) and PN (TSI EEPS) experimental data.

8CO.2

Emissions of IVOC and SVOC from Mobile Sources Using Online Electron Impact Mass Spectrometry. JONATHAN FRANKLIN, Eben Cross, Jesse Kroll, *Massachusetts Institute of Technology*

Intermediate-volatility organic compounds (IVOCs) and semivolatile organic compounds (SVOCs) are efficient precursors to secondary organic aerosol (SOA). However, a detailed understanding of such compounds in the atmosphere has been limited by the lack of fast and reliable measurements targeting I/SVOCs. In order to better understand the emissions of I/SVOCs from mobile sources, here we utilize a recently-developed online electron impact mass spectrometric (EI-MS) technique to characterize the emissions from multiple engines. This instrument targets I/SVOCs by cryo-trapping samples and then thermally desorbing them into a high-resolution time-of-flight mass spectrometer. The mass spectrometer not only quantifies the volatility-separated sample, but also provides ensemble chemical composition (e.g., elemental ratios) with high time resolution, on the order of 10-15 minutes. I/SVOC emissions from both gasoline and diesel fuel engines have been measured as a function of engine operating state and the results will be intercompared with other co-located I/SVOC measurement techniques.

8CO.3

Influence of Jet Fuel Composition on Aircraft Engine Emissions: A Synthesis of Aerosol Emissions Data from the NASA APEX, AAFEX, and ACCESS Missions. RICHARD MOORE, Michael Shook, Andreas Beyersdorf, Chelsea Corr, Scott Herndon, Berk Knighton, Richard Miake-Lye, Kenneth Thornhill, Edward Winstead, Zhenhong Yu, Luke Ziemba, Bruce Anderson, *NASA*

We statistically analyze the impact of jet fuel properties on aerosols emitted by the NASA McDonnell Douglas DC-8 CFM56-2-C1 engines burning fifteen different aviation fuels. Data were collected for this single engine type during four different, comprehensive ground tests conducted over the past decade, which allow us to clearly link changes in aerosol emissions to fuel compositional changes. It is found that the volatile aerosol fraction dominates the number and volume emissions indices (EIs) over all engine powers, which are driven by changes in fuel aromatic and sulfur content. Meanwhile, the naphthalenic content of the fuel determines the magnitude of the non-volatile number and volume EI as well as the black carbon mass EI. Linear regression coefficients are reported for each aerosol EI in terms of these properties, engine fuel flow rate, and ambient temperature, and show that reducing both fuel sulfur content and napththalenes to near-zero levels would result in roughly a ten-fold decrease in aerosol number emitted per kg of fuel burn. This work informs future efforts to model aircraft emissions changes as the aviation fleet gradually begins to transition toward low-aromatic, low-sulfur alternative jet fuels from bio-based or Fischer-Tropsch production pathways.

8CO.4

Predicting Particle Number Emissions from Hybrid-Electric Vehicle Engine Restart Events. KAREN SENTOFF, Britt Holmén, Matt Conger, *University of Vermont*

Particle emissions from motor vehicles have been associated with local air quality issues and human health concerns. Epidemiological studies have indicated exposure to ultrafine particles, measured as particle number as opposed to mass, are linked to cardiovascular and respiratory diseases. Although hybrid-electric vehicles (HEV) have an increasing presence in the on road fleet and have been designed to minimize emissions and energy consumption, little has been done to quantify the real-world tailpipe emissions from these vehicles. Second-by-second data were collected from the tailpipe of a Toyota 2010 Camry hybrid and a conventional vehicle (CV) model equivalent along a 32-mile route in Vermont over an 18-month study period. The vehicles were instrumented with the Total Onboard Tailpipe Emissions Measurement System (TOTEMS), capable of measuring particle number size distributions (TSI EEPS), exhaust flow rate (custom tailpipe adapter), spatial information (Garmin and Geologger GPS), and vehicle engine control unit information (Toyota Techstream Scantool). The HEV, on average, had higher particle number emission rates than the CV, particularly for the urban portion of the route where the HEV was expected to demonstrate improvements over the CV. It has been observed that the HEV internal combustion engine restarts produce peak emissions four times that of stable HEV engine-on operation and 3.5 times that of stable operation in the CV. With many of these restart events occurring in areas with frequent stop-and-go and in close proximity to human activity and pedestrians, closer examination was necessary. The goal of this work was to predict the particle size distributions at HEV engine restart events. Particle size distributions at engine restart were predicted as a function of engine-off time preceding a restart, motor torque, generator torque, vehicle speed, and calculated load. The ability to predict these high emission events may allow for adjustments to the control algorithms of the HEV drivetrain to further prevent restart particle emissions and potential human exposures.

8CO.5

Physicochemical Assessment of Exhaust Emissions from a Light-duty Gasoline Direct Injection Engine Operated with Conventional and Ethanol-blended Fuels. NAOMI ZIMMERMAN, Manuel Ramos, Cheol-Heon Jeong, Krystal J. Godri-Pollitt, James S. Wallace, Greg J. Evans, *SOCAAR, University of Toronto*

Gasoline vehicles are increasingly being equipped with direct injection (GDI) engines in lieu of traditional port fuel injection engines to meet regulatory limits on fuel economy and carbon dioxide emissions in North America and Europe, respectively. Analogous to diesel engines, GDI engines emit large quantities of particles; however, unlike diesel, there are currently no regulatory limits on GDI particulate matter (PM) emissions. Accordingly, future legislation of PM emissions from GDI vehicles requires a comprehensive understanding of GDI exhaust emissions, including the impact of ethanol-blended fuels, which are expected to reduce PM exhaust concentrations.

In this ongoing study, a light-duty GDI engine (2012 Ford Focus) was operated with an engine dynamometer under five driving conditions: cold start, hot start, simulated urban driving, simulated highway cruise, and a simulated passing maneuver. Emissions were generated using ethanol-gasoline blends of commercially available gasoline and anhydrous ethyl alcohol ranging from E0 (0% ethanol) to E85 (85% ethanol).

Exhaust emissions were characterized along three sampling lines: 1) real-time measurement of gaseous regulated (NOx, THC, CO) and unregulated pollutants with an MKS MultiGas 2030-HS FTIR; 2) collection of PM on filters for gravimetric analysis and offline measurement of metal species and elemental and organic carbon concentrations; and 3) dilution in a rotary disk diluter (TSI 379020A) for real-time measurement of particle number concentration and size distribution (TSI 3090), and black carbon concentration (DMT PASS-3). Exhaust concentrations were normalized to fuel-based emission factors for a direct comparison to on-road emission factors measured from GDI-equipped vehicles. This study aims to help forecast the impact of increasing GDI and biofuel integration on traffic-related air pollution levels.

8CO.6

Physical and Chemical Characterization of Fine Particles from Biomass Burning Process (Woods and Rice Straw). HEE-JOO CHO, Shila Maskey, Arom Seo, Kihong Park, *GIST*

Biomass burning process, which includes natural open burning and prescribed burning, is one of the largest source of atmospheric aerosols. Most of the volume is in the accumulation mode (~ 80-90%), consisting of organic carbon (~80%), elemental carbon (~5-9%), and other trace inorganic species (~12-15%) (Reid JS et al., 2005). Chemical and physical properties of biomass burning aerosols mainly varied with fuel types and combustion phases (e.g., flaming combustion versus smoldering combustion). Once they emitted into the ambient atmosphere, their properties will also change with atmospheric aging. In this study, a biomass burning chamber with a dilution system was constructed to simulate various burning processes. Pine and oak woods and agricultural products (e.g., rice straw) obtained from Korea are used as fuel types. Particle size distribution, and hygroscopicity, volatility, and mixing state of biomass burning aerosols are measured with the scanning mobility particle sizer (SMPS) and hygroscopicity and volatility tandem differential mobility analyzer (HVTDMA), respectively. Due to existence of various refractory and non-refractory species in the biomass burning aerosols, our own type of AMS (GIST-AMS), recently developed by our group was used. This AMS employs both thermal vaporization-electron impact ionization and single step laser desorption ionization methods enabling us to measure non-refractory (sulfate, nitrate, ammonium, organics, and etc.) and refractory components (black carbon and heavy metals). Our progress on physical and chemical properties of biomass burning aerosols with varying fuel types and burning conditions will be presented.

8CO.7

Light-Duty Diesel Biodiesel Particle Number Emissions Relative to Blend Ratio and Engine Conditions. 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) (EPA, 06JUL2011). 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 petrodiesel as opposed to neat petrodiesel.

The objective of this research was to quantify the differences in particle number (PN) emissions for a single light-duty diesel engine operating on 5 different fuel blends (B0, B10, B20, B50, and B100). PN 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 and ASTM grade waste cooking oil biodiesel with a TSI Engine Exhaust Particle Sizer (EEPS, 32 channels, 5.6-560nm range). 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 driving conditions in the New England landscape.

The data collected by the EEPS in the UFP range show an increase compared to petrodiesel in particle number throughout the UFP size range for B10, a decrease UFP throughout the size range for B20, followed by subsequent increases of UFP for B50 and B100 below 60nm. This leads to changes in total UFP emissions by factors of 2, 0.85, 1.8, and 3 relative to petrodiesel for B10, B20, B50, and B100 respectfully. In addition to investigating possible mechanisms that could cause such a relationship, the effect of engine operating conditions on UFP emissions were examined.

8EP.1

Development of New PM Test Protocol and Characterization of PM Formation and Growth from Natural Gas Turbines. NICHOLAS GYSEL, William A. Welch, Chia-Li Chen, J. Wayne Miller, David R. Cocker III, *University of California Riverside*

The low levels of PM from natural gas fired turbines present a large challenge for particulate characterization and regulatory control. Current methodology for characterization of PM from stationary sources is limited due to inherent biases. This coupled with inaccuracies, lack of precision and sensitivities to current measurement methods necessitate the need for improved measurement capabilities. This all affects the development of new power plants, as many sites in Southern California are labeled as non-attainment sectors. Ultimately this means that newer power plants must offset the emissions of existing plants to meet the regulated emission requirements. Current protocol methods have limitations due to inherent biases involved with the measurement methodology. The Environmental Protection Agency (EPA) mandated a revision to the definition of PM2.5 in 40 CFR Parts 51 and 52 to include condensable PM (CPM) when referring to New Source Review (NSR) regulations. EPAs implementation of the Clean Air Act (CAA) requires the measurement of total primary particulate matter. That is the filterable portion of PM (FPM) as well as the condensable fraction of PM (CPM). It is therefore necessary to understand the parameters that affect CPM formation and growth and develop a single test protocol that has the capabilities of measuring total primary PM accurately and precisely as current protocol methodology for PM measurements from stationary sources contain biases.

In this study we have developed a dilution method capable of characterizing the instantaneous effects of dilution parameters such as dilution ratio, residence time, dilution temperature and relative humidity on PM growth and formation. Real-time electronic PM instrumentation was used including a nano scanning mobility particle spectrometer (SMPS) and a long column SMPS downstream of the dilution tunnel. We have used this method and have compared it with current protocol methods on a 65 kW micro-turbine, 14 MW and 50 MW commercial turbines equipped with oxidation catalysts and selective catalytic reduction (SCR) aftertreatment control technologies.

8EP.2

Particle Number and Composition Differences From Conventional and Emerging Vehicle Technology on Varying Aromatic and High Octane Fuels. DANIEL SHORT, Diep Vu, Tyler Berte, Georgios Karavalakis, Thomas D. Durbin, Akua Asa-Awuku, *University of California, Riverside*

Engine knock is the abnormal combustion of fuel due to increased fuel pockets that combust after or before the normal combustion window. High fuel octane ratings can reduce knock in the gasoline internal combustion engine. Ethanol and specific aromatic compounds are octane boosters found in gasoline today. Changes of fuel aromatic compounds can have significant impacts on particle composition such as Water-Soluble Organic Carbon (WSOC) and Black Carbon (BC). These particular particle compositions could alter Cloud Condensation Nuclei (CCN) activity and have detrimental human health effects when inhaled.

Our study has measured the Particulate Matter (PM) emissions from a 2012 Honda Civic Hybrid, 2012 Nissan Altima, 2012 Kia Optima, and 2012 Ford F150. Four distinct fuel blends were used which include 15%, 25%, and 35% aromatics content with an additional fuel of 35% aromatics with a high octane rating. These vehicles were driven on the Unified cycle (UC), which is the primary California Air Resources Board (CARB) vehicle certification test cycle. In addition, the vehicles were driven at three steady-state speeds of 30, 50, and 70 MPH. Particle number and gravimetric PM mass were measured and analyzed. Particle size distributions were measured with an Scanning Mobility Particle Sizer (SMPS) when the vehicles were driven at steady state speeds. The water-insoluble mass fraction was estimated using a unique method of interpreting differences between a water and butanol CPC particle counts. WSOC and real-time BC was also measured. Results show that high speeds have significant effects on the water-insoluble particle composition. Collectively, this study discusses the impacts high octane fuels have on vehicle particle emissions.

8EP.3

The Impact of Radioactive Charging on the Microphysical Evolution and Transport of Radioactive Aerosols. PETROS VASILAKOS, Yong-Ha Kim, Sotira Yiacoumi, Costas Tsouris, Jeffrey Pierce, Athanasios Nenes, *Georgia Institute of Technology*

This study focuses on the influence of radioactive charging on the vertical transport of radioactive aerosols in the atmosphere. The TwO-Moment Aerosol Sectional (TOMAS) microphysics model was extended to account for radioactive charging effects in a computationally efficient way. Simulations of the deposition of radioactive aerosols were performed, as well as sensitivity analyses to evaluate effects of radioactive charging on the transport patterns of radioactive aerosols, using a one-dimensional version of the TOMAS model. Here, we present results of vertical transport characteristics of aerosols containing 131I and 137Cs, assumed to be released from radioactive sources in cases of radiological events, in a column consisting of 5 layers.

The results indicate that radioactive charging may facilitate or suppress coagulation of radioactive aerosols, thus influencing the amount of mass deposited on the ground and suggesting that no consideration of the radioactive charging may introduce uncertainties in the modeling of radioactive aerosol transport.

8IM.1

Evaluating Elemental and Organic Carbon composition of Size-Segregated Combustion Particles Using the Electrical Low Pressure Impactor. PATRICIA FRITZ, Shida Tang, David Guerrieri, Brian P. Frank, Marilyn Wurth, Daniel Hershey, *New York State Dept. of Environmental Conservation*

The composition and morphology of aerosol particles continue to be poorly characterized with respect to their health impacts and their potential impact on atmospheric processes and climate forcing. Previously, we reported using a Combustion Aerosol Standard (CAST, Jing, Ltd.) system to generate emissions targeted to specific impactor stages of the Electrical Low Pressure Impactor (ELPI, Dekati, Ltd.) to describe particle size distributions in real time and to collect samples for development of post-sampling methodologies for morphological and chemical analysis. Manipulation of combustion parameters allowed precise control of both particle size (median particle diameters of 30, 109, or 267 nanometers) and loading on the stages.

In the current set of experiments we used the ELPI to measure particle concentrations and to collect particles on a series of stages to characterize elemental carbon (EC) and organic carbon (OC) content of emissions from different combustion aerosol sources (e.g. CAST and a Tier IV-compliant 14 kW diesel generator (Mitsubishi Corporation /Marathon Electric) and with different particle loadings. In addition to real-time data on particle size distributions, this method provides corresponding measurements of EC/OC ratios on a size-resolved basis. Evaluating the EC/OC ratio of emissions has been suggested as a tool for particulate source attribution and to estimate their potential influence on radiative forcing. Atmospheric EC and OC inputs are of interest to climate science due to their ability to absorb or reflect sunlight. These inputs are likely to increase with continued reliance on generators during storm and disaster recovery efforts, and with conversion of existing appliances and vehicles from petroleum and gas to biomass fuels.

8IM.2

Design of a Novel Open-path Aerosol Extinction Cavity Ringdown Spectrometer and Initial Data from Deployment at NOAA's Atmospheric Observatory. TIMOTHY GORDON, Nick Wagner, Mathews Richardson, Daniel Law, Daniel Wolfe, Charles Brock, Frank Erdesz, Daniel Murphy, *NOAA*

The ability to frame effective climate change policy depends strongly on reducing the uncertainty in aerosol radiative forcing, which is currently nearly as great as best estimates of its magnitude. Achieving this goal will require significant progress in measuring aerosol properties, including aerosol optical depth, single scattering albedo and the effect of relative humidity on these properties for both fine and coarse particles. However both ground- and space-based instruments fail or are highly biased in the presence of clouds, severely limiting quantitative estimates of the radiative effects of aerosols where they are advected over low-level clouds. Moreover, many in situ aerosol measurements exclude the coarse fraction, which can be very important in and downwind of desert regions.

By measuring the decay rate of a pulsed laser in an optically resonant cavity, cavity ringdown spectrometers (CRDSs) have been employed successfully in measuring aerosol extinction for particles in relative humidities below 90%. At very high humidities (as found in and near clouds), however, existing CRDSs perform poorly, diverging significantly from theoretical extinction values as humidities approach 100%. The new open-path aerosol extinction CRDS described in this poster measures extinction as aerosol is drawn through the sample cavity directly without inlets or tubing for channeling the flow, which cause particle losses, condensation at high RH and other artifacts. This poster presents the key elements of the new open-path CRDS design as well as comparisons with an earlier generation closed-path CRDS and preliminary data obtained during a field study at the 300 meter tower at NOAA's Boulder Atmospheric Observatory (BAO) in Colorado.

8IM.3

Advances in Speciating Highly Oxygenated Organic Aerosol Using In-situ Thermal Desorption Semi-volatile Aerosol Gas Chromatography (SV-TAG) with On-line Derivatization. Gabriel Isaacman, NATHAN KREISBERG, Lindsay Yee, David Worton, Rebecca Wernis, Susanne Hering, Allen H. Goldstein, *University of California, Berkeley*

Speciation at the molecular level is necessary to more fully understand the sources, sinks, transport and transformation of organic matter in the atmosphere. The Thermal desorption Aerosol Gas chromatograph (TAG) is a mature instrument successfully deployed in seven distinct field campaigns and offers a proven method for in-situ, hourly speciation of organic aerosols. To measure the highly polar fraction of semi-volatile organics, which are important to secondary aerosol formation, a new version of the instrument has been developed to simultaneously collect both particle and semi-volatile vapor phases (Zhao et al., 2013; Isaacman et al., 2014) using a dual cell SV-TAG system with on-line derivatization of hydroxyl functional groups. Parallel samples collected on a reusable metal-fiber filter with and without removing the gas phase provide direct partitioning measurements of organic compounds. Hydroxyl groups are replaced with more stable trimethylsiloxyl groups using a standard silylation technique to provide quantitative recovery of highly oxygenated compounds by minimizing interactions with the chromatography column. Two recent field campaigns, in rural Alabama, US (2013) and in Amazonia, Brazil (2014), offer unique data sets for evaluating the field performance of this instrument. Using perdeuterated internal standards injected with every sample, the recovery of compounds ranging from pure non-polar hydrocarbons to highly oxygenated SOA can be evaluated for two very different environments to determine the role of aerosol composition, environmental factors and small changes in sampling protocols in instrument performance. Results show that these highly polar species can be measured with comparable precision to that obtained with off-line filter samples but now at hourly time resolution. While the extremely wet Amazonian environment presented unique challenges operationally, instrument performance is shown to be improved over that observed in Alabama, demonstrating that field performance of TAG instruments with derivatization can be expected to match prior capabilities for non-polar compounds.

8IM.4

Inversion of Multi-channel Light Scattering Data for Particle Size Distribution Measurements. MARK KANAPARTHI, Ishara Jayasuriya, Suresh Dhaniyala, *Clarkson University*

Aerosol size distribution measurements are routinely made using optical techniques, by relating single particle light-scattering response to its equivalent particle size. Light-scattering based size distribution measurements can be made over a wide particle diameter range of ~ 55 nm to ~ 70 µm using a range of commercial instruments. While single-particle light scattering instruments can provide accurate size information and near real-time size distribution measurements, these instruments are often expensive and large in size because of the need to have precise control of particle passage through a small detection volume. The design requirements that allow for effective detection of small (sub-100 nm) single particles also limit the dynamic range of measurement of an instrument. With the increasing availability of inexpensive and powerful optical sensor arrays, the possibility of particle measurements over a wide size range at low cost is becoming possible. A detector array configuration allows for a collection of a richer data set that could be analyzed for particle size distribution measurements. Such analysis is, however, made challenging by the complexity of inversion of the system response function matrix for size distribution calculation. In this presentation, we investigate the possibility of using optical detector arrays for size distribution measurements by understanding the practical limits of such systems. Our results from theoretical system modeling and preliminary experiments will be presented.

8IM.5

Real-time and On-line Screening Method for Outgassing-materials Using Soft X-ray. CHANG HYUK KIM, Young Tae Sul, David Y. H. Pui, *University of Minnesota*

In the semiconductor industry, avoiding particles is critical to enhancing the production yield of semiconductor chips. Therefore, most particulate contaminations have been eliminated by filtration systems. In spite of these efforts, as shorter wavelength ultraviolet (UV) light sources are used in photolithography to increase the number of semiconductor chips in a single wafer, the semiconductor industry has encountered new contamination problems from airborne molecular contaminations (AMCs). Even though the concentration of AMCs in the cleanroom air is very low, down to ppb or ppt, they can destroy semiconductor chips by producing particles and haze under the UV irradiation, thus increasing manufacturing costs. AMCs can originate from everywhere and outgassing from construction materials such as adhesives is an good example. However, a famous method to evaluate outgassing-materials, thermal desorption gas chromatography mass spectroscopy (TD-GC-MS), is time-consuming and not suitable for frequent measurements of outgassing.

The objectives of this study were to develop a fast screening method for outgassing-materials and to apply this method for evaluating materials. For the screening method, an outgassing chamber was made of stainless steel, which can be heated up to 200 °C. Outgassing from materials in the chamber was carried by nitrogen gas into the soft X-ray conversion chamber and converted into particles assisted by soft X-ray. Size distributions of generated particles were measured by a scanning mobility particle sizer (SMPS). Particle number and volume concentrations were obtained from the measured size distributions. This method showed good repeatability at different conditions such as mass, residence time, detection range, temperature and relative humidity. Different adhesives will be further evaluated at the same condition using this method and compared to find low outgassing-materials. By this method, time for screening materials can be saved and used to evaluate the low outgassing materials in detail combined with TD-GC-MS.

8IM.6

Evaluation of Nano-sized Silica Size Standards. SHIGERU KIMOTO, William Dick, David Y. H. Pui, Daryl Roberts, *University of Minnesota*

In this study, we evaluated a new series of nano-sized silica particle suspensions synthesized with modal diameters in the size range 20-200 nm. These silica particles are primarily used as size standards for calibration of wafer surface scanning devices in semiconductor industries. To be used as size standards, important microphysical properties of the particles must be known. Therefore, we characterized the nanosized silica particles in terms of size, effective density, and refractive index. We used calibration procedures developed by the National Institute of Advanced Industrial Science and Technology (AIST) in Japan in our evaluation methods for size and effective density measurements, made with the Scanning Mobility Particle Sizer (SMPS) (TSI, Model 3080) and the Aerosol Particle Mass Analyzer (APM) (Kanomax, APM-II). For refractive index measurements, we used a laser particle counter (LPC). We will report details for this study.

8IM.7

Design and Operational Optimisation of Pneumatic Sampler for Resuspension Chamber.

MIROSLAV KLÁN, Jan Hovorka, Martin Civiš, *Charles University in Prague*

The generation, capture and measurement of aerosol particles in a controlled laboratory environment are very important for determining the emission potentials of different sources of dust and for defining the physical characteristics, chemical composition and toxicological risk connected with the emission of particles into the atmosphere from specific locations or source materials. Therefore, we constructed metallic cylindrical resuspension chamber (V=0.437 m^3, S=0.35 m^2) to disperse solid samples under well-defined temperature and humidity. The chamber allows on-line measurements of particle number size distribution of aerosolized samples and subsequent sampling of size segregated particles on filter media. Repeatability of the resuspension experiments strongly depends on the way of introduction of a solid sample into the chamber. For this purpose a pneumatic sampler was optimised. The sampler was positioned at centerline near the upper third of the chamber and consists of electronically controlled air-jet and rotating five-hole carousel. Optimal air pressure and injection time of the jet were 15 bars and 10 milliseconds respectively. Optimal sample mass was about 5 mg. Ultrapure SiO_2 and Al_2O_3 of well-defined grain size were used as a standards. Environmental samples were dried at 48°C for 24h and pre-sieved with Tyller sieve (mesh size 38 micrometer). Fully automatic regime of the sampler allows conducting consecutive dispersion of five samples. Since each of resuspension experiments usually takes about two hours, use of the sampler allows about 10 hours of conducting experiments without the need to open the chamber, which greatly improved experiment repeatability.

The financial support by the Czech Grant Agency (P503/12/G147) is greatly acknowledged.

8IM.8

Online Particle Separation and Shape Measurement Using Pulsed-Field DMA.

MINGDONG LI, George Mulholland, Michael Zachariah, *University of Maryland*

One of the major challenges in particle measurement is to extend the dimensionality measurement beyond the assumption of spherical symmetry. For a nonspherical particle, a standard differential mobility analyzer (DMA) measurement yields a mobility-equivalent spherical diameter, but provides no information about the degree of sphericity. However, given that the electrical mobility for nonspheres is orientation-dependent, and that orientation can be manipulated using electric fields of varying strength, one can, in principle, extract shape information through a systematic measurement of mobility as a function of particle orientation. Here, we describe the development of a pulsed-field differential mobility analyzer (PFDMA) which enables one to change the peak E-field experienced by the particle to induce orientation, while still maintaining the same particle transit time. The instrument is validated with polystyrene latex (PSL) spheres with accurately known size, and gold rods with dimensions accurately determined by transmission electron microscopy (TEM). We demonstrate how the instrument can be used for particle separation and extraction of shape information. In particular, we show how one can extract both length and diameter information for rod-like particles.

The most important class of non-spherical particles are aggregates. Recently, we have demonstrated how this instrument can be applied to aggregates, and demonstrate that the mobility size of soot non-spherical aggregates showed a clear alignment effect. Since the mobility size of spheres is constant, the experimental results demonstrate that PFDMA could be used to separate spherical particles from non-spherical aggregates. This generic approach can be used to obtain shape information for nonsphercial particles and separate particles based on their shape.

8IM.9

Characterization of an Humidified Tandem DMA System: Size and Humidity Dependent Efficiencies and Dispersion. XERXES LOPEZ-YGLESIAS, Ming Chee Yeung, Fred Brechtel, Chak K. Chan, *Brechtel Manufacturing Inc.*

Hygroscopicity is a critical property of atmospheric aerosol that describes particle response to changing ambient humidity. It governs the water content, optical properties and CCN activity of a particle by controlling the size at different relative humidity (RH) conditions. Comprehensive studies of hygroscopicity are necessary to elucidate aerosol impacts on global climate and regional visibility. The Tandem Differential Mobility Analyzer (TDMA) technique coupled with aerosol humidification has been widely used for studying aerosol hygroscopicity. In this study, we evaluate the performance of a commercial Humidified TDMA (BMI HTDMA, Model 3002) with respect to DMA sizing, particle transmission and dispersion as functions of size and relative humidity (RH), RH control, and growth factor (GF) measurements. The results of these experimental studies are compared to model predictions. Unique features of this particular HTDMA include a diffusion-based particle humidifier, a DMA design allowing selection of particles up to 2 µm diameter at only 5600 volts, and the ability to study the complete deliquescence and efflorescence cycle.

8IM.10

Development of a High Throughput Wind Tunnel Evaluation Method for Ultra-Coarse Inlet Testing. QUENTIN MALLOY, Andrew Dart, Jonathan Thornburg, Carlton Witherspoon, Zora Drake-Richmon, Jonathan Krug, Robert Vanderpool, *RTI International*

The current data concerning ambient Pb containing particle size distributions is sparse primarily due to complexities associated with sampling the “total” suspended particle concentrations. An exceedingly difficult aspect of “total” particle sampling is measurement of those particles with large aerodynamic diameters, termed ultra-coarse particles. Measurement of these ultra-coarse particles is difficult due to their inherently high inertia and sedimentation velocities. These aspects of ultra-coarse particles require application of specifically designed inlets with large geometries and operating at high flow rates. We have developed a method for generation and analysis of test atmospheres within a wind tunnel for analysis of an inlet sampling effectiveness particle sizes upwards of 30 micro-meters. CV’s for aerosol uniformity with our procedure for wind speeds up to 24 Km hr^{-1} was less than 5 percent. Evaluation of two candidate inlets displayed fall-off sampling effectiveness beginning at approximately 5 micro-meters, with degree of fall-off being a function of inlet and wind speed.

8IM.11

Evaluation of Granular Bed with Glass Beads for Use in a Nanoparticle Respiratory Deposition (NRD) Sampler. JAE HONG PARK, Levi Mines, Imali Mudunkotuwa, T. Renee Anthony, Vicki Grassian, Thomas Peters, *University of Iowa*

The objective of this work was to broaden the applicability of an innovative nanoparticle respiratory deposition (NRD) sampler by identifying sampling media alternatives to the eight nylon mesh screens used, in the original NRD sampler, to collect and quantify multiple metals in nanoparticle aerosol samples. The new sampling media consisted of a granular bed with three layers of glass beads held in place by two coarse mesh screens (mesh/1-mm beads/200-µm beads/1-mm beads/mesh). The solidity of the total glass beads layers was 0.740. The collection efficiency by size was measured with a scanning mobility particle sizer in triplicate for metal particles generated from a spark discharge system. Measured collection efficiencies were compared to those calculated from theory. The number median diameter and total number concentration of test particles from the spark discharge system were 100 nm and 1.5×10^5 particles/cm^3, respectively. The particle collection efficiency of the granular bed was 80(±2)% at 30 nm, 45(±2)% at 100 nm, and 34(±7)% at 300 nm, yielding a 50% cutoff diameter of approximately 85 nm. The shape of the measured collection efficiency curve was similar to that estimated from theory, although measured collection efficiencies were considerably higher than theory (e.g., the 50% cutoff diameter from theory was 35 nm). These results show that a granular bed can be used as a diffusion media in the NRD sampler. Compared to the use of screens, this granular bed approach opens up a wide array of different materials that can be used for sampling media in the NRD sampler and more broadly, use in other diffusion-based samplers.

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8IM.12

Development Of An Online Measurement For Soluble And Total Cu In PM2.5. DONGBIN WANG, Martin Shafer, James Schauer, Constantinos Sioutas, *University of Southern California*

A novel monitor for online, in-situ measurement of copper (Cu) in ambient fine and ultrafine particulate matter (PM) was developed based on a recent published high flow rate Aerosol-Into-Liquid Collector. This Aerosol-Into-Liquid Collector operates at 200 liters per minute (L/min) flow and collects particles directly as highly concentrated slurry sample. The Cu concentration in slurry samples is subsequently determined by a cupric Ion Selective Electrode (ISE). Laboratory tests were conducted to evaluate the performance of the cupric ISE. The calibration curve of the cupric ISE was determined using Cu(NO3)2 standard solutions prepared by serial dilution. As part of the evaluation, the effect of ionic strength, temperature and pH of the aerosol slurry sample on the cupric ISE measurement was also evaluated. The Cu measurement system performance was evaluated by collecting and measuring samples of lab generating Cu(NO3)2 aerosols with known mass concentration. Overall, very good agreement between the theoretical and measured Cu concentrations was obtained, indicating the excellent overall collection efficiency and measurement accuracy of the Cu measurement system. Field evaluations of the cupric ISE measurements demonstrated very good agreement for total and water-soluble Cu concentrations with on-line measurements by inductively coupled plasma mass spectrometry (ICPMS) and demonstrated no interferences from other components of particulate matter in real world sampling. Moreover, the field tests indicated that the new Cu measurement system could achieve near-continuous (i.e. 3-4 hours) and unattended collection and measurements for at least 4 to 7 days without any obvious shortcomings in its operation. Both laboratory and field evaluations of the online Cu measurement system suggest that it is an effective and valuable technology for collection and characterization of ambient aerosols and provides the foundation for the wider use of ISE for metal analysis and speciation of aerosols.

8IM.13

Charge Distributions of Arbitrary Shaped Particles Charged by the Unipolar Diffusion Charger in the EAD and NSAM. DREW THOMPSON, David Y. H. Pui, *University of Minnesota*

Unipolar diffusion chargers are commonly used in aerosol instrumentation, such as in exposure monitors where a particle concentration is inferred from the electrical current produced by the deposition of charged particles or as a charge conditioner in a differential mobility analyzer (DMA) where predictable charge distributions are needed for the determination of particle size distributions. However, it has been reported that particle morphology affects the ion-particle collision rate, which in turn would affect the performance of any aerosol instrument employing a unipolar diffusion charger. An expression for the charge distributions of arbitrary shaped particles charged by the opposed flow unipolar diffusion charger used in the Electrical Aerosol Detector (EAD) and the Nanoparticle Surface Area Monitor (NSAM) will be presented. The particle charge distribution was found using the analytical solution of the birth-and-death theory where the ion-particle collision kernel was calculated using a recently published expression for arbitrary shaped particles in the transition regime (Gopalakrishnan, Thajudeen, Ouyang, and Hogan. (2013) J. Aerosol Sci.; 64: 60). Calculated charge distributions for spherical and cylindrical particles are compared to that measured using a tandem DMA (TDMA) system after correcting for experimentally determined size-, shape-, and preexisting charge-dependent particle losses in the charger.

8IM.14

Generation of Monodisperse Aerosols by Aerodynamic Flow Focusing. HONGXU DUAN, Amir Naqwi, Francisco Romay, Benjamin Liu, *MSP Corporation*

A novel approach has been developed for generating highly monodisperse aerosol particles. The generator applies a vibrating perturbation to a micro-liquid jet generated by aerodynamic flow focusing (Gañán-Calvo, 1998). The aerosol generated by this approach is charge neutralized with bipolar ions generated by a non-radioactive, electrical ionizer to achieve a charge equilibrium state. We have demonstrated that droplets in the 20 to 200 micro-meter range can be generated from a single 100 micron nozzle. Both oleic acid/ethanol and sodium chloride/water solutions have been used to generate highly monodisperse aerosols of liquid and solid particles in the 1 to 20 micro-meter range. The size of the monodisperse particles can be calculated from the operating parameters and agrees with measurements made with an Aerodynamic Particle Sizer. The new monodisperse aerosol generator is capable of stable operation over an extended period of time without experiencing nozzle clogging.

Gañán-Calvo, Alfonso M. "Generation of steady liquid microthreads and micron-sized monodisperse sprays in gas streams." Physical Review Letters 80.2 (1998): 285.

8IM.15

Particle Losses with a Large Diamater Nafion Air Sample Dryer. Alfred Wiedensohler, EUGENE BOHENSKY, Paul Smith, Craig Sunada, *Perma Pure LLC*

Controlling relative humidity of an ambient aerosol sample flow is critical to obtain consistent results for physical and optical aerosol particle measurements. Gas sample dryers using Nafion membrane technology have been shown to control the relative humidity well in many analysis applications. However, especially bundle dryer used for higher flow rates might have enhanced particle losses due to diffusion. In this development, particle losses are characterized for Nafion dryers with large diameter membrane, which can be employed for a wide range of flow rates. Users and researchers performing aerosol research and analysis will have an effective option to control humidity while improving measurement accuracy and limiting particle losses.

8IM.17

A Nanoparticle Nebulizer for Generation of Aerosolized Colloid Particles with Reduced Interference from Non-Volatile Residue. DEREK OBERREIT, Gary Van Schooneveld, David Blackford, *Fluid Measurement Technologies, Inc.*

Dispersion of colloid nanoparticles into an aerosol first requires nebulization of the colloid into fine droplets and subsequent evaporation of the solvent from them. Following solvent evaporation, droplets that did not contain a colloid particle form particles composed of non-volatile solvent residue. Droplets that do contain colloid particles result in aerosolized colloid particles with a coating of non-volatile residue. To reduce the interference by non-volatile residue particles as well as effect on the colloid particle properties (surface chemistry, size), it is desirable to create droplets containing a low volume of solvent. This is especially true for aerosolization of nanoparticles that approach the size of the non-volatile residue particles. Nebulization is typically accomplished using either pneumatic or electrospray methods. While electrospray methods do provide sufficiently small droplets (~0.3 μm), there are several limitations to the method including poor long term stability and necessity for a conductive solvent. Common pneumatic nebulizers create droplet distributions with a peak diameter near 2.0 μm which leads to a significant amount of non-volatile residue interference in the aerosol. We present a new commercially available pneumatic nebulizer that is designed to produce a high number concentration of small droplets with a peak diameter less than 0.5 μm. We compare the performance of this nebulizer with existing aerosolization methods for a variety of colloids. We also show additional applications of this device for monitoring colloid concentrations in dilute systems such as ultrapure water systems and in liquid filter efficiency testing.

8IM.18

Measuring Aerosol Scattering and Absorption - Limitations of the Extinction-Minus-Scattering Method. SUJEETA SINGH, Damon Smith, Marc Fiddler, Solomon Bililign, *North Carolina A&T State University*

Aerosols from biomass burning represent a significant source of particles in the atmosphere. An accurate measurement of the optical properties of these aerosols is critical for measuring their effect on climate, since they represent a large uncertainty. Optically dark aerosols, such as soot, affect the climate system by both cooling (due to scattering) and by warming (due to absorbing), dependent on the aerosol's size, composition, and shape. The aim of this work is to quantitatively determine the absorption and scattering cross-section, single scattering albedo, and angstrom coefficient of soot. Particle extinction (absorption + scattering) was measured with a cavity ring-down spectrometer (CRDS), scattering was measured with an integrating nephelometer, and a condensation particle counter (CPC) measured particle number density. In this work, we perform an assessment of the contributions to systematic and random errors for CRDS extinction measurements. Cross section measurements are limited by the accuracy of the CPC and, to a lesser extent, measurement variability and cell geometry. Statistical fluctuations of aerosol particles, recapturing of forward-scattered light, laser mode noise, and laser bandwidth effects are negligible. For nephelometer measurements, scattering cross section errors resulting from extrapolation between measured values limits the accuracy of this method. A comparison between CRDS, nephelometery, and Mie Theory predictions for non-absorbing polystyrene latex spheres shows mean measured cross section values at 584 nm to have an excellent agreement, though all were systematically larger than predicted values. Backscatter values showed poor agreement, and all nephelometer cross sections were limited by fitting errors (those from extrapolating between measured wavelengths). The resulting effects of propagated errors on the accuracy of absorption cross section and single scattering albedo will be discussed along with preliminary measurements on absorbing polystyrene and reaerosolized soot.

8IM.19

Development and Evaluation of Real-time Nano-particle Counter. KANG-HO AHN, Hong-Ku Lee, *Hanyang University, R. of Korea*

Measuring particle size distribution is one of the primary concerns in aerosol studies. For a nano-particle size distribution measurement, many scientists use a combination of a differential mobility analyzer (DMA) and a condensation particle counter (CPC) system, which is a called scanning mobility particle sizer (SMPS). Although it has a very high particle size resolution, some issues still remain. One of a main problem is a long scanning time during the measurement. In particular, long scanning time is not adequate for measuring fast changing particle concentration during the measurement. Previous effort to overcome these problems has been performed by some researchers (Chung et al. 2006; Chen et al. 2007; Kim et al. 2007; Lee et al. 2013).

In this study, we developed a radial exhaust multi-port system (REM-system) with no scanning to measure real-time particle size distribution. This system consists of multi-condensation particle counter (M-CPC) and multi-port DMA (MP-DMA), which has a variable cross sectional area electrode. We also evaluated size distribution of the system using mono-dispersed NaCl particle. The average geometrical standard deviations (σg) of MP-DMA is 1.041, which is considered to be mono-disperse. After the evaluation, the system performance is compared with the commercial SMPS. The performance test was conducted under steady and unsteady particle concentration conditions.

As a result of this research, it is considered that this system is more suitable for measuring rapidly changing aerosol concentrations than SMPS.

8NM.1

3D Label-Free Prostate Specific Antigen Immunosensor Based on Graphene-Gold Nanocomposites.

HEE DONG JANG, Sun Kyung Kim, Hankwon Chang, *Korea Institute of Geoscience and Mineral Resources*

Highly sensitive and label-free detection of the prostate specific antigen (PSA) remains a challenge in the diagnosis of prostate cancer. Here, a novel three-dimensional (3D) electrochemical immunosensor capable of sensitive and label-free detection of PSA is reported. This unique immunosensor is equipped with a highly conductive graphene (GR)-based gold (Au) nanocomposite modified electrode. The GR-based Au nanocomposite is prepared using aerosol spray pyrolysis and the morphology of the nanocomposite is the shape of a crumpled GR ball decorated with Au nanoparticles. Unlike previous research, this novel 3D immunosensor functions very well over a broad linear range of 0-10 ng/mL with a low detection limit of 0.005 ng/ml; furthermore, it exhibits a significantly increased electron transfer and high sensitivity toward PSA. The highest rate of current change according to the PSA concentration is 49 µA. Satisfactory selectivity, reproducibility, and stability of the 3D immunosensor are also exhibited.

8NM.4

Modelling of Fluid-Dynamic Transport of Growing Nanoparticles with a Turbulent-Like Plasma Jet.

MASAYA SHIGETA, *Osaka University*

The mass-production of nanoparticles is still practically arduous by conventional methods. To overcome that problem, thermal plasmas have been anticipated as a promising tool for efficient fabrication of nanoparticles because thermal plasmas offer a very-high-temperature field with steep gradients at their fringes where many small nanoparticles are generated rapidly from the material vapor. However, it is still difficult to investigate the formation mechanism of nanoparticles generated in/around a thermal plasma because the process involves rapid phase conversions and transports by complicated convection due to fluid-dynamic instability as well as diffusion and thermophoresis.

Hence, this study performs numerical simulation to visualize the dynamic behavior of a thermal plasma flow and the transport of nanoparticles in growth. A model is developed to express the simultaneous nonequilibrium processes of the nanoparticles' growth and transports. The model is simple but consistent so that it is suitable to transient problems which usually require high computational costs. Furthermore, an original simulation code with higher accuracy is developed to express a turbulent-like behavior of a thermal plasma jet and to capture shock-like steep gradients in the spatial distribution of nanoparticles.

8PH.1

Vibrational Spectra of Individual Dust Particles Obtained from the International Space Station and New York 9/11 Disaster.

ANTRIKSH LUTHRA, Aruna Ravi, James Coe, *The Ohio State University*

The concentration of dust particles inhaled into people's lungs is correlated with public health. Particles of the size range 2-5 microns are amongst the biggest by volume that get through to the lungs, hence characterizing their chemical composition is important. This research focuses on IR spectroscopic analysis to characterize the individual dust particles collected from the International Space Station and New York 9/11 disaster (~1 mile away from ground zero). These particles are trapped in the holes of a plasmonic metal mesh (12.6 microns square lattice and 5 microns hole size). This allows us to take scatter-free infrared absorption spectra whose peaks provide an insight on the identity of infrared active components. The study of single dust particles provides non-destructive chemical information of not only the major components, but also of minority components. This information is different and complimentary to the analysis of bulk samples.

8PH.2

Development of a Microfluidic Instrument for the Real-time Measurement of Aerosol Oxidative Potential Using DTT (Dithiothreitol) Assay.

TING FANG, Vishal Verma, Rodney Weber, *Georgia Institute of Technology*

The aerosol oxidative potential has gained increasing importance due to its possible relevance to adverse health effects of ambient particles (PM). One of the most widely used measures of oxidative potential of particles is the DTT (Dithiothreitol) assay. This assay monitors the consumption rate of DTT as catalyzed by the redox-active species in PM. The major concern with the assay is the substantial PM concentration, required to yield a detectable signal. While filter-based collection approaches with long sampling duration are commonly used, they could entail artifacts due to losses of DTT-active semi-volatile species during sampling and handling procedures. Besides, composite samples collected over a long period of time cannot capture short time scale variations in the aerosol oxidative potential that could provide unique insights on sources and atmospheric processes affecting DTT activity. Based on the flow injection analysis (FIA) technique, we aim to adapt the DTT assay to an online system coupled to a particles-into-liquid sampler (PILS) for continuous real-time measurement of aerosol oxidative potential. In this approach, PM2.5 ambient particles are directly collected into Deionized water via PILS at an air-flow of 16.7 L/min and carrier DI water flow of 0.1 mL/min. The aqueous sample, after filtering through a PTFE syringe filter (pore size = 0.45 micro-meter), is injected into a flowing carrier stream containing DTT. Varies reagents are mixed by generating a turbulent flow using super serpentine reactors (Global FIA). The consumption rate of DTT is monitored using a Liquid Wave-guide Capillary Cell (LWCC-3250; World Precision Instruments, Inc., Florida) with optical path length of 2.5 m, coupled to an online spectrophotometer (Ocean Optics, Inc., Dunedin, Florida, USA), which included a UV-VIS light source (Ocean Optics DT-Mini-2), multi-wavelength light detector (USB4000 Miniature Fiber Optic Spectrometer), and a data acquisition software (SpectraSuite). The performance of this online DTT system and field application will be discussed.

8PH.3

Distribution of Ambient Atmospheric Water-soluble Metals in the Southeastern United States and Insights into Their Complexation States. TING FANG, Vishal Verma, Richard E. Peltier, Hongyu Guo, Laura King, Rodney Weber, *Georgia Institute of Technology*

Water-soluble metals in ambient particles have been shown to generate reactive oxygen species (ROS) by Fenton reactions. Certain metals such as Cu, Mn, and Fe have even been associated with the response of various oxidative assays such as the Ascorbate (AA), Dithiothreitol (DTT) and macrophage ROS assays, typically used to measure the toxicological properties of ambient particles. As part of the Southeastern Center for Air Pollution & Epidemiology (SCAPE) project, we measured the concentration of water-soluble metals in PM2.5 in southeastern United States. In this study, 530 PM2.5 filter samples were collected over a yearlong period from contrasting environments, i.e. urban (Atlanta), rural (Yorkville and Centreville), industrial (Birmingham) and roadside (near I-85 freeway in Georgia Tech) sites. Water-soluble metals in the filter extracts were measured using an online XRF (X-ray fluorescence) instrument (Xact™ 625 Monitoring System) by coupling to an ultrasonic nebulizer (CETAC, U5000 AT+) to aerosolize filter extracts and the system was automated by using a Dionex autosampler (Dionex 40AS). The oxidative potential (ROS generating capability) of these particles were also measured using the dithiothreitol (DTT) assay. As an additional step to identify the oxidative particle components, we passed these extracts through a C-18 solid phase extraction (SPE) columns (octadecyl carbon chain bonded silica, Sorbent Technologies) and measured the metals concentration in both passed-through (hydrophilic) and retained on the column fraction (hydrophobic). Among all sites, industrial (Birmingham) and roadside sites have the highest levels of water-soluble metals (e.g. Ca, Mn, and Zn), while the concentrations are generally low in the rural environment (Yorkville and Centerville). Urban background sites in Atlanta have moderate levels of the water-soluble metals. Some of these metals, particularly Fe, Mn and Zn were well correlated with the DTT activity in urban and roadside sites. The partitioning behavior of these metals on the C-18 column would further help to understand the complexation states of these metals with organic compounds and their availability to induce the oxidative stress in biological cells.

8PH.4

Spatial and Seasonal Variation in the Molecular Composition of the Humic-Like-Substances (HULIS) Fraction of Ambient Aerosols: Clue for the Sources of Aerosol Oxidative Potential. YING WANG, Vishal Verma, Ting Fang, Rodney Weber, *Georgia Institute of Technology*

Atmospheric Humic-like substances (HULIS) are an operationally defined, polar, acidic and chromophoric material, isolated from ambient aerosols or fog and cloud samples. They are ubiquitously present in the troposphere and make up a major fraction of the continental fine-sized water-soluble organic compounds (WSOC). HULIS is often regarded as a complex mixture of organic compounds. However, structural information at the individual component level is rather limited. Recent studies also show that HULIS is closely associated with the production of reactive oxygen species (ROS) in aerosols which is known to exert oxidative stress via inhalation.

In the present study, we characterized the HULIS fraction from different locations and seasons using gas chromatography mass spectrometry (GC-MS). Aerosol samples with an aerodynamic diameter of 2.5 microns or less (PM2.5) were collected using High Volume samplers at an urban site, a rural site and a highway site around Atlanta, Georgia, during the period of June 2012 to April 2013. High volume quartz-fibers filters were extracted by water and passed through C-18 columns to separate the HULIS fraction. Hydrophobic compounds retained on the column were eluted by methanol and analyzed by GC-MS. The chromatographs are dominated by multifunctional hydroxyl and carbonyl compounds. Biomass burning biomarkers, including monosaccharide derivatives such as levoglucosan, are prominent in winter urban sites. Secondary aerosol compounds derived from terpenoids are found to be widely present in HULIS with compound types varying with seasonality. These variations in HULIS molecular composition provide useful information on the sources of organic aerosols in different seasons in southeast US. The possible contribution of these HULIS compounds to aerosol oxidative potential would be further investigated by correlating the compound concentrations with the ROS generation capability of these samples which was analyzed in a previous study using a dithiothreitol (DTT) assay.

8PH.5

Estimating the Public Health Impacts of Ultrafine Particulate Matter in the San Francisco Bay Area. CUONG TRAN, Saffet Tanrikulu, David Fairley, Su-tzai Soong, Yiqin Jia, Jeffery Matsuoka, Eric Stevenson, Henry Hilken, *Bay Area Air Quality Management District*

Ultrafine particulate matter (UFPM) is currently an unregulated pollutant, but has harmful effects on human health. The Bay Area Air Quality Management District (BAAQMD) has been studying UFPM with the goal of reducing its emissions, ambient levels and health impacts in the Bay Area. The key components of that study include continuous ambient monitoring since 2012, data analysis, emissions inventory development, air quality simulation, and estimation of exposure and health burdens. Here, we summarize the preliminary estimation of the public health burdens and associated monetary costs of UFPM for the San Francisco Bay Area. To our knowledge, this is the first study to estimate regional health impacts of UFPM.

The BAAQMD, in collaboration with the California EPA's Office of Environmental Health Hazard Assessment (OEHHA), has compiled health impact functions for UFPM from an extensive literature review. We incorporated them into the US EPA's BenMAP model to analyze the health burdens of UFPM. To estimate-region wide UFPM levels, we utilized co-located measurements of UFPM and other species at four air monitoring stations. UFPM correlated reasonably well with NO2; therefore, we estimated region-wide ambient UFPM levels by applying correlations between UFPM and NO2, derived from the simultaneous measurements of both pollutants, to simulated NO2 concentrations. We used detailed population data from the 2010 US Census with BenMAP to estimate exposure and total incidences of premature mortality, asthma-related emergency room visits (ERV), respiratory hospitalizations, and cardiovascular hospitalizations.

Our analysis shows 800 excess mortalities per year and about $300M in direct costs of illness (COI) for UFPM. We compared these findings to previous results for PM2.5, which indicated 1700 premature deaths and $1B COI per year in the Bay Area. There were also spatial and seasonality differences between these pollutants, implying that different approaches to mitigating their impacts are needed.

8RA.1

Characterization of Arctic Aerosol Particles during the Arctic Ocean Expedition in 2013. GIBAEK KIM, Young Jun Yoon, Hee-joo Cho, Kihong Park, *Gwangju Institute of Science and Technology*

The Arctic region, isolated from anthropogenic sources, is one of the pristine places to study natural aerosol processes and evaluate various anthropogenic impacts on the atmosphere. The investigation of climate change in the Arctic may provide a decisive clue to predict climate change on a global scale. Atmospheric aerosols have an important role in the radiation balance and the formation of cloud condensation nuclei. However, they represent large uncertainties in their contribution to climate change. Therefore, it is necessary to determine the physicochemical properties of the Arctic aerosols.

Herein, differential mobility particle sizer (DMPS), hygroscopicity and volatility tandem differential mobility analyzer (HVTDMA), transmission electron microscopy/energy dispersive spectroscopy (TEM/EDS), and laser induced breakdown spectroscopy (LIBS) techniques were applied to characterize aerosol samples measured/collected at the Korean research icebreaker, ARAON, during the Arctic Ocean Expedition in 2013. The size distribution of aerosol particles ranging from 28 to 594 nano-meter was observed by DMPS. Furthermore, the hygroscopic and volatile properties were determined by using the HVTDMA technique under controlled RH (85 percent) and temperature (100 degree Celsius) conditions, respectively. Occasionally, the heating temperature was gradually elevated up to 250 degree Celsius for the investigation of existence of non-volatile core particles. In addition, morphological and elemental analyses, and multi-elemental analysis for occasionally collected $PM_{2.5}$ aerosol particles were performed by TEM/EDS and LIBS, respectively.

Atmospheric aerosol particles were classified into several groups based on their morphology and elemental composition. Several elements such as Mg, Ca, Na, and K were detected by LIBS, and their variations were investigated. Chlorophyll a concentrations observed from satellite data indicate that the biological activity was relatively intense around the cruise route. HVTDMA measurement data suggest that particulate organic matters were ubiquitous during the measurement period.

8RA.2

The Characteristics of Long-range Transboundary Inorganic Secondary Aerosols in Northeast Asia.

YOO JUNG KIM, Gregory Carmichael, Jung-Hun Woo, Zhang Qiang, Young Sunwoo, Young-il Ma, *University of Iowa*

Northeast Asia is suffering recurrently severe air pollution issue due to large amounts of anthropogenic emissions. The emitted compound influences downwind region by long-range transboundary transport. Most of SO2 and NOx emissions come from the industrialized regions along the East China coast. The Korean Peninsula is located on the eastern edge of the continent of Asia and lies in a belt of prevailing westerlies. Korea is a suitable location for studying the interaction of emissions from the Northeast Asia region. According to many previous studies, the long-rang transport of air pollutants contributes to Korean, but there are many uncertainties regarding the impact of long-range transport.

Inorganic secondary aerosols (sulfate, nitrate and ammonium) are dominant ionic contributors to Particle matter. High relative contributions of inorganic secondary aerosols appear under westerly wind cases at Korea. The major pathway of inorganic secondary aerosols production is converting from SO2 and NOx during the long-range transport, but the contribution varies dramatically depending on season and wind pattern. So far, sulfate is the primary contributor to PM2.5, but nitrate levels are increasing because that NOx emissions in China are increasing dramatically since 2000 due to the growth in power, industry, and transport sector, while SO2 emissions are trending downward since 2005.

We will present inorganic secondary aerosol characteristics of PM2.5 by westerly long-range transport, tracking their transport pattern, and production pathway in order to better understand regional air quality modeling of the long-range transport. This study will be performed based on the international study, MICS-Asia phase III, initiated with many researchers. Results using CMAQ with the modeling domain covering Northeast and Southeast China, Korea, and Japan with 15km resolution will be discussed.

8RA.3

Frost Flower Aerosol Effects on Arctic Wintertime Longwave Cloud Radiative Forcing.

Li Xu, LYNN RUSSELL, Richard Somerville, Patricia Quinn, *Scripps Institution of Oceanography*

Frost flowers are clusters of highly saline ice crystals growing on newly formed sea ice or frozen lakes. Based on observations of particles derived from frost flowers in the Arctic, we formulate an observation-based parameterization of salt aerosol source function from frost flowers. The particle flux from frost flowers in winter has the order of 10^6 m^{-2} s^{-1} at the wind speed of 10 m s^{-1}, but the source flux is highly localized to new sea ice regions and strongly dependent on wind speed. We have implemented this parameterization into the regional WRF-Chem model initialized for two wintertime scenarios. The addition of sea salt aerosol emissions from frost flowers increases averaged sea salt aerosol mass and number concentration and subsequent cloud droplet number. This change of cloud droplet number concentration (CDNC) increases downward longwave cloud radiative forcing through enhanced cloud optical depth and emissivity. The magnitude of this forcing of sea salt aerosols from frost flowers on clouds and radiation, however, contributes negligibly to surface warming in Barrow, Alaska, in the wintertime scenarios studied here.

8RA.4

Source Attribution of Aerosol Size Distributions and Model Evaluation Using Whistler Mountain Measurements and GEOS-Chem-TOMAS Simulations. STEPHEN D'ANDREA, Jessica Ng, Michael Wheeler, Annie-Marie Macdonald, Richard Leaitch, Jeffrey Pierce, John Kodros, *Colorado State University*

Remote and free tropospheric aerosols represent a large fraction of the climatic influence of aerosols; however, aerosol in these regions is less characterized than those polluted boundary layers. We evaluate aerosol size distributions predicted by the GEOS-Chem-TOMAS global chemical transport model with online aerosol microphysics using measurements from the peak of Whistler Mountain, BC, Canada (2182 m.a.s.l.). We evaluate the model to predictions of aerosol number, size and composition during periods of free tropospheric and boundary-layer influence. Additionally, we perform GEOS-Chem-TOMAS simulations without Asian anthropogenic emissions and without biomass burning emissions to quantify the contribution of these sources to aerosols at Whistler (through comparison with simulations with these emissions on). The combination of measurements and modeling gives us insight into the sources and processes that shape the aerosol at Whistler.

8RA.5

Individual Particle Chemistry during the Summer in Remote Northern Michigan. MATTHEW GUNSCH, Nathaniel May, Daniel Gardner, Stephanie Schmit, Andrew Ault, Kerri Pratt, *University of Michigan*

Northern Michigan is a remote, heavily forested area with minimal local pollution. Therefore, it is important to characterize the types and sources of local and transported particles impacting the region to determine air quality and climate effects. Nearby metropolitan areas include Milwaukee (230 miles southwest), Detroit (located about 240 miles south), and Chicago (located about 290 miles southwest). In addition, Canadian wildfires (located to the north and northwest) frequently impact the area, and particles generated from the surface of the Great Lakes (located to the west, north and east) may be a source of particles to the area. However, there have been very few studies that measure atmospheric particles in the upper mid-western United States. During summer 2014, an aerosol time-of-flight mass spectrometer (ATOFMS) measured the size and chemical composition of individual 0.4-2 micrometer particles above the mixed forest canopy at the University of Michigan Biological Station (UMBS) near Pellston, MI. Size-resolved atmospheric particle concentrations were measured using a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer (APS). In addition, collected particles will be analyzed using scanning electron microscopy with energy disperse X-ray spectroscopy (SEM-EDX) for morphology and elemental composition determination. The major particle types observed included biomass burning, organic carbon-sulfate, mineral dust, and sodium chloride salts, suggested to be produced from the surface of the Great Lakes. The source regions and meteorological conditions under which various chemical mixing state particles were observed will be discussed.

8SA.1

Elemental and Individual Particle Analysis of Atmospheric Aerosols from New Delhi, India. HONGRU SHEN, Thomas Peters, Gary Casuccio, Naresh Kumar, Andrew Ault, *University of Michigan*

The Indian capital, New Delhi, is one of the most polluted cities with respect to particulate matter. Deaths due to respiratory disease are now second only to cardiovascular disease and without a concerted effort this condition will only worsen. However, few particulate matter studies conducted in New Delhi have focused on individual atmospheric particles, with most studies confined to bulk particles analysis. The lack of such studies in New Delhi has motivated this work investigating the particle sources and processing in the atmosphere. Atmospheric particles were passively sampled at 50 sites across New Delhi, in October through December 2008. These samples were analyzed using computer controlled scanning electron microscopy (CCSEM) to determine the physical (size and morphology) and chemical properties (energy dispersive spectrometry (EDS) of 18 elements) of individual particles. The particles analyzed in the study were primarily < 10 µm, with most < 2.5 µm. All sample particles were classified into distinct groups, using the k-means clustering algorithm on the EDS spectra. The predominant particle types were mineral dust, different types of fly ash, and lead-rich particles. The main sources of anthropogenic particles are likely motor vehicle traffic, domestic fuel burning, industrial sources, and power plants. Lead-rich particles were distributed heterogeneously among the sites, and identification of the precise source, likely combustion of leaded fuel, is ongoing. Future studies will focus on characterizing the physical properties of the different types of particles spatially to determine sources, atmospheric history, reactivity, and transport. This detailed single particle identification of sources and spatiotemporal trends can be used as part of future efforts to evaluate particulate matter exposure city-wide in New Delhi.

8SA.2

Investigation of Sources of Particulate Matter through Trace Metal Measurements Near the Oil Sands Field in the Athabasca Region, Alberta. CATHERINE PHILLIPS-SMITH, Cheol-Heon Jeong, Robert Healy, Ewa Dabek-Zlotorzynska, Valbona Celo, Jeff Brook, Greg J. Evans, *SOCAAR, University of Toronto*

Trace metals in particulate matter smaller than 2.5 µm (PM2.5) have been measured as part of the Joint Canada-Alberta Implementation Plan for Oil Sands Monitoring (JOSM) Program since 2010. Under the Enhanced Deposition Component of this program, measurements have been made by Environment Canada near oils sands activities at three sites run by the Wood Buffalo Environmental Association. An intensive measurement campaign was also executed at a location near one of these sites in the summer of 2013. Together these data should help elucidate and resolve the relative contributions of the multiple PM2.5 generating sources and activities in this region.

Positive Matrix Factorization (PMF), combined with wind sector analysis was applied to determine the sources of metals in close proximity to oil sands processing activities. In addition to 24-hour filter collected PM2.5 (once every six days for two years), an Xact625 X-ray fluorescence based instrument provided hourly time-resolution measurements of trace metal species from August 10 to September 5, 2013. This higher time resolution enabled the investigation of short-lived events. Overall the elements examined included; Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Br, and Sr, with additional elements determined in the filter samples. Elements such as Se, V, and S, were examined for their relationships with different anthropogenic sources, including oil or coal combustion. Si, Ca, and Fe, usually associated with crustal material, were also examined due to the extensive mining, and other dust producing activities in the area. This poster will present the interpretation of these data in regards to the identification and apportionment of sources such as dust, road dust, oil combustion, mining, and coal combustion.

8SA.4

Relating Stack Height to Regional Pollutant Exposures.

KRISTINA WAGSTROM, Fatema Parvez, *University of Connecticut*

Estimating the inhalation intake fraction for emissions from a variety of sources provides a means by which to determine the relative impact between different emissions sources. For instance, it is likely that emissions from an elevated stack will have a lower intake fraction than ground-level emissions. In this study, we compare the ground level concentration contributions and inhalation fraction for different heights of point source emissions to those estimated using dispersion modeling approaches.

This study employs a regional chemical transport model, CAMx (ENVIRON 2013), to extend this analysis over an entire region. The Particulate Matter Source Apportionment Technology, PSAT, (Wagstrom et al. 2008), is available in CAMx and is used to specifically track the contributions from each grouping of stack heights within the domain. This allows a more thorough estimation of total potential exposure by accounting for the transport of pollutants on regional scales.

In addition to estimating intake fraction of primary pollutants, as is common, we also provide estimates of the inhalation intake fraction for secondary pollutants. The intake fraction for secondary pollutants is calculated based on the commonality between the precursor and product. For instance, the intake fraction of SO_2 and particulate sulfate would actually be calculated as the intake fraction of the sulfur atom treating SO_2-sulfate as a complete system. This approach can also be applied to the NOx-nitrate system, the ammonia-ammonium system, and similar systems of organic species. This approach provides a more thorough and complete estimation of what fraction of the original emissions are eventually inhaled by the human population.

8SA.6

Seasonal Variations and Regional Sources of Ultrafine Particulate Matter at a Semi-Rural Site on the Olympic Peninsula.

LAUREN WHYBREW, Cassandra Gaston, Felipe Lopez-Hilfiker, Odelle Hadley, Honglian Gao, Fran McNair, Dan Jaffe, Joel A. Thornton, *University of Washington, Seattle, WA*

Currently, there are air quality standards for the mass concentration of particles less than 2.5 micrometers in diameter, PM2.5. However, there are no standards for ultrafine particles, i.e. those smaller than 0.1 micrometers, even though studies have shown that ultrafines can cause negative respiratory health effects beyond that of PM2.5 due to their smaller size. The mass and number concentrations of ultrafines, and therefore their sources, are not well characterized. To address this, we use a Scanning Mobility Particle Sizer (SMPS) to measure ultrafine particle concentrations and size distributions in Port Angeles, Washington, a region that has many local sources such as traffic, residential biomass burning, ship emissions, and industrial biofuel operations. The SMPS has been operating continuously since December 2013, providing us with measurements at a five-minute time resolution. In addition to the SMPS, we include a compositional analysis obtained from a high resolution, time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS) equipped with a FIGAERO inlet capable of measuring chemical compounds in both the gas and particle phases. The goals of this project are to gain insights into the primary sources of ultrafine particles in this region by using the observed diurnal and seasonal variations in ultrafine particle abundance, together with auxiliary data sets that include meteorological parameters and other chemical tracers of various pollutant sources. We observed seasonal differences in the diurnal profile and total number concentrations of ultrafine particles at this site due to differences in meteorological conditions and sources. Higher concentrations observed in winter were likely due to emissions from residential biomass burning as confirmed by observed biomass burning markers obtained by the FIGAERO HR-ToF-CIMS. These insights will then be used to evaluate the effectiveness of local air quality regulations.

8UA.1

Impact of Land Use on Atmospheric Quasi-Ultrafine Particles in Houston TX. INKYU HAN, Yuncan Guo, Masoud Afshar, *University of Texas School of Public Health*

A large number of urban populations in the world are exposed to ambient particulate matter (PM), a mixture of natural and anthropogenic pollutants. The association between the adverse health outcomes and exposure to atmospheric fine and coarse PM are well known whereas the health effects of exposure to airborne ultrafine particles (UFPs) are much less understood. Yet due to its small size and large number of particles, UFPs can be deposited at a much higher efficiency in the alveolar region than fine and coarse PM and this enhances potential risks associated with exposures to particles in this size range. An important reason for this gap in knowledge regarding increased health risks associated with exposure to UFPs is the lack of exposure assessment in urban areas. Unlike fine and coarse PM available from the national air monitoring stations across the United States, measurement of ambient UFP can be only evaluated by investigators directly conducting air sampling in the field. The main objective of the study was to examine the impact of land use on ambient quasi-UFP mass (particle size less than 0.25 micro-meter) and polycyclic aromatic hydrocarbons (PAHs) in quasi-UFP in Houston, TX. Quasi-UFP was concurrently collected at two different monitoring sites between January 2013 and December 2013. The measurements included 40 weekly integrated particle mass and PAHs. Preliminary results showed that weekly average concentrations of quasi-UFP were 5.8 ug/m3 (Industrial site) and 4.7 ug/m3 (Background). The weekly average concentrations of sum of particle bound PAHs in quasi-UFP were 2.86 ng/m3 (Industrial site) and 1.63 ng/m3 (Background). There were significant differences of weekly average of quasi-UFP mass and PAHs in quasi-UFP between the two sites. The large spatial variability in the mass and PAHs in quasi-UFP suggested the effect of local emission sources by different land use types.

8UA.2

Contribution of Tailpipe Emissions of Gas Phase Precursors to Secondary Aerosol Formation. BEHDAD YAZDANI BOROUJENI, Chance Spencer, Don Collins, *Texas A&M University*

On-road vehicle emissions are a significant source of ambient air pollution. Laboratory and real-world based emission measurements of heavy duty diesel vehicles (HDDV) show that they are important sources of primary aerosols. However, emitted gaseous species, especially those from light duty gasoline vehicles (LDGV), can undergo photochemical reactions and act as precursors for secondary aerosol formation. Recent studies suggest that the contribution of gasoline vehicles to transportation-related aerosol mass in the atmosphere may dominate over that from diesel vehicles.

This study used near-roadway portable captive aerosol chambers to assess the contribution of gas phase vehicle emissions in formation of secondary aerosol. Two identical cylindrical chambers, each 1 m3 in volume, were used along with integrated scanning mobility particle sizers (SMPS). The cylindrical wall and top portion of each chamber is made of 0.025 mm transparent fluorinated ethylene propylene (FEP) film. The bottom portion of each chamber is a permeable membrane of expanded polytetrafluoroethylene (ePTFE), which allows gases to diffuse into the chamber and react inside it while preventing penetration of particles. The experiments were performed near a major arterial road in College Station, TX. One of the chambers was located upwind and the other downwind of the roadway. In both chambers, monodisperse seed particles were injected and their growth rate evaluated using the SMPS systems. The difference between measured upwind and downwind captive aerosol growth rates is interpreted as the contribution of gaseous vehicle emissions in formation of secondary aerosol mass. Complementary measurements of the primary emissions size distributions were made by sampling ambient air with both SMPS systems. Preliminary results based on 10 days of experiments conducted under varying meteorological conditions will be presented.

8UA.3

Elucidating Emission Sources and Atmospheric Processes of Aerosols in Fresno, CA: Results from 2013 Winter NASA DISCOVER-AQ Study. CAROLINE PARWORTH, Hwajin Kim, Shan Zhou, Sonya Collier, Xiaolu Zhang, Christopher Cappa, Qi Zhang, *University of California, Davis*

From January – February 2013 an intensive field study sponsored by NASA called Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) took place throughout central California. This work focuses on elucidating sources and processes of aerosols in Fresno, CA. Ionic $PM_{2.5}$ and gases were characterized with a particle-into-liquid sampler coupled with ion chromatography (PILS-IC) and gas denuders. The mass concentration and size-resolved composition of non-refractory PM_1 (NR-PM_1) were measured with an Aerodyne high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS).

From the PILS-IC the total mass concentration of ionic $PM_{2.5}$ was determined to be 17.5 micro-grams per cubic meter, where NH_4NO_3 dominated mass concentration. From gaseous measurements of HNO_3 and NH_3 it was determined that formation of NH_4NO_3 in the particle phase is limited by gaseous HNO_3 concentrations. Instrument intercomparisons show that ~90% of $PM_{2.5}$ mass is made up of NR-PM_1 species, and highlights the importance of measuring NR-PM_1 composition.

From the HR-ToF-AMS the average mass concentration of NR-PM_1 was determined to be 32.13 micro-grams per cubic meter, and was dominated by organics (56% of total mass concentration), followed by nitrate (28%), ammonium (10%), sulfate (4%) and chloride (1%). Positive matrix factorization (PMF) was performed on the HR-ToF-AMS mass spectra and several types of primary organic aerosols (POA) and oxygenated organic aerosols (OOA) were obtained. The elemental compositions, temporal and diurnal variations, correlations with tracer compounds, and size distributions of these components have been investigated to characterize the sources and processes of PM_1 in Fresno during winter time. Diurnal variations of mass concentrations for secondary aerosols (i.e., nitrate, sulfate, OOAs) show evidence of daytime enhancements associated with boundary layer breakage and mixing down of particles that were formed the previous night.

8UA.4

Monitoring Stations to Assess Near-Road Air Pollution. NATHAN HILKER, Cheol-Heon Jeong, Jon M Wang, Naomi Zimmerman, Robert Healy, Kelly Sabaliauskas, Greg J. Evans, Tony Munoz, Al Melanson, Andrew Warner, Michael Noble, Jerzy Debosz, Yushan Su, Dennis Herod, Celine Audette, Luc White, Daniel Wang, Dave Henderson, *SOCAAR, University of Toronto*

Exposure to air pollution near major roadways has been identified as a risk factor for a number of diseases and other adverse health outcomes. A pilot study within the Greater Toronto Area (GTA) has been initiated to better assess population exposure to traffic-related Criteria Air Contaminants (CACs) as well as emerging pollutants. Four separate stations are being created, each housing a common suite of instruments to measure traffic-related pollutants, many in real time. Supporting data including meteorology and traffic counts will also be collected. Traffic density differs greatly between sites, allowing the assessment of pollutant concentrations across a range of near-road conditions. This poster describes the design of these stations including the selection of sites and the suite of instruments. Preliminary data collected from an urban background and near-road site are presented. Different strategies are explored for mining the inherent spatial and temporal patterns, including differences in weekday vs. weekend patterns, roadside vs urban background diurnal patterns, and resolution of individual vehicle plumes measured using high time resolution instruments. These methods are being developed in order to estimate the contribution of traffic emissions to local air quality over multiple scales ranging from individual vehicles to fleet averages.

8UA.5

Vertical and Horizontal Aerosol Profiling Over Residential Areas. VERONIKA DOCEKALOVA, Jan Hovorka, Filip Kobrzek, Petr Marecek, *Charles University in Prague*

Ultrafine, fine and coarse particulate matter influence both air quality and human health. Particle concentration in the air is usually measured at the ground level and aerosol dispersal is only estimated based on modelling.

Therefore, the aim of this study was to measure size-segregated atmospheric aerosol (coarse, fine and ultrafine particles) near specific sources by airborne measurements. Data analysis provides information on vertical and horizontal size-segregated aerosol dispersal from source and its contribution to the air pollution in the surroundings.

Unmanned airship, remotely controlled with GPS 10Hz position tracking, electrically powered with propulsion vectoring which allows average cruising speed of 4 ms^{-1}, was used. The airship was equipped with specially designed gondola carrying three aerosol monitors and temperature sensor. The monitors acquired 1Hz data on TSP of PM10, PM2.5 and PM1 and number concentration of fine and ultrafine particles. Flights were made in February/March 2014 in the Moravian-Silesian region over urban and suburban areas of Ostrava city (Czech Republic). They were: small village near Czech-Polish state border down-wind of Ostrava city, residential district in the city near large complex of heavy industry and small settlement up-wind of the city. Repeated flights were carried out in several height levels up to 500 m above ground.

In the village locality, the measurement were conducted from midday to late afternoon, while in the residential district and small settlement there were rather very early morning flights conducted to record morning air boundary layer inversion stratification. As an example, in the village coarse aerosol concentrations were low and concentrations did not vary significantly nor with flying height nor over residential or field area. Number of nanoparticles slightly decreased with increasing altitude but no distinctive vertical profile was observed.

This project is supported by the Czech Grant Agency (P503/12/G147).

8UA.6

Long-term Trends in Criteria Pollutant Concentrations within the South Coast Air Basin of California. SCOTT A. EPSTEIN, Kalam Cheung, Sang-Mi Lee, *South Coast Air Quality Management District*

The South Coast Air Basin (SCAB) is an area of 10,743 square miles that encompasses Orange County and major portions of Los Angeles, Riverside, and San Bernardino counties. Topographical barriers to pollutant transport outside of the Basin along with intense photochemistry, emissions from a strong industrial presence, and a passenger and goods movement transportation infrastructure reliant on fuel combustion lead to significant pollution problems. Major portions of the SCAB are in federal non-attainment of 8-hr ozone and $PM_{2.5}$ standards. However, conditions within the SCAB have improved significantly since the advent of modern air pollution control measures. The South Coast Air Quality Management District maintains a network of 38 permanent monitoring stations within the SCAB to continuously measure criteria pollutant concentrations. This extensive network allows for a detailed spatial and temporal analysis of pollutant concentrations. We will explore seasonal and weekly variations in pollutant concentrations as a function of location along with regional trends over the past four decades. Meteorological variations and the location of emission sources can be used to explain a large fraction of the spatial and temporal variation in concentrations throughout the Basin.

8UA.7

Modeling the Spatial Variability of Traffic Related Pollutants and the Contribution of High Emitting Vehicles in Pittsburgh, PA. YI TAN, Timothy Dallmann, Allen Robinson, Albert A. Presto, *Carnegie Mellon University*

The highly time-resolved data from a recent mobile monitoring campaign in Pittsburgh, PA showed substantial spatial variability of traffic related pollutants. High emitting vehicles caused short-duration plume events, and contributed a disproportionately large fraction of the near road exposures of particle-bound polycyclic aromatic hydrocarbons (PAHs) and BC.

In this study, we developed a two-layer statistical model to predict the spatial variability of PAHs and BC. The two-layer model was based on highly time-resolved data from 42 Phase I sites. The plume layer provided a simplified estimation on the near road decay of pollutant plumes, and the base layer modeled the spatial patterns of background PAHs and BC using the traditional land use regression (LUR) method. When the two layers were combined, the model successfully predicted the mean concentrations of PAHs and BC. We validated our model using measurements collected from 36 Phase II sites which covered a broader area than Phase I sites. The two-layer model reasonably predicted concentrations of PAHs and BC and the impact of high emitting vehicles at Phase II sites. Traditional single layer LUR models were also developed using mean concentrations from the 42 Phase I sites. The two-layer model performed better than the traditional LUR model in capturing the spatial variability of PAHs and BC.

The two-layer model found that around 20% residential units in the study domain were considerably impacted by PAH plumes from high emitting vehicles (i.e., plumes contributed more than 40% of the total PAH exposure). High emitting vehicles had smaller impacts on BC exposures, contributing to less than 20% of the total BC exposure at ~90% residential units. BC exposures were more driven by regional emissions such as coke production.

8UA.8

High-spatial Resolution Profiling of Aerosol Size Distribution Aloft a Highway. VERONIKA DOCEKALOVA, Jan Hovorka, Filip Kobrzek, Petr Marecek, Jan Bendl, *Charles University in Prague*

Dispersal of aerosol particles from specific sources within atmospheric boundary layer is usually calculated from earthbound measurements. Therefore, we conducted airborne measurements to experimentally determine spatial variability of number size distributions of atmospheric aerosol aloft a busy highway. Unmanned airship, remotely controlled with GPS 10Hz position tracking, electrically powered with propulsion vectoring and average cruising speed of 4 ms^{-1}, was used. The airship manoeuvrability allows data localisation within 5m both vertically and horizontally but depends on wind speed and strength of thermal vertical motion. Therefore, airship measurements were conducted from early morning to about midday for two days in June 2014 above the D1 highway SE of Prague (Czech Republic). There was a traffic flow from 4500 up to 7500 cars per hour at the D1 during the measurements. The airship carried temperature sensor and a TSI's NanoScan SMPS and an Optical Particle Counter - OPC. Each monitor was connected to a separate heated inlet. First, longitudinal flights aloft a highway and nearby field situated up-wind were conducted with 60s integration time at heights from 40 to 200m. Two modes at 15 and 30nm were clearly distinguishable in the NanoScan size spectra with normalised PNC in the range of 10-6200cm^{-3} varying significantly with a flight height. Second, transversal flights aloft the highway with data acquisition frequency of 1Hz for 15nm particle sizes and for the OPC full size range were conducted at height from 40-200m. Vertical profiles aloft a highway for various particle sizes were constructed.

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9AC.1

Vapor Wall Loss of Semi-Volatile Organic Compound in Smog Chamber. PENGLIN YE, Xiang Ding, Ellis Shipley Robinson, Neil Donahue, *Carnegie Mellon University*

We have investigated the vapor wall loss of semi-volatile organic compounds (SVOCs) in the CMU smog chamber. Wall loss is a key factor influencing organic aerosols behavior in chamber experiments. Previous studies of wall loss focused on the loss of particles to the chamber wall. However, little knowledge is available about vapor wall loss that is due to the condensation of organic vapors on or into Teflon chamber walls. Matzunaga and Ziemann showed that organic vapors could sorb reversibly into Teflon chamber walls, but direct observations of semi-volatile vapor wall losses are lacking. We have studied the passive decays of alkanes (hexacosane, pentacosane, docosane, eicosane, d62-squalane) and an organic acid (oleic acid) in single-component and binary-component (organic) systems, using ammonium sulfate (AS) seeds to constrain particle wall loss (WLp). The organic to sulfate ratio (O:S) is a robust measure of mass loss; for pure organics coating AS, the coated aerosols sustain SVOCs at their saturation concentration, and so mass loss of organics from the suspended particles reflects vapor wall loss. For all organics studied here, O:S decreased steadily, clearly indicating significant vapor wall loss (WLv). This confirms that it is important to characterize WLv of SVOCs in chamber experiments. The WLv of the alkanes increased decreasing carbon number. Eicosane had the highest WLv and hexacosane showed quite small WLv. This indicated WLv was positively related to the volatility of SVOCs. The WLv of pure oleic acid and the mixture of oleic acid and d62-squalane were also studied. Pure oleic acid showed larger WLv than in the mixture. And the WLv of oleic acid in the mixture was positively correlated with the fraction of oleic acid in the mixture. Our results confirm that WLv needs to be considered in smog-chamber study, especially when evaluating the secondary organic aerosol (SOA) formation from SVOCs as well as OA evolution.

9AC.2

Parameterizing Vapor Wall Loss Rate in a Teflon Chamber. XUAN ZHANG, Rebecca Schwantes, Hanna Lignell, Matthew Coggon, Richard Flagan, John Seinfeld, *Caltech*

Understanding the impact of secondary organic aerosol (SOA) on climate change and human health requires an accurate representation of SOA formation from biogenic and anthropogenic emissions. The chamber measured SOA yields from the photochemistry of individual volatile organic compounds (VOC) provide the standard parameterization in atmospheric 3-D models for simulating the SOA budget in regional and global scales. However, field measurements indicate that the SOA abundance is routinely underpredicted when the traditional chamber derived parameterizations are used. One potential reason for this low bias is the unaccounted chamber wall effects, in particular, the deposition of gas-phase SOA precursors onto chamber walls, other than partitioning onto existing particles. In this study, we report the wall loss rates of ~ 30 organic vapors generated from the photochemical oxidation of isoprene, toluene, alpha-pinene, and dodecane at 298 and 318 K. These organic vapors span a wide range in volatilities and oxidation states, thus representative of intermediate- and semi-volatile compounds produced under typical chamber experimental conditions. A vapor wall loss model is developed to describe the observed vapor-wall interactions. We find that the Teflon chamber walls serve as a large reservoir of absorbing organic materials. The partition of vapors on chamber walls is a reversible process, which might be explained by the equilibrium sorption mechanisms of glassy polymers. The accommodation coefficient of a specific vapor on chamber walls is related to its volatility: vapors with lower vapor pressures tend to be more accommodated by the Teflon walls. The impact of vapor wall loss on the SOA yield is evaluated by comparing the equilibrium time scales between vapor-wall and vapor-particle partitioning.

9AC.3

Main Parameters Controlling Equilibration Time Scales of Atmospheric Semi-Volatile Aerosols.

ANDREY KHLYSTOV, *Desert Research Institute*

Air quality models assume semi-volatile organic compounds (SVOC) in atmospheric aerosol to be in thermodynamic equilibrium with the gas phase. Recent experimental data suggested a possibility of very slow thermodynamic equilibration due to mass transfer limitations in solid or highly viscous particles. Thus, time scales of gas-particle equilibration need to be studied to verify assumptions made by the current air quality models. Understanding kinetics of gas-particle partitioning is also of great importance for interpretation of laboratory and ambient studies of aerosol volatility using thermodenuders.

In this presentation, I will revisit main parameters that control kinetics of aerosol equilibration to demonstrate that aerosol equilibration depends only on the aerosol size distribution characteristics and, if one accounts for particle size changes due to condensation/evaporation, on the ratio of the initial aerosol mass concentration to the saturation vapor concentration of the condensing species. I will also provide an estimate of the relative influence of this ratio on the equilibration time. Equilibration of the total mass of a multi-component aerosol and the effect of chemical reactions will also be discussed. Finally, the effect of intra-particle transport will be considered. I will use this analysis to provide estimates of the equilibration time scales for ambient aerosols to delineate the region of applicability of the thermodynamic equilibrium assumption. Contribution of different parameters to the overall uncertainty in estimating aerosol characteristic times will also be discussed.

9AC.4

A Critical Evaluation of Proxy Methods used to Estimate the Acidity of Atmospheric Particles.

CHRISTOPHER HENNIGAN, Jessica Izumi, *University of Maryland, Baltimore County*

Aerosol acidity is an important parameter that impacts human health, ecosystems, and biogeochemical cycles. Aerosol acidity also affects many chemical and physical processes in the atmosphere, including aerosol water uptake and the gas/particle partitioning of many semi-volatile compounds. Despite its importance, the acidity of atmospheric particles is generally quite poorly constrained. This is due to both the difficulty in measuring non-conservative H^+ and to the general disagreement among proxy methods commonly used to estimate aerosol acidity. In this study, five proxy methods of aerosol acidity are evaluated and compared using as inputs a month of ambient measurements collected in Mexico City during the MILAGRO study. The proxy methods evaluated include: 1) the ion balance method; 2) the $NH_4^+/(Cl^- + NO_3^- + 2*SO_4^{2-})$ molar ratio; 3) the ISORROPIA and AIM thermodynamic equilibrium models run in reverse mode (aerosol composition only); 4) the ISORROPIA and AIM thermodynamic equilibrium models run in forward mode (gas + aerosol inputs); and 5) gas-aerosol phase partitioning of the semi-volatile NH_3/NH_4^+ and HNO_3/NO_3^- systems. It is shown that the two most common measures of aerosol acidity – the inferred H^+ loading (in nmol/m^3) and aerosol pH – have no correlation, a finding that has important implications for the interpretation of many ambient studies. We further highlight major differences and investigate the largest sources of uncertainty across the various proxy methods. Ultimately, the accuracy of each method is assessed and recommendations are made for their appropriate use based on the limitations observed under different atmospheric conditions.

9AC.5

Probing Aerosol Particle Interfaces with Biphasic Microfluidics. CARI DUTCHER, Andrew Metcalf, *University of Minnesota, Twin Cities*

Aerosol particles are complex microenvironments, which can contain multiple interfaces due to internal liquid – liquid phase partitioning and the external vapor – liquid surface. These aerosol interfaces have profound effects on particle morphology, species uptake, equilibrium partitioning, activation to cloud condensation or ice nuclei, and optical properties. Many factors play a role in determining a particle's internal structure, such as ambient environmental conditions and the chemical composition of the respective phases, resulting in many possible particle configurations. For example, the aqueous and organic phases in a single aerosol particle may align in a side-by-side nodule morphology, whereas in other cases, the organic phase may form a film that can completely surround the aqueous phase. In order to fully predict a particle's internal structure at a given temperature, relative humidity, and chemical composition, fundamental studies of interfaces observed in atmospheric aerosol particles are essential.

In this talk, a novel method using biphasic microscale flows will be introduced for generating, trapping, and perturbing complex interfaces at atmospherically relevant conditions. These microfluidic experiments are conducted using phase contrast and fluorescence microscopy on a temperature-controlled inverted microscope stage with high-speed imaging to monitor interfacial phenomena at the microscale. Chemical compositions of the aqueous and organic phases studied here include electrolyte and water soluble organic acid species often observed in the atmosphere, such as mixtures containing ammonium salts (e.g., $(NH_4)_2SO_4$, NH_4NO_3) and dicarboxylic acids (e.g., malonic, glutaric, and maleic acid). From these measurements, important thermodynamic, kinetic, and rheological properties of the atmospheric aerosol mimics can be explored, yielding insight into multiphase aerosol particle dynamics.

9BA.1

Effect of Sampling Flow Rates on Virus Collection Efficiencies of a BioSampler vs. an All-Glass Impinger. John Lednicky, Julia Loeb, Kevin Fennelly, Diandra Anwar, Sewon Oh, CHANG-YU WU, *University of Florida*

The dynamics of airborne virus transmission are not well understood, especially since it is not easy to collect virus aerosols with high efficiencies using air samplers that are commonly deployed for the microbiological assessment of air quality. One reason for the challenge in collecting virus aerosols is the design of the air samplers that primarily targets the collection of airborne bacteria and fungi and their spores; such a design is relatively inefficient for collecting smaller-sized particles. In this study, methods to improve the efficacies of the collection of viral aerosol particles by common air samplers were explored. The collection efficiencies of an SKC BioSampler® and an All-Glass Impinger 30 (AGI-30) operated under variable flow rates and sampling times were evaluated using laboratory-generated aerosols of MS2 bacteriophage. The BioSampler's efficiency was higher than the AGI-30 when it was used at a collection flow rate lower than the manufacturer's recommended rate of 12.5 L/min, whereas the opposite was true for the AGI-30. In follow-up work, we opportunistically tested whether we could detect airborne viruses using BioSamplers operated for the same length of time but at two different flow rates in the vicinity of sick office workers. For both field trials, virus collection was better when the BioSamplers were operated at a flow rate of 8 L/min instead of the recommended flow rate of 12.5 L/min.

9BA.2

Application of ATP-based Bioluminescence for Bioaerosol Quantification: Effect of Sampling Method. TAEWON HAN, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

An adenosine tri-phosphate (ATP)-based bioluminescence method can offer a quick and affordable solution for quantifying bioaerosol samples and could be applied to estimate the efficacy of various bioaerosol samplers. As part of our continuing development of this method, here we investigated how different bioaerosol sampling methods affect the intensity of ATP-based bioluminescence reactions. The following bioaerosol sampling methods we investigated when sampling Pseudomonas fluorescens and Bacillus atropheus aerosolized by a Collison nebulizer (BGI, Inc.): (1) Button Aerosol Sampler (SKC, Inc.) used with polycarbonate, PTFE, and cellulose nitrate filters, (2) BioSampler (SKC, Inc.) with 5 mL and 20 mL of collection liquid, and (3) our newly developed Electrostatic Precipitator with Superhydrophobic Surface (EPSS). All three samplers were tested for 15 and 60 minute sampling times. All bioaerosol samples were quantified using a ratio (R): luminescence intensity produced by the bacterial ATP (indicative of the total ATP content) vs. cell counts determined by microscopy.

The effect of sampling was quantified as a dimensionless ratio, RR (|1-R_sample/R_nebulizer|), which represents a change in microorganism condition before and after sampling. For B. atrophaeus, the RR when sampled with BioSampler ranged from 0.79 to 0.93; for Buttons sampler RR ranged from 0.51 to 0.90; the EPSS showed the lowest range RR values, from 0.32 and 0.55. Differently from B. atrophaeus, the average RR value for P. fluorescens was 4.2. We hypothesize that the drastic change has to do with damage to P. fluorescens during sampling, thus resulting in the release of ATP and a more efficient interaction of ATP and bioluminescence reagents. The results indicate that the intensity of ATP bioluminescence depends on a sampling method and amount of stress to microorganisms. Future studies will investigate the reactions of different species in more detail.

9BA.3

Characterization of Gelatin Filters for Sampling Bacillus Anthracis. KRISTIN BOWER, John Yeager, Paul Dabisch, *NBACC*

There are many types of samplers that can be used to estimate the concentration of viable microorganisms present in an aerosol. Within the sampling process, there are many possible sources of loss, both physical and biological. Characterization of such losses is an important since losses which are unaccounted for will lead to an underestimation of dose in animal inhalation studies. In this study, the use of a gelatin filter to sample aerosolized Bacillus anthracis – both spores and vegetative cells – was characterized. Losses in viability associated with impaction velocity onto the filter medium and retention of collected microorganisms in a viable state for the duration of sampling were assessed. To this end, preparations of B. anthracis spores and vegetative B. anthracis were aerosolized into a small test system and sampled with 25-mm gelatin filters. The filters were operated at flow rates ranging from 0.25 L/min to 1.0 L/min to vary impaction velocity at the filter face. For a subset of samplers, additional clean air was pulled through the filter post-collection to examine the effect of airflow on the viability of collected bacteria. Gelatin filters were dissolved and bacterial concentrations were determined by enumeration on trypticase soy agar plates. For both vegetative and spore preparations of B. anthracis, no significant difference in the measured aerosol concentration was observed among the different flow rates, suggesting that the filter face velocity does not affect the viability of the collected bacteria in the range of flows examined. Similarly, no significant change in the measured aerosol concentration was observed following additional airflow across the filter for either preparation, suggesting that desiccation of the collected bacteria does not occur during the durations tested. These results suggest that gelatin filters can be used for efficient sampling of both vegetative and spore preparations of B. anthracis.

9BA.4

Effect of Bioaerosol Sampling Stress on 16S rRNA/rRNA-gene Ratio of Airborne Bacteria. HUAJUN ZHEN, Valdis Krumins, 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. A higher cellular ribosome content (often represented as 16S rRNA normalized to 16S rRNA-gene) is interpreted as greater potential for metabolic activity of bacteria. The same methodology could be applied to investigate metabolic activity of bacteria in the airborne phase. However, airborne bacteria experience mechanical and/or desiccation stress during sampling, which may affect rRNA stability, raising questions regarding representativeness of measured rRNA content in bioaerosol samples.

To simulate the stress during sampling by filtration, fresh E. coli cultures were aerosolized and collected on filters. Particle-free air was then passed through the filters for 0, 2, 4 and 6 hours. Our initial results showed high variability in rRNA/rRNA-gene ratio as function of sampling time. We determined that this inconsistency was largely due to the losses of rRNA and rRNA-gene (up to 90%) during sample processing.

To overcome this issue, a dual-internal-reference technique was developed utilizing exogenous Pseudomonas fluorescens 16S rRNA and DNA as internal standards to control for losses of E. coli rRNA and DNA during sample processing. This technique was applied to investigate the change of rRNA/rRNA-gene ratio during growth of E. coli in Tryptic Soy Broth at 37 °C. Results showed that the ratio increased rapidly to ~104 during the initial 3 hours of exponential growth phase, and then gradually decreased and finally leveled off at around 5000 after 16 hours. This confirmed the positive correlation between bacterial growth and cellular ribosome content as demonstrated by previous studies.

Tests with sampling devices that utilize collection mechanisms of filtration, impingement and electrostatic precipitation are currently ongoing. The preliminary data indicate that the choice of sampling technique might bias the amount of rRNA detected in bioaerosol samples.

9BA.5

Genomic RNA as a Physical Tracer in Filovirus Aerosol Studies. TAMIKA KNIGHT, Michael Schuit, Shanna Ratnesar-Shumate, Paul Dabisch, *NBACC*

Non-labile tracers are important in aerosol studies examining the persistence of microorganisms. The co-aerosolization of a tracer which can be quantitated in parallel with the biological activity of a microorganism allows for separation of physical losses from losses of biological activity, and calculation of a biological decay rate, which can be utilized to estimate the spread of disease and ultimately inform preparedness and response efforts. Substances commonly used as tracers in aerosol studies include fluorescent microspheres, soluble fluorescent salts, and, more recently, nucleic acids measured using quantitative PCR (q-PCR). Use of nucleic acids as a physical tracer is desirable as chemicals commonly added as tracers have occasionally been shown to be toxic to the microorganism or alter the aerodynamic properties of the aerosol. The objective of this study was to examine the use of filovirus genomic RNA quantitated with q-PCR as a physical tracer in aerosol studies. Filovirus suspensions containing a fluorescent microsphere were aerosolized into a small aerosol chamber and periodically sampled with both an Aerodynamic Particle Sizer (APS) and 25-mm gelatin filters. Gelatin filters were dissolved and utilized for both q-PCR and fluorescence measurements. The dissolved filter samples were diluted in Trizol LS and viral RNA for real-time reverse transcription-PCR (RT-PCR) amplification was extracted using a Direct-zol RNA MiniPrep kit. Primers for Ebola and Marburg were obtained from the US-DoD Critical Reagents Program. The physical decay rate of the aerosols generated within the chamber was estimated from APS particle counts, genomic equivalents as determined by q-PCR, and microsphere fluorescence. Results comparing the use of genomic RNA as physical tracer to results obtained using either the APS or a fluorescent microsphere to track physical losses will be presented. These data will be utilized to support future studies examining the biological decay rate of aerosolized filoviruses.

9IM.1

Determining the Absolute Concentration of Proteins Using ES-DMA. MINGDONG LI, Jiaojie Tan, Michael Tarlov, Michael Zachariah, *University of Maryland*

A fast and accurate assay to determine the absolute concentration of proteins is described based on direct measurement of droplet entrapped oligomer formation in electrospray. Here we demonstrate the approach using electrospray differential mobility analysis (ES-DMA) which can distinguish monomers and dimers from higher order oligomers. A key feature of the method is that it allows determination of the absolute number concentration of proteins eliminating the need for specific protein calibration. The method was demonstrated by measuring the concentration of a NIST Standard Reference Material 927e, Bovine Serum Albumin, and a NIST candidate reference material 8670, immunoglobulin G.

9IM.2

Bio-nanoparticles as Candidate Reference Materials for Mobility Analysis of Nanoparticles. RIAN YOU, Mingdong Li, Suvajyoti Guha, George Mulholland, Michael Zachariah, *University of Maryland*

We propose bio-nanoparticles as a candidate reference material for determining the mobility of nanoparticles over the range of 6×10^{-8} $m^2/V\cdot s$ to 5×10^{-6} $m^2/V\cdot s$. Using an electro-spray differential mobility analyzer (ES-DMA), we measured the empirical distribution of several biomaterials. All of them show monomodal distributions that are more than two times narrower than the currently used calibration particles for mobility larger than 6×10^{-8} $m^2/V\cdot s$ (diameters less than 60 nm). We also present a numerical method to calculate corrected distributions of bio-nanoparticles by separating the contribution of the diffusive transfer function. The corrected distribution is about 20 % narrower than the empirical distributions. Even with the correction, the reduced width of the mobility distribution is about a factor of two larger than the diffusive transfer function. The additional broadening could result from the non-uniform conformation of biomaterials and from the presence of volatile impurities or solvent adducts. The mobilities of these investigated biomaterials are stable over a range of buffer concentration and molarity, with no evidence of temporal degradation over several weeks.

9IM.3

A New Paradigm for Size Distribution Measurements Relevant to Aerosol Health Studies. AMANDA GRANTZ, Johannes Leppä, Richard Flagan, *California Institute of Technology*

With regard to particle size, evidence suggests that fine particles play a substantial role in affecting human health. Associations between PM2.5 and health endpoints are consistent, yet the role of ultrafine particles within this class has yet to be fully resolved. A research gap still exists in the development and deployment of inexpensive and widespread real-time monitoring instruments and methods for aerosol size distribution measurement. Size determinations are crucial for proper exposure assessments because particles of different sizes may deposit in different compartments of the human respiratory tract upon inhalation and possibly affect health in different ways. This study discusses whether high resolution measurements are necessary for prediction of lung dose in epidemiological time series studies or if there is potential for a new paradigm for collecting aerosol particle size measurements more simply and cost-effectively for health effects studies.

The arguments presented in this study are based on synthetic data describing aerosol populations measured in the environment. Particle number size distributions are simulated from published data and used as input for modeled measurement systems. These systems are modeled to recover size distributions with varying resolution. The ICRP model of particle deposition is then used to calculate deposition patterns in the human respiratory tract based on these measured particle size distributions. The deposited dose of particles is estimated for different regions of the human respiratory tract. Predicted deposition values are compared to ideally known deposition values, as calculated directly from the simulated input particle size distribution. Calculated dose biases are within ±10% even for measurement systems modeled to classify particle sizes with resolution values down to 3.

9IM.4

Concentrated Particle Collection in to Liquid for Toxicological Studies. 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 concentrated particle collection into liquid for toxicological studies. We use a three-stage Growth Tube system which has a low output temperature and dew point, greatly decreasing water condensation from the sampling flow in to the collection medium. Particles as small as 8 nm can be activated and grown without exceeding 25 deg C in the majority of the flow. By increasing the number of delivering nozzles we are capable of depositing ambient aerosols into a liquid volume of less than 150 uL. Liquid collection allows for sampling of water-soluble, vapor-phase components as well as particles, mimicking exposure in real environmental conditions.

This approach has several advantages over standard filter collection. The concentrated nature of the suspension greatly reduces sample collection time and the direct collection into suspension limits morphological and chemical changes that may happen during extraction and re-suspension from filters. The sampler is portable, and can run unattended for several days. Particle collection efficiencies over 95% are measured for sizes between 10 nm and 2.5 um.

9IM.5

A New Instrument for Direct Cellular Exposure to Ambient Aerosols. ARANTZAZU EIGUREN FERNANDEZ, Ning Li, Steven Spielman, Susanne Hering, *Aerosol Dynamics Inc.*

A new instrument has been developed for direct cell exposure to ambient aerosols. Vapors and particles are delivered directly into the cell culture providing a realistic exposure scenario for in-vitro toxicity studies. Particles and vapor-phase components are collected into the liquid without disturbing the cells, reducing possible cellular stress produced during collection.

This new system is based on water condensational growth of ambient particles. It samples at 8 lpm. To minimize surface disruption and maximize collection, aerosols are delivered through 32 impaction nozzles, each carrying 0.25 lpm. The exposure chamber is kept at 37^{o}C for optimum cell survival. As cell cultures require a 5% CO2 environment, a 0.4 lpm CO2 flow is added at the inlet and mixed with the incoming flow.

By challenging the system with monodisperse particles, collection efficiencies >95% were demonstrated for particles between 10nm and 2.5µm.

Preliminary studies evaluating cell viability after exposure to aerosols were conducted using mouse macrophage cell line RAW 264.7 and human bronchial epithelial cell line BEAS-2B. Both lines have been widely used as in-vitro models to study the adverse effects of various air pollutants. Two exposure conditions were evaluated, high and low particle concentrations. For low concentrations (~3x103#/cc) no difference between control and exposed cells were observed after 1 hr, 3 hr and 6 hr exposures. For high concentrations, cells were exposed to emissions from burning incense with particle concentrations over 5x105#/cc. After 5, 20, and 120 min exposure cells were viable; however, after overnight incubation with the exposed medium, cell viability was determined to be 80%, 20% and 0%, respectively. These results showed a dose-response effect to extremely high exposure conditions.

These preliminary results suggest that the new system may provide a new tool for direct cellular exposure to ambient aerosols, allowing a realistic study of the toxicity of aerosols.

9NP.1

Atmospheric Nanoparticle Growth: From Nano- to Global Scale. ILONA RIIPINEN, Jan Julin, Taina Yli-Juuti, Silja Häkkinen, Lars Ahlm, Juan-Camillo Acosta Navarro, Ivica Crljenica, Katrianne Lehtipalo, Stephen D'Andrea, Jeffrey Pierce, *Stockholm University*

The way that condensable material is distributed to the atmospheric aerosol size distribution is among the key factors defining the properties and impacts of atmospheric particulate matter. Specifically, the number concentrations of ultrafine particles and CCN are largely governed by whether the secondary compounds can grow newly-formed clusters and particles to larger sizes or whether they condense primarily to the larger (> 100 nm) fraction of the atmospheric aerosol population. Knowledge on 1) the identities of the condensing molecules; 2) their thermodynamic (e.g. volatility) and kinetic (e.g. accommodation coefficients) properties is needed develop mechanistic models describing the nanoparticle growth process. Using detailed mechanistic growth models together with observational data from laboratory and field has enabled us to constrain the processes and molecules responsible for the growth of atmospheric nanoparticles – as well as related them to total formed the secondary aerosol mass. In this presentation I review our recent findings about the volatility of atmospheric nanoparticles and the thermodynamic and kinetic properties of the molecules growing these particles to climatically relevant sizes – covering both secondary organics as well as systems containing sufuric acid, ammonia and amines. Furthermore, I discuss the options of simplifying the growth process in atmospheric large-scale models in a physically and chemically consistent manner.

9NP.3

The Contribution of Sub-Grid, Plume-Scale Nucleation to Global CCN Concentrations. ROBIN STEVENS, Jeffrey Pierce, *Dalhousie University*

New-particle formation in the plumes of coal-fired power plants and other anthropogenic sulfur 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 kilometers and larger. The predictive power of these models has thus been 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 developed 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 sulfur-rich plumes based on large-scale mean meteorological parameters, emissions of SO_2 and NO_x from the source, and mean background pollutant concentrations.

We implement the P6 parameterization in the GEOS-Chem global chemical-transport model in order to evaluate the contribution of coal-fired power plants globally to particle number and CCN concentrations. We find that sub-grid scale new particle formation is sensitive to preexisting aerosol condensation sink. For constant SO_2 emissions, fewer new particles are formed in more polluted regions. Additionally, we see a seasonal cycle in sub-grid scale new-particle formation rates due to changes in SO_2 oxidation rates from changes in OH production from photolysis.

9NP.4

Difference in Particle Formation at a Mountain-top Location in Colorado during the Spring and Summer: Modeling and Comparison with Observations. FANGQUN YU, Anna Gannet Hallar, *University at Albany*

New particle formation (NPF) is a major source of atmospheric particles with important climatic and environmental impacts, and a firm understanding of dominant mechanism(s) of NPF in the atmosphere remains to be achieved. NPF has been observed frequently at Storm Peak Laboratory (SPL), a high elevation mountain-top observatory in Colorado. Analysis of recently available continuous measurements of condensation nuclei larger than 10 nm as well as particle size distributions reveals significant difference in the NPF during the Spring and Summer at SPL. Model simulations based on a global chemical transport model (GEOS-Chem) coupled with a size-resolved (sectional) advanced particle microphysics (APM) model are used to interpret in-depth the nucleation phenomena at SPL, focusing in this study on one Spring month (March 2012) and one Summer month (July 2012). The model, with nucleation rates calculated based on the ion-mediated nucleation mechanism, captures well the observed persistent daily nucleation events in March (almost every day) and very few NPF in July. While UV-B flux is ~ 50% higher in July, OH concentrations of the two months are comparable, probably as a result of much larger concentration of volatile organic carbons (VOCs) in the summer. Based on the model simulations, the monthly mean sulfuric acid gas concentration in July is a factor of ~ 2.5 lower than that in March but the concentration of condensable (low volatile highly oxidized) secondary organic gases is a factor of 4 higher in July. The high nucleation rates in March and the lack of nucleation in July indicate that sulfuric acid plays a much more important role in the initial nucleation process although organics compounds contribute significantly to the particle growth. Other factors contributing to the large difference in NPF at SPL during the Spring and Summer will also be discussed.

9NP.5

Simulation of Nucleation in the Global Atmosphere Based on CERN CLOUD Chamber Measurements. KEN CARSLAW, Eimear Dunne, Andreas Kuerten, Francesco Riccobono, Kamalika Sengupta, Catherine Scott, Joao Almeida, *University of Leeds*

Our understanding of global aerosol formation is based on models that use nucleation rates derived empirically from field campaigns or from extrapolation of thermodynamic and kinetic models. No global model predictions of particle formation throughout the atmosphere have been based on laboratory kinetic measurements. Here, we use nucleation rate measurements from the CERN cloud chamber for the sulfuric acid/ammonia system and the sulfuric acid/oxidized organic system to simulate particle formation throughout the troposphere using the GLOMAP global aerosol model. Measurements for the sulfuric acid/ammonia system cover a wide range of conditions of the free troposphere: temperatures of 208-298 K, sulfuric acid concentrations of <106-109 cm-3, ammonia concentrations of a few ppt to ~1 ppb, and ionisation rates for conditions between the lower and upper troposphere. In the organic experiments, a broad range of oxygenated compounds of biogenic origin was produced from oxidation of pinanediol ($C_{10}H_{18}O_2$, a first-generation oxidation product of α-pinene), thus the compounds can be considered as representative of oxidation products of biogenic monoterpenes. The model predictions are in good agreement with measured particle concentrations. In the boundary layer, we show how our biogenically influenced nucleation rate can help to explain the observed seasonal cycle in particle concentrations. This behavior is not captured by a model that assumes that only sulfuric acid controls the rate, an assumption that is anyway ruled out by experimental results from CLOUD. Nevertheless, such a biogenic mechanism underpredicts particle concentrations outside the biologically active seasons, suggesting that ternary inorganic nucleation or other organic compounds contribute to nucleation rates.

9PH.1

The Effects of Atmospheric Oxidation on the Levels of Aerosol Reactive Oxygen Species. JONATHAN ABBATT, *University of Toronto*

The term reactive oxygen species (ROS) is used to collectively describe species that are potentially good oxidants. Whereas it is believed that ROS are important in affecting the oxidant balance within the body, it is not known the degree to which atmospheric processing of aerosol before inhalation affects the abilities of particles to give rise to ROS. This talk will focus primarily on the ability of particulate matter to participate in redox cycling reactions which oxidize reduced aqueous species, such as anti-oxidants. Our group has been exploring how atmospheric oxidation gives rise to redox-active products in secondary organic aerosol formed from gas phase precursors (i.e. naphthalene, two-stroke engine exhaust) and from particulate precursors (i.e. diesel exhaust). The diesel black carbon results are intriguing because they illustrate that the majority of the redox-cycling ability is associated with the particle and not with small soluble species, and that redox abilities increase with simulated atmospheric oxidation. Such black carbon (“soot”) particles are known to translocate through the body, potentially allowing oxidative stress effects to be felt beyond the pulmonary system. A second topic is the level of peroxide species formed within particles through oxidation chemistry, focusing on their abundance in secondary organic aerosol. Overall, there is the need to better understand the fundamental chemistry generating ROS, so that a mechanistic connection of potential health effects can be made to atmospheric chemistry.

9PH.3

In Vitro Exposures to Isoprene-Derived Secondary Organic Aerosol: Assessing the Effects of Cytotoxicity and Inflammation on BEAS-2B using Resuspension and Direct Deposition Approaches. MAIKO ARASHIRO, Ying-Hsuan Lin, Kenneth Sexton, Ilona Jaspers, Rebecca Fry, Avram Gold, Jason Surratt, *University of North Carolina at Chapel Hill*

Although gaseous isoprene has been classified by the International Agency for Research on Cancer (IARC) as "possibly carcinogenic to humans (Group 2B), little is known about the health effects of isoprene-derived secondary organic aerosol (SOA) due to being recently recognized as an SOA precursor. Recent work from our laboratory has shown that anthropogenic pollutants, such as nitrogen oxides (NO_x) and sulfur dioxide (SO_2), enhance isoprene oxidation leading to SOA formation. Current understanding of the effects of gaseous products from oxidation of isoprene and its analog, 1,3-butadiene, on cytotoxicity and inflammation suggests that there may be similar effects associated with inhalation of isoprene-derived SOA. This study focuses on investigating the health effects associated with the inhalation of isoprene-derived SOA formed in the presence of acidified sulfate aerosol and initially high nitric oxide (NO) conditions. The objective of this study is to examine toxicity of these isoprene-derived SOA through a resupension exposure method and a direct deposition exposure method.

Outdoor smog chamber experiments were conducted to systematically generate SOA from the photochemical oxidation of isoprene. Human bronchial epithelial cells (BEAS-2B) were exposed to the chemical mixture generated in the chamber in two ways: (1) resuspension of particles collected onto filters; and (2) direct deposition of particles directly from air onto the air-liquid interface of cells using an instrument called the electrostatic aerosol in vitro exposure system (EAVES). Cytotoxicity and inflammatory biomarkers (IL-8 and COX-2) measured from the exposed cells will highlight benefits and limitations of each exposure method. Biological measurements together with complementary chemical measurements will identify potential toxicity associated with inhalation of isoprene-derived SOA.

9PH.4

Application of Aerosol Mass Spectrometry to infer the Sources of the Reactive Oxygen Species Generating Properties of Organic Aerosols in the Southeastern United States. VISHAL VERMA, Ting Fang, Lu Xu, Nga Lee Ng, Rodney Weber, *Georgia Institute of Technology*

Organic aerosols (OA) comprise a substantial fraction of the particulate mass in ambient atmosphere. Recently many of the bulk organic aerosol species have been associated with the markers of adverse health effects in humans. Mechanistic studies indicate that the reactive oxygen species (ROS) generated by organic aerosols can serve as the starting link for understanding these associations. Certain groups of the organic compounds such as secondary organic aerosols (SOA) and HULIS (Humic-like-substances) have been shown as highly oxidative; however, the specific components responsible for the ROS generation have not yet been identified. As part of a multi-institutional and collaborative center (Southeastern Center for Air Pollution & Epidemiology) study, we investigated the oxidative properties of organic aerosols in the southeastern US, in different seasons of the year when a particular source dominates the mass concentrations. For example, in summer, SOA is the strongest source while biomass burning dominates in winter. ROS-generation properties of these organic fractions were measured using the DTT (dithiothreitol) assay, which measures capability of the particles to generate superoxide radicals. Various factors of the organic aerosols were inferred from aerosol mass spectrometry, i.e. hydrocarbon-like OA (HOA), semi-volatile oxygenated OA (SVOOA), low-volatility OOA (LVOOA), isoprene OA, and biomass burning OA (BBOA). The contribution of each of these factors in the DTT activity of organic aerosols will be assessed using multiple linear regressions and positive matrix factorization tools. Our goal is to identify the specific organic components most responsible for driving the PM ROS generation, to trace their emission sources and to quantify their individual contribution in the aerosol oxidative potential.

9PH.5

Formation and Transformation of Hazardous Components in the Atmosphere: Reactive Oxygen Species, Polycyclic Aromatic Compounds and Allergenic Proteins. MANABU SHIRAIWA, Andrea Arangio, Kathrin Selzle, Christopher Kampf, Ulrich Poeschl, *MPIC*

Epidemiological studies show correlations between air particulate matter and adverse health effects of air pollution including allergy, asthma, cardiovascular and respiratory diseases, but the causative relations and mechanisms of interaction on the molecular level are still unclear. Based on kinetic experiments and model simulations, we found that long-lived reactive oxygen intermediates (ROIs) are formed upon heterogeneous reactions of ozone with aerosol particles, such as hazardous polycyclic aromatic hydrocarbons and allergenic proteins. ROIs are defined as the subset of reactive oxygen species (ROS), including organic and inorganic species with reactive oxygen atoms or groups (O, RO, RO2 and so on). ROIs generated by photochemical and heterogeneous reactions in the atmosphere seem to play a key role in aerosol health effects and provide a direct link between atmospheric and physiological multiphase processes through various interfaces, such as plant surfaces and the human respiratory tract. Recent kinetic experiments showed that the nitration reaction of proteins with ozone and nitrogen dioxide proceeds through long-lived ROI, most likely phenoxy radical derivatives of tyrosine (tyrosyl radicals). Allergenic proteins are efficiently oxygenated and nitrated upon exposure to ozone and nitrogen dioxide in the polluted air, leading to an enhancement of their allergenicity.

9UA.1

Impacts of Complete Street Retrofit on On-road Fine and Ultrafine Particles Concentrations: A Case Study in Santa Monica, California. Shi Shu, Nu Yu, YIFANG ZHU, *UCLA*

Abstract: The California Complete Streets Act of 2008 requires local governments to update general plans so that new construction or modification of roadways considers all transportation modes, which include but are not limited to walking, cycling, and driving. This work evaluates the effect of a complete street retrofit on Ocean Park Boulevard (hereafter referred to as “the retrofit”) in Santa Monica, California, in terms of ultrafine particle (UFP) and fine particle (PM2.5) concentrations. The retrofit, which cost 4.4 million dollar, was constructed on the Ocean Park Boulevard in Santa Monica, CA between December 2011 and February 2013. The pre-retrofit on-road air quality study had been completed in March and April of 2011 and the data have been published. This post-retrofit study replicated the experimental design in April 2013 after the construction was finished, to provide air quality data comparable to those in pre-retrofit study. The meteorological conditions were similar in these two studies. After subtracting background concentrations, UFP decreased after the retrofit by 4200 particles cm-3 while PM2.5 had no statistically significant change. The raw traffic volume was manually counted based on video footages captured during each test session. The emission-weighted traffic volume was calculated based on vehicle categorization and the pollutant-emitting capacities of each category, same as it was done in the pre-retrofit study. The emission-weighted traffic volume decreased 26% after retrofit, which may explain why UFP reductions were observed while total traffic flow remained the same. Although no causality could be reached, this study observed improved air quality on street after retrofit. Nonetheless, a full evaluation of the health impacts of the retrofit requires further information about how travel behavior, not just traffic, has changed.

9UA.2

Airborne Metal Concentrations during and After Pollution Restrictions in Beijing.

NITIKA DEWAN, Brian Majestic, YuanXun Zhang, *University of Denver*

The 16th Universiade, an international multi-sport event, was hosted in Shenzhen, China from August 12th - 24th, 2011. During this time, officials instituted the Pearl River Delta action plan in order to enhance the air quality of Shenzhen, Beijing. The current study examined the total and water-soluble trace elements in atmospheric particulate matter (PM) during and post-Universiade. $PM_{2.5}$ samples were collected at two sites in China: “LG”- top of 31st floor residential building in the Longgang District of Shenzhen City and “BS”- top of Building E of Peking University Shenzhen Graduate School in the Nanshan District of Shenzhen. During the Universiade, the monitored $PM_{2.5}$ mass concentrations were 12.99 ± 3.73 ug/m^3 at the LG site and 25.24 ± 5.20 ug/m^3 at the BS site. After the Universiade, when the control measures were eased, significant increases in the $PM_{2.5}$ mass concentrations were observed (LG= 48.01 ± 8.73 ug/m^3 and BS= 54.05 ± 6.53 ug/m^3). Results from this study showed a significant increase in the concentrations of total metals post-event. For instance, samples at the LG site showed (“during” to “post” event) concentrations (in ng/m^3) of: As (57.3 to 385), Pb (13.1 to 78.9), and Zn (125 to 309). Similarly, samples at the BS site showed (“during” to “post” event) air concentrations (in ng/m^3) of: As (1.03 to 7.95), Pb (10.3 to 55.5), and Zn (18.1 to 75.4). Water-soluble metals were also elevated post-Universiade. LG samples showed average soluble Fe as 5% (9.35 ng/m^3) during the event and 10% (39.1 ng/m^3) post-event. BS samples showed average soluble Fe as 26% (28.1 ng/m^3) during the event and 34% (83.1 ng/m^3) post-event for the total measured Fe.

9UA.3

Predicting the Effectiveness of Vegetation Barriers on Near-Road PM.

JONATHAN STEFFENS, K. Max Zhang, *Cornell University*

Roadside vegetation barriers have been suggested as a potential mitigation strategy for near-road air pollution. However, there is still a lack of mechanistic understanding of how roadside barriers affect pollutant transport and transformation on and near roadways. In this talk, we present the recent advancement of modeling capability in predicting the effectiveness of vegetation barriers on near-road PM. We adopt the Large Eddy Simulation (LES) model to resolve the plume transport across vegetation barriers, coupled with an improved aerosol dynamics model to capture the particle deposition. The results show a significant improvement over our previous attempt described in Steffens and Zhang (2012). The modeling sensitivities to the height, width, depth, and leaf area density of vegetation barriers as well as meteorological conditions are investigated. The implications on green infrastructure designs will also be discussed.

9UA.4

Contamination of Urban Stormwater Runoff in Syracuse, NY by Previously Deposited Atmospheric Aerosol. CLIFF DAVIDSON, Emily Procopio, Jeremy Tamargo, *Syracuse University*

It is well known that runoff from streets, parking lots, and other hardscape can bring contaminants to receiving waters. Some of this runoff is contaminated by tire wear, tailpipe emissions, and material falling into the street from vehicles, as well as by trash lying in the street. However, much of the runoff during major storms comes from the surrounding land and buildings that can cover a sizeable surface area. As a result, aerosol dry deposition on urban surfaces can provide significant amounts of contamination that ends up in waterways.

In this research, we examine chemical contaminants in urban runoff and attempt to identify those constituents that originated from atmospheric deposition. We have collected runoff directly from streets and other impermeable surfaces at selected locations around the City of Syracuse and Onondaga County. We have also targeted two large buildings in downtown Syracuse for collection of runoff, namely the Convention Center which has a large (0.56 hectare) green roof, and the Onondaga County War Memorial Arena which has a similarly sized traditional roof. In both of these buildings, pipes have been added to the stormwater drainage system to enable collection of the water flowing off the roof during rainstorms. Fresh precipitation is sampled simultaneously. Collection is accomplished in real time during the storms, and the samples are analyzed chemically for a variety of constituents.

This research is part of a larger program to examine water management challenges facing urban areas as suburbs expand and increasing land area is covered with impermeable surface material. Water flowing over surfaces contaminated by atmospheric deposition as well as other pollution sources is channeled into storm sewers and ultimately receiving waters which can result in health and ecosystem effects.

9UA.5

Spatial Distribution of and Correlation between Noise And Particulate Matter near Two Freeways in Los Angeles, California. SHI SHU, Yang Pu, Yifang Zhu, *UCLA*

Near-freeway environments are important from public health and environmental justice perspectives. Because both the traffic emitted air pollution and noise are associated with cardiovascular disease, there is a knowledge gap on how they distributed in space and if they are correlated with each other. This study investigated the spatial profile of particle concentrations and noise levels near Interstate 405 and Interstate 710, two major freeways in Los Angeles, CA. Besides ultrafine particle (UFP) number concentrations and fine particle (PM2.5) mass concentrations, A-weighted equivalent continuous sound level (LeqA) was measured simultaneously at increasing distances from the freeways on four streets with or without sound wall. Twenty sampling sessions were conducted on nine different days from February to June 2013. For the 405 site, the sampling sessions were scheduled at different hours of daytime to cover different traffic and meteorological conditions. For the 710 site, the sampling sessions were scheduled during both daytime and nighttime to capture different meteorological conditions. Generally, LeqA levels showed a more symmetrical profile on both sides of freeways than particulate matter concentrations did. Under upwind conditions, UFP showed relatively low concentrations and no obvious gradient, while LeqA showed decay with increasing distance as it did under downwind conditions. Moderate correlations (Pearson correlation coefficients ranged from 0.39 to 0.72) between LeqA and UFP were observed under downwind conditions on all four streets. The presence of a sound wall was found to effectively reduce LeqA but not UFP and PM2.5. Both the LeqA level and UFP concentrations at a fixed location increased with increased traffic volume, but at different rate. These data may be used to study the independent and synergistic health impacts of noise and air pollutants near roadways.

10BA.1

Contribution of Bioaerosols to PM10 and PM2.5 in the Southeastern United States. TRACI LERSCH, Gary Casuccio, Stephanie Shaw, Annette Rohr, *RJ Lee Group, Inc.*

The nature and origin of carbonaceous aerosols and their contribution to ambient particulate matter (PM) mass were evaluated to better understand the contribution of bioaerosols to ambient air quality. Ambient PM10 and PM2.5 samples were collected in Atlanta and Yorkville, GA as part of the Southeastern Aerosol Research and Characterization Study (SEARCH). The 2010 sampling program was conducted at both an urban and a rural site to provide insight on the seasonal influences of bioaerosols. The ChemPass Personal Environmental Monitoring System (PEMS) developed by the Harvard School of Public Health was used to collect the samples over 24 hour periods.

Single particle morphology and compositional information from scanning electron microscopy (SEM) were applied to measure primary particle mass concentrations. SEM methods were used to quantify and speciate carbonaceous aerosols based on distinctive morphological features and trace characteristic elements. Particle volume and density were estimated and used to calculate the mass of bioaerosols, elemental carbon (soot), and other particle constituents. In addition, samples were subjected to thermal-optical reflectance (TOR) analysis to quantify total (TC) and organic carbon (OC).

SEM carbon measurements were compared to TOR results of co-located filters. On average, the PM10-2.5 TC SEM results were within 10% of the PM10-2.5 TC TOR measurements. Biological aerosols were a significant component of PM10-2.5 at the urban and rural sites during the spring and fall 2010 campaigns. The average weight percent of vegetative particles ranged from 8.7 to 18.4 percent at the urban and rural sites, respectively. However, the SEM underestimated the OC in the PM2.5 fraction. The difference may be due, in part, to the loss of volatiles over time. Further examination of the filters using high resolution SEM detected carbon-rich deposits under specific operating conditions. Given reasonable assumptions, these deposits could account for the ‘missing’ PM2.5 carbon mass in the SEM analysis as compared to the TOR data on the co-located filters.

10BA.2

On the Use of Organic Molecular Markers for the Apportionment of Aerosols - Insight from PMF Analysis at 3 French Urban Sites. ANTOINE WAKED, Olivier Favez, Jean-Luc Jaffrezo, Jean-Luc Besombes, Benjamin Golly, Laurent Alleman, Tiphaine Delaunay, Géraldine Guillaud, Pierre-Yves Guernion, Eva Léoz-Garziandia, *Univ. Grenoble Alpes, CNRS, LGGE, F-38000 Grenoble, France*

Organic molecular compounds are used as markers of many anthropogenic and biogenic sources. Some ambient air biogenic aerosols sources could be identified and quantified using organic markers such as arabitol, mannitol, sorbitol and methane sulfonic acid (MSA) into receptor models such as Positive Matrix Factorization model (US EPA PMF v3.0). The quantification of these biogenic sources is still only performed in very few studies in the literature. In this work, source apportionments of ambient particulate matter (PM10) collected over one year period at three urban background sites (Lens, Bordeaux and Lyon) in France were conducted using PMF. The components measured and used in these PMF solutions included soluble ionic species, trace elements, sugar alcohols, sugar anhydride, organic carbon OC and elemental carbon EC. The sources identified in those sites were secondary organic aerosols (Sulfate-rich and Nitrate-rich), primary biogenic emissions and marine biogenic emissions, fresh and aged sea salt, mineral dust, traffic and biomass burning as well as petrochemical and metallurgical industries. The results obtained showed an important contribution for the biogenic aerosols sources in the 3 urban sites and a comparable temporal variations with contributions exceeding 10% of the total PM10 mass. In addition, a strong seasonal variation was also observed for these sources accounting for more than 20% of the total PM10 mass in summer. It indicates that these sources are not negligible and calls for more investigations using source apportionments studies in general.

10BA.3

Species Variations in Airborne Bacterial Communities in Asian Dust Downwind Area during a Dust Event. TERUYA MAKI, Fumihisa Kobayashi, Kazunori Hara, Chen Bin, Yasunobu Iwasaka, *Kanazawa University*

Asian dust (Kosa) events transport airborne microorganisms, which significantly impact biological ecosystems, human life, and ice-cloud formation in downwind areas. However, composition and abundance dynamics of airborne bacteria have rarely been investigated in downwind area during Kosa events. In this study, air samplings were sequentially performed on the top of building (10-meter altitude) within the Kosa arrival area (Kanazawa City, Japan) from May 1 to May 7, 2013, when a dust event occurred. The particle concentrations of bacterial cells and mineral particles increased ten times during Asian dust event comparing non-dust event days. A 16S rDNA clone library prepared from the air samples mainly belonged to the three phyla, such as Firmicutes, Cyanobacteria, and Alpha-proteobacteria. Cyanobacteria mainly including a marine type of Synechococcus species dominated at the first phase of dust event and were continuously detected during dust event. The clones belonging to Alpha-proteobacteria were mainly detected at the initial and last periods of dust events and clustered with marine bacterial clade (SAR clade) and Shingomonas spp. In the midst of dust event, sequences of Bacillus subtilis and B. pumilus in Firmicutes predominately appeared, and they are known to dominantly inhabit atmospheric area in KOSA source area (Chinese desert). The clones obtained after the dust event finished were mainly related to B. megaterium, which are thought to originate from local terrestrial areas. Our results suggest that airborne bacterial communities on the surface ground changed their species compositions during dust event, and are composed of terrestrial and pelagic bacteria which, are transported from East Sea and China continental area by Kosa event.

10BA.4

Hunting Sources of Biogenic Ice Nucleating Particles in Soils, Sea Spray and Air. PAUL DEMOTT, Thomas Hill, Yukata Tobo, Christina S. McCluskey, Ezra Levin, Kaitlyn Suski, Douglas Collins, Gavin Cornwell, Christopher Lee, Camille Sultana, Jessica Axson, Francesca Malfatti, Kimberly Prather, Sonia Kreidenweis, Tinkara Tinta, *Colorado State University*

We posit that an important proportion of ice nucleating particles (INP) in air that have previously been distinguished only as having a carbonaceous source have biogenic sources. These INP may include microbes and organic materials that are products of biological activity. This study describes efforts toward defining the numbers and compositions of biogenic INP in air, their general sources from soils and oceans, and their compositions.

Complementary real-time and offline measurement methods are applied. Measurements with a continuous flow diffusion chamber allow for isolation of INP via impaction for electron microscopic examination, and linking to a single particle time-of-flight aerosol mass spectrometer via a pumped counterflow virtual impactor for real-time compositional analyses. Offline immersion freezing methods following collection of particles onto substrates or directly into liquid provide for large sample volume assessment of INP number concentrations, extending the measurable range over several orders of magnitude and 35 C supercooling. Filtration, heat, and chemical treatment permit exploring the size and relative organic content of INP.

Arable soils are strong potential sources for atmospheric biogenic INP of at least three types. At warmer than about -12 C, microbial INP can sometimes dominate. At lower temperatures, unidentified stable organic materials dominate as INP. Clay mineral particles are the least effective particles contained in arable soils, unlike desert soils where mineral particles dominate INP.

Marine aerosol INP studies are exploiting realistic sea spray generation in the laboratory and sampling from the marine boundary layer. A certain category of sea salt particles is often associated with ice nuclei of marine origin, but detailed investigations of the ice nucleating “units” within seawater and the sea surface microlayer indicate that these INP are often between 20 and 200 nm in size. Continuing studies to isolate the compositions of these INP as bacterial, viral, or simply molecular will be described.

10BA.5

Hydrophilicity and CCN Activity of Atmospheric Bacteria Isolates and Implications for Cloud Formation. NATASHA DELEON-RODRIGUEZ, Aikaterini Bougiatioti, Nimmy Mathew, Arnaldo Negron-Marty, Michael Bergin, Konstantinos Konstantinidis, Athanasios Nenes, *Georgia Institute of Technology*

The abundance of bacterial cells in the atmosphere can reach relatively high numbers, but the role of airborne cells in atmospheric chemistry, cloud formation, and precipitation remains to be quantified. A few studies exist that report the activity of bacterial cells as cloud condensation nuclei (CCN), and there is no understanding about the origin of this activity and its relation to the properties of a bacterial cell. The objective of this study was to determine whether the affinity of different bacterial cells to water (hydrophilicity) alone is sufficient to explain cell ability to act as CCN. To this end, we collected samples from rainwater and ambient air at different locations (urban cities and rain forest) and altitudes (>10 km and surface air). Over 20 bacterial isolates were obtained using different minimal and rich media and were identified based on sequencing of the 16S rRNA gene. Bacteria in rain samples from forested areas were typically known plant-associated bacteria, in contrast to those isolated from other environments, which were typically from soil. The hydrophilicity of different bacterial isolates was evaluated based on their contact angle with water. Measurements of contact angle were performed using a sessile drop over a bacterial lawn using a KSV CAM-200 goniometer. A wide range of contact angles were reported, ranging from very hydrophilic to very hydrophobic bacteria; the majority of the isolates however were found to be very hydrophilic. Finally, the CCN activity of each isolate is studied by introducing aerosolized bacteria into a continuous flow streamwise thermal-gradient CCN counter.

10BA.6

Emission Rates of Biological Aerosol Particles in a Montane Pine Forest. STEPHAN NORDMANN, Hang Su, J. Alex Huffman, Ulrich Poeschl, Yafang Cheng, *MPIC*

The formation and transportation of primary biological aerosol particles (PBAP) are important to understand its climate, ecological and health effects. Although PBAP may significantly contribute to the aerosol burden on a regional scale, they are not considered in atmospheric models. Their explicit description in models is difficult due to the lack of their emission mechanisms. In the Beachon-RoMBAS campaign, which took place in a homogeneous pine forest in Colorado, USA, PBAP were intensively characterized by various techniques. In this study, Huffman et al. (2013) found elevated PBAP concentrations during and after rain and attributed this to particle bursts in the beginning of several rain events and active biota growing on wetted surfaces (e.g. spores from fungis, cryptogamic covers). In the present study we use the Weather Research and Forecast model (WRF) coupled with a chemistry module to derive emission rates of PBAP for the campaign period covering both precipitation and non-precipitation conditions. Two nested model domains were chosen with horizontal resolutions of 3 km and 1 km, respectively. The PBAP in the model were assumed to have the same density and hygroscopicity as bioaerosols described in Bauer et al. (2008). The particle size distribution consists of 8 model bins. We divided the simulation period in July and August 2011 into a non-precipitation and precipitation episode, and examined the emissions from different classes of ecosystems as represented by the Normalized Vegetation Index (0.1-0.4, 0.4-0.7 and 0.7-1). For both episodes, the best correlation between model and observation was found for emissions from NDVI of 0.4- 0.7, which was considered as the major source of observed PBAPs. The emission rates from this class were then retrieved from the regression results between model and observation for the different model bins for precipitation and non-precipitation episodes, respectively. As a result, observed concentration patterns can be simulated by the retrieved emissions and its diurnal variation is mainly due to the diurnal cycle in meteorological variables. Distinct peaks in the time series of observed PBAP were attributed by Huffman et al (2013) to particle bursts when the rain starts. We will simulate this by increasing the emissions at locations and times where and when rain occurred by using a gridded precipitation product from radar and rain gauge observations.

10BB.1

Impact of the Economic Crisis on Wintertime Air Quality in Thessaloniki, Greece. ARIAN SAFFARI, Nancy Daher, Constantini Samara, Dimitra Voutsa, Athanasios Kouras, Evangelia Manoli, Olga Karagkiozidou, Christos Vlachokostas, Nicolas Moussiopoulos, Martin Shafer, James Schauer, Constantinos Sioutas, *University of Southern California*

During the period of Greek financial crisis, switching from fuel oil burning for domestic heating to uncontrolled biomass burning has caused significant air quality deterioration in Thessaloniki. In this study, urban PM2.5 samples were collected in Thessaloniki during the wintertime of 2012 and 2013 along with a subset of morning and evening samples to determine the diurnal variations. Chemical composition including metals and elements, ions, carbonaceous species and speciated organic compounds were quantified. Redox activity was also assessed by the biological reactive oxygen species (ROS) assay. PM2.5 mass concentration increased by 2-fold during the evening compared to the morning, likely due to the increased emissions from residential heating sources. PM2.5 mass concentration in 2013 has also increased by 30% compared to 2012. Organic matter (OM) was the dominant PM constituent with higher evening-time contribution to the total mass compared to the morning, which is mostly due to the increased wood smoke emissions in the evening time. Concentrations of V and Ni (tracers of residual/fuel oil combustion) dropped by 30-50% in 2013. The concentration of K, on the other hand, increased by 2-fold in 2013 suggesting that the residential heating method in Thessaloniki is changing from the conventional fuel oil burning to the less expensive wood and biomass combustion. Concentrations of levoglucosan, mannosan and galacsosan (organic tracers of wood smoke), were considerably (4-6 fold) higher in 2013 compared to 2012, which implies a significant increase in wood and biomass burning in 2013 compared to 2012. Concentrations were also 3-4 times higher in the evening compared to the morning. Moreover, positive correlations were observed between ROS activity and water-soluble potassium, levoglucosan and galactosan (R=0.74, 0.72 and 0.75, respectively), which indicates a potentially significant effect of wood smoke emissions on the redox activity of PM2.5.

10BB.2

2013 Southeast Asian Smoke Haze: Speciation of Size-resolved Aerosols and Associated Health Impacts. RAJASEKHAR BALASUBRAMANIAN, Raghu Betha, Sailesh Behera, *National University of Singapore*

Occurrence of biomass burning-induced smoke haze has become an annual phenomenon in tropical South East Asia (SEA) over the past several decades, but with different duration, intensity and impacts depending on prevailing weather conditions. Uncontrolled forest and peat land fires resulting from land clearing activities in Indonesia release large amounts of airborne particulate matter (PM) with unique chemical composition into the atmosphere. The resultant PM emissions from these wild fires are transported by trans-boundary winds and transformed into regional haze episodes affecting several countries in SEA, most notably, Singapore, Malaysia, Indonesia and Thailand. One of the worst haze episodes in the history of SEA occurred in June 2013. Size-segregated particulates (2.5 – 1.0 µm; 1.0 – 0.5 µm; 0.5 – 0.2 µm and < 0.2 µm) were collected during both hazy and non-hazy periods, and subjected to chemical fractionation of particulate-bound trace elements (B, Ca, K, Fe, Al, Ni, Zn, Mg, Se, Cu, Cr, As, Mn, Pb, Co, Cd). PM2.5 concentrations were elevated (up to 329 µg/m3) during the haze episode, compared to those during the non-haze period (11 – 21 µg/m3). There was a 10-fold increase in the concentration of K, an inorganic tracer of biomass burning. A major fraction (>60%) of the elements was present in oxidizable and residual fractions while the bio-available fraction accounted for up to 20% for most of the elements except K and Mn. Deposition of inhaled potentially toxic trace elements in various regions of the human respiratory system was estimated using a Multiple-Path Particle Dosimetry model. The particle depositions in the respiratory system tend to be more severe during hazy days than those during non-hazy days. A prolonged exposure to finer particles can cause adverse health outcomes during hazy days as revealed by quantified risk analysis.

10BB.3

Characterizing Cookstove Emissions in South Asia. RYAN THOMPSON, Cheryl Weyant, Tami Bond, *University of Illinois at Urbana-Champaign*

Solid fuel cookstoves of South Asia are responsible for indoor air pollution that affects hundreds of millions of people. Black carbon emissions from South Asia cookstoves are of special concern for climate forcing due to their proximity to the Himalayan glaciers. Despite this, cookstove emissions have not been adequately quantified or characterized because they often occur in remote villages that are inaccessible with conventional semi-portable emissions equipment. A portable emission sampling system was taken inside homes and on roofs throughout rural villages in Nepal, Tibet, and Yunnan to measure the emissions of over 120 cooking events in 60 homes, burning wood, dung, coal, and several types of agricultural residue. The portable sampling system consists of a partial capture sample probe, PTFE filter, quartz filter, and real-time sensors to measure optical scattering, optical absorption, CO, and CO2. Real-time emission factors were calculated using the carbon balance method, as well as single scattering albedo and modified combustion efficiency. The PaRTED approach (Patterns of Real-Time Emission Data) was used to identify patterns and variability of PM emissions between cooking tasks, stove types, fuel types, homes, villages, and regions. This study provides regional and situation-specific emission factors to improve global emission inventories. The real-time data allow exploration of major factors that determine the magnitude and characteristics of emissions. For example, most of the PM is emitted during the start of the cooking event, when the stove is first lit, and the optical properties of this PM are dependent on fuel type. The results can be used to evaluate and improve how well laboratory tests represent actual field usage.

10BB.4

Chemical and Physical Characterization of Particulate Emissions from Different Phases of an Improved Cookstove Operation. Raul Martinez, SAMEER PATEL, Anna Leavey, Dhruv Mitroo, Ruijie Yu, Brent Williams, Pratim Biswas, *Washington University in St. Louis*

Three billion people worldwide rely on biomass to cook their food; and due to the inefficient combustion in cookstoves (Sahu et al. 2011), this results in a serious public health and climate issue. The World health organization reported that the exposure to air pollution led to 7 million deaths in 2012, making it the world's largest single environmental health risk. Indoor air pollution accounted for more than half of the deaths. At the same time, biomass is emerging as a sustainable and carbon-neutral energy resource and thus its use is receiving attention.

Biomass combustion in cook stoves typically results in higher PM, mostly organic, which deteriorates air quality and impacts health adversely. The goal of this study was to characterize the particulate emissions from an improved cookstove during three operating phases viz. startup, steady state and extinguishing phase. Chemical characterization was conducted using a Thermal Desorption Aerosol Gas Chromatograph (TAG) to obtain detailed organic speciation and an Aerosol Mass Spectrometer (AMS) for organic and inorganic mass loadings. Real-time measurements of $PM_{2.5}$, particle number size distribution, total number concentration and lung-deposited surface area concentration were conducted for physical characterization of the particulate emissions. Effect of fuel type on emissions during each of the three combustion stages was studied by measuring emissions from different biomass and fossil fuel types. Data presented in this study will facilitate a better understanding of the environmental and health impacts of pollution from biomass combustion.

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10BB.5

Online Characterization of Biomass-derived Cooking Fuel Emissions with a Soot Particle Aerosol Mass Spectrometer. EBEN CROSS, Dan Sweeney, Amy Banzaert, Amy Smith, Timothy Onasch, John Jayne, Douglas Worsnop, Jesse Kroll, *MIT*

Nearly half of the world's population is dependent on solid biofuels for heating their homes and cooking their food. Lack of sufficient ventilation within many living spaces results in extremely high concentrations of particulate matter (PM) within indoor environments. Real-time chemical characterization of biomass particulate combustion emissions is a critical step toward designing improved combustion sources, assessing alternative biomass-derived fuels, and pinpointing the combustion stages at which human exposure to PM is highest. In this paper, we will present recent laboratory results obtained with a soot particle aerosol mass spectrometer (SP-AMS). The SP-AMS was used to characterize the composition and variability of particulate emissions from a large set of field-relevant cookstove designs and biomass-derived fuel types. The SP-AMS enables online, highly time-resolved measurements of both black carbon and organic carbon, as well as specific aerosol components of interest (e.g., PAHs). In this paper, we will present species-specific emission indices for each burn cycle with the aim of better understanding the health and climate impacts of biofuel combustion practices.

10BB.6

Evolution of the Aerosol Size Distribution and Cloud Condensation Nuclei (CCN) Within Smoke Plumes during the Biomass Burning Observation Project (BBOP). JASON TOMLINSON, Fan Mei, Jian Wang, Jennifer Comstock, John Hubbe, Mikhail Pekour, John Shilling, Edward Fortner, Duli Chand, Arthur J. Sedlacek, Lawrence Kleinman, Gunnar Senum, Beat Schmid, *Pacific Northwest National Laboratory*

Biomass burning from wildfires and controlled agricultural burns are estimated to be a major contributor of fine particles and organic aerosol at northern temperature latitudes during the summer months. However, the evolution of the physicochemical properties of the aerosol during transport and the potential impact of the aerosol on cloud condensation nuclei (CCN) activity has rarely been studied. During the DOE Biomass Burning Observation Project (BBOP) in 2013, over 20 research flights were conducted within biomass burn plumes from wildfires in the Northwestern United States and agricultural burns in the Mid-South region of the United States.

A large suite of instruments aboard the DOE G-1 measured the chemical and physical properties of the aerosol with an emphasis on black carbon. A Fast Integrated Mobility Spectrometer (FIMS), Ultra High Sensitivity Aerosol Spectrometer (UHSAS-A), and Passive Cavity Aerosol Spectrometer (PCASP) measured the aerosol size distribution from 15 – 3,000 nm at 1-Hz. A dual column CCN counter measured the CCN number concentration at supersaturations of 0.25% and 0.50% at a time resolution of 1-Hz. The aerosol chemical composition was measured using high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) that has that has been configured to measure refractory aerosol particles. Utilizing the aforementioned measurements, a CCN closure study is used to investigate the emitted aerosol hygroscopicity and potential impacts on cloud microphysics from the different fuel sources.

10CA.1

Wavelength Dependence of the Optical Properties of Primary Combustion Aerosols. Luka Drinovec, GRISA MOCNIK, Ian Arnold, Rajan K. Chakrabarty, Anthony D.A. Hansen, Hans Moosmuller, *Desert Research Institute*

Optical properties of emitted aerosols were investigated for combustion under laboratory conditions. We have characterized emissions from the burning of mustard oil, incense, and Ponderosa Pine needles during flaming and smoldering combustion phases. Burning of mustard oil lamps and incense finds wide-scale usage during Asian rituals, while Ponderosa pine needles are a common fuel in western United States and Canadian forest fires. We measured aerosol absorption spectra, single scattering albedo, and the filter loading parameter, combining the data from an Aethalometer (model AE33) and a photo-acoustic spectrometer (model PASS-3). The combustion regime was monitored by measurements of carbon monoxide, carbon dioxide, black carbon concentrations and thermo-optical OC/EC measurements. Size distribution and geometry of emitted particles were analyzed using SMPS and SEM.

Optical properties of emitted aerosols varied greatly. Emissions from the mustard oil lamp featured absorption spectra with the Absorption Angstrom Exponent (AAE) close to 1. Emitted aerosols were optically and morphologically similar to soot emitted by diesel engines. For incense, the AAE was much higher as also observed for incomplete biomass burning. During combustion of needles, aerosol spectral properties depended on the burning type – featuring higher AAE during the smoldering phase compared to the flaming phase. The type of combustion also influenced the filter loading parameter, which is attributed to different particle coating thickness.

This compares well with ambient measurements apportioned to different fuels based on emission measurements of diesel engines, biomass combustion, and combustion of propane with different fuel/air mixtures. We hence propose the mustard oil lamp as stable laboratory proxy for flaming combustion producing mostly fractal-like chain aggregates with AAE of 1. Similarly, incense can be used as proxy for carbonaceous aerosols emitted by smoldering biomass burning.

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10CA.2

Determining Aerosol Volatility Parameters using a 'Dual Thermodenuder' System: Application to Laboratory-generated Organic Aerosol. PROVAT SAHA, Andrey Khlystov, Andrew Grieshop, *North Carolina State University*

A thermodenuder (TD) is a widely used tool for measuring aerosol volatility in the lab and field. Although the TD is a simple system, extraction of the parameters dictating aerosol volatility from TD data is challenging due to long equilibration times and uncertainties concerning potential kinetics limitations to mass transfer and components' enthalpies of evaporation (Hvap). To address these limitations, we have developed a 'dual TD' based experimental approach in which one line consists of a temperature-stepping TD (TS-TD) with a relatively long residence time and the other operates isothermally at variable residence time (VRT-TD). The TD system was characterized for axial temperature distributions, distribution of measured residence time using pulses of CO2 and temperature-dependent and size-resolved particle losses using non-volatile sodium chloride (NaCl) aerosols. An optimizing evaporation kinetics model based on the volatility basis set (VBS) was used to extract the values of parameters dictating volatility (e.g., distribution of materials at different volatility bins and associated Hvap and mass accommodation coefficient). Initial evaluation of the system measured the volatility of laboratory generated di-carboxylic acid aerosols (e.g., adipic acid, succinic acid, and glutaric acid); excellent agreement with previously published results was observed. For example, our results reconfirm the mass accommodation coefficient (alpha) of approximately order of 0.1 determined by the other groups via curve fitting approaches. The volatility of alpha-pinene ozonolysis secondary organic aerosols (SOA) in a smog chamber was then studied. Approximately 35-45% SOA mass evaporated at 50° C with RT of 50 s indicating that a substantial portion of SOA is highly semi-volatile, whereas about 8-10% SOA mass remained at 120° C indicating that some portion of SOA mass consisted of relatively low volatility material. A multi-component model was adapted to model SOA and modeling effort suggests that the VRT data provides additional constraint on the feasible Hvap and alpha values. This method will be applied in future studies to characterize the volatility of organic aerosol from different sources (e.g., cook stoves emission, near road environment, and ambient atmospheric conditions).

10CA.3

Quantitative Evidence of Ultraviolet Organic Peroxy Radical Photochemistry in a Photochemical Flow Cell. W. SEAN MCGIVERN, Joseph Klems, *National Institute of Standards and Technology*

The use of ultraviolet light in laboratory experiments to study processes that lead to organic aerosols in the atmospheric is extensive. Recently, we have provided qualitative evidence that peroxy radical photochemistry can play a significant role in determining the composition of organic aerosols formed in the presence of ultraviolet light. This work provides quantitative evidence for the relevance of these processes by examining the condensed-phase products formed in the extreme oxidation of dodecanoic acid by OH generated from the 254 nm photolysis of ozone in the presence of water. The products were analyzed using high-performance liquid chromatography (HPLC) with both ultraviolet (UV) absorption and tandem mass spectrometric (MS-MS) detection utilizing derivatization to specifically probe hydroxyl and carbonyl functional groups. The complex product spectrum for hydroxy-substituted species was broken in three distinct classes: singly substituted parent, multiply substituted parent, and products derived from decomposition of the parent. An a priori lumped kinetics model of the product distribution successfully reproduces the experimental product distribution only when photochemical processes, including both decomposition of the peroxy radical to form an alkyl radical and O_2 and isomerization, are active. Two separate ultraviolet exposure conditions were also studied by shading a portion of the flow cell; modeling of this system, particularly in the low-exposure case, requires an understanding of the fate of alkyl hydroperoxides (R-OOH). The analysis of these compounds using HPLC/UV and MS-MS methods and their respective impact on measured product distributions from condensed-phase filter extracts will also be discussed.

10CA.4

Application of Positive Matrix Factor Analysis in Heterogeneous Kinetics Studies: OH Initiated Oxidation of Organophosphate Flame Retardants in PM. JOHN LIGGIO, Yongchun Liu, Shao-Meng Li, *Environment Canada*

Organophosphate flame retardants (OFRs) are widely used in North America and Europe to depress the formation of flames in various commercial products despite the inherent toxicity of some of these compounds. These compounds are increasingly being measured in ambient particulate matter around the globe, suggesting that they are rather persistent in the atmosphere. However, there remains very little kinetic data on the heterogeneous processing of these compounds on ambient PM. In the current study, a mixed-phase relative rate approach for determining organic aerosol particle heterogeneous reaction kinetics been improved by performing Positive Matrix Factor (PMF) analysis of Aerosol Mass Spectrometry data. PMF analysis thereby removes the influence of m/z fragments from reaction products on the reactant signals used to derive kinetics. To demonstrate the advantages of this approach, the heterogeneous reaction between OH radicals and citric acid (CA) and several organophosphate flame retardant compounds was investigated using a photochemical flow tube coupled to a compact time-of-flight aerosol mass spectrometer (C-ToF-AMS). The measured heterogeneous rate constant (k2) for particulate-phase organophosphates (TPhP, TDCPP, and TEHP), were found to be greater than previously reported utilizing individual m/z fragments. The effect of particle size, relative humidity, and the internal/external mixture of OFRs with other ambient organics is also investigated and found to have a significant effect on the ultimate particle phase lifetime of these, and presumably other toxic PM components.

10CA.5

Relative Importance of Black vs. Brown Carbon Absorption in Biomass Burning Plumes. SHANE MURPHY, Rudra Pokhrel, Eric Beamesderfer, Daniel Lack, Nick Wagner, Justin Langridge, Daniel Murphy, *University of Wyoming*

Biomass burning represents one of the largest global sources of absorbing aerosol. Despite the importance of biomass burning emissions on the Earth's radiative balance, there remains significant uncertainty about the optical properties of emitted particles. Of particular interest is the impact of lensing on black carbon absorption and the impact of brown carbon. This presentation describes results from the Fire Lab at Missoula Experiment-4 (FLAME-4), which occurred in October 2012. Multi-channel photoacoustic (PAS) and Cavity Ringdown (CRDS) spectrometers were used to measure absorption, extinction, and absorption enhancement of aerosols particles produced from a wide range of globally relevant biomass fuels. Measurements were made at 405, 532, and 660 nm with duplicate channels at 405 and 660 measuring denuded particles, allowing for direct observation of the enhancement of absorption by black carbon particles caused by clear and brown organic coatings. Fuels were chosen based on their contribution to global wildfire and cooking emissions. Data from fresh biomass burning emissions and from emission photochemically oxidized in a smog chamber will be presented. The impact of photochemical aging on the absorption and single scattering albedo (SSA) of organic aerosols produced by biomass burning will be discussed. The SSA and absorption angstrom exponent (AAE) of different biomass fuels will be explored and the relative importance of black and brown carbon emitted from different biomass fuels will be assessed.

10CA.6

Comparison of Near-Roadway PAH Measurements via Multiple Methods. STEVEN BROWN, David Olson, Taehyoung Lee, Paul Roberts, Gary Norris, Jeffrey Collett, *Sonoma Technology, Inc*

We measured polycyclic aromatic hydrocarbon (PAH) concentrations at Fyfe Elementary School, 18 m from the US 95 freeway soundwall, in Las Vegas, Nevada, during January 2008. We collected PAH data via three methods: (1) from a high-resolution aerosol mass spectrometer (HR-AMS), at 2-minute resolution, termed APAH; (2) from a Photoelectric Aerosol Sensor (PAS) instrument, at 5-minute resolution, starting January 15, 2008, termed PPAH; and (3) from gas chromatography-mass spectroscopy (GC-MS) analysis of extracts from quartz fiber filters collected at various times during January 2008, termed FPAH. PPAH data showed a similar pattern to black carbon (BC) (r2=0.86), while APAH data were more similar to organic matter (OM) (r2=0.79). There was modest agreement between PPAH and APAH measurements (r2=0.49). Somewhat surprisingly, neither PPAH nor APAH showed a good correlation with hydrocarbon-like organic aerosol (HOA), despite the fact that the PAHs originated from primary emissions, similar in concept to what HOA represents. Of 26 filter samples, 17 had both coincident PPAH and APAH measurements, while an additional 9 filter samples had coincident APAH measurements. Neither PPAH nor APAH measurements compared well with the sum of total measured FPAH or of total measured hopanes. APAH had a high correlation with chrysene (r=0.80) and modest correlation with benzo(b)fluoranthene (r=0.69) and benzo(e)pyrene (r=0.66). PPAH did not have a correlation higher than 0.48 with any individual FPAH. Results indicate that PPAH measurements are more closely related to BC concentrations than OM, APAH, or specific FPAHs, while APAHs are closely related to chysene concentrations. PAH measurements correlated modestly with hopanes and levoglucosan, indicating PAH are from a mix of mobile, biomass burning, and other possible urban sources.

10CO.1

Temperature Effects on Secondary Organic Aerosol Formation from Gasoline Vehicle Exhaust.

MARY KACARAB, David R. Cocker III, *University of California, Riverside*

Exhaust from gasoline vehicles has recently been targeted as a potential significant source for anthropogenic secondary organic aerosol (SOA). This work quantifies the significant effects of environmental temperature on SOA formation from gasoline vehicle emissions. SOA from oxidized gasoline vehicle exhaust was studied in the University of California Riverside (UCR) College of Engineering Center for Environmental Research and Technology (CE-CERT) dual 90m^3 environmental chambers in a series of experiments ranging in temperature from 5^{O}C to 40^{O}C. Aerosol size distribution, number and mass concentrations, volatility, density, and fractal dimensions were measured over the course of aging and through different temperature change cycles. Aerosol formed at the "cold" temperature of 5^{O}C gave a 1.4x greater yield than aerosol formed at the "hot" temperature of 40^{O}C. Significant aerosol mass is lost from the system when SOA formed at 5^{O}C is heated to 40^{O}C, however no aerosol mass is gained when SOA formed at 40^{O}C is cooled to 5^{O}C. The density and fractal dimension of the particles are also affected by temperature, with cold temperature aerosol having a density of ~2g/cm^3 yet decreasing to ~1.5g/cm^3 when temperature is increased to 40^{O}C. For hot temperature aerosol, the density remains constant at ~1.5g/cm^3 even when cooled. The results of these experiments indicate a clear hysteresis effect in aerosol mass, density, and fractal dimension as well as the presence of thermally labile compounds in gasoline vehicle exhaust. The effect of temperature seen on vehicle exhaust aerosols does not follow the same trends observed for biogenic aerosols.

10CO.2

On the Black Carbon Content of Soot from Flames and Engine Exhaust.

MATTI MARICQ, *Ford Motor Company*

Black carbon is of environmental interest for its contributions to climate change, air quality, and visibility. Its predominant source is from combustion; thus, it represents an important component of PM emissions from power plants, motor vehicles, aircraft, construction and agricultural equipment as well as biomass burning.

The solid carbonaceous component of combustion PM is variously described as soot, elemental carbon (EC), and black carbon (BC). The latter two generally reflect the measurement method, with EC relying on oxidation of soot into CO2 and BC relying on optical absorption. Often these terms are used interchangeably, not just colloquially but with practical implications. The latter is illustrated by the reliance on instruments such as the photo-acoustic soot sensor, laser induced incandescence, and the smoke meter to serve as the basis of soot measurements in engine exhaust. And conversely, soot is being looked at as a standard material for the calibration of PM measurement instruments.

It is known that condensation of organic material will modify the relationship between soot and BC. However, a recent study (Mamakos et al. Aerosol. Sci. Technol. 47, 927, 2013) revealed that even after volatile removal with a catalytic stripper the BC from a commercial propane diffusion flame soot generator (Combustion Aerosol Standard) was generally lower than the EC. The work presented here will examine in more detail the relationship between BC and soot mass from premixed and diffusion flames, and in motor vehicle exhaust. This reveals that the BC content increases with the age of the soot in the flame, likely due to increased carbonization. Motor vehicle soot has a high BC content, which is attributed to the higher temperature environment of engine combustion. The results have implications on the use of optical methods to measure PM emissions and the use of soot for instrument calibration.

10CO.3

Determination of Suspended Exhaust PM Mass for Light Duty Vehicles Using IPSD Method. HEEJUNG S. JUNG, Yang Li, Jian Xue, Kent Johnson, Thomas D. Durbin, Mark Villela, Liem Pham, Seyedehsan Hosseini, Zhongqing Zheng, Daniel Short, Georgios Karavalakis, Akua Asa-Awuku, Xiaoliang Wang, David Quiros, Shaohua Hu, Tao Huai, Alberto Ayala, *University of California Riverside*

In line with stricter PM emission standards for heavy-duty vehicles, the United States Environmental Protection Agency and the California Air Resources Board will implement stricter PM standards on light-duty vehicles. California's new PM emission standard will be reduced to 1 mg/mile, which poses a challenge to the current gravimetric measurement method. The European Union (EU) will implement a particle number (PN) emission standard and has proposed to use the Particle Measurement Programme's PN measurement protocol as a complementary measurement to the PM mass standard. The current EU PN standard excludes sub 23 nm particles which are mostly volatile but may be responsible for significant adverse health effects. There is limited information regarding associations between human health effects and PN emissions. Also PN and PM do not necessarily correlate with each other over a variety of test conditions, which poses questions to regulators regarding whether particle number is an appropriate metric to replace current particle mass-based measurement protocols.

This study presents determination of suspended exhaust PM mass as opposed to filter captured PM mass as a possible alternative metric to complement current gravimetric method. One example is the integrated particle size distribution (IPSD) method which combines particle size distribution with size dependent particle effective density. The method allows for simultaneous determination of particle mass, particle surface area, and particle number. As IPSD can simultaneously obtain PM as well as PN, it has the potential to explain discrepancies between current gravimetric method and particle number method. The paper presents comparison of suspended PM mass determined by the IPSD method with gravimetric PM mass. Final goal of this project is to assess repeatability and accuracy of alternative methods to determine suspended PM mass to examine appropriateness as future regulatory measurement methods.

10CO.4

Detailed Characterization of Particulate Matter (PM) Emitted by Lean-Burn Gasoline Direct Injection (GDI) Engine. JACQUELINE WILSON, Alla Zelenyuk, Mark Stewart, George Muntean, John Storey, Vitaly Prikhodko, Samuel Lewis, Mary Eibl, *Pacific Northwest National Laboratory*

Limited fossil fuel resources and upcoming U.S. fuel economy and emission standards are major challenges in current engine development. We present the results of a study in which we characterized the properties of PM emissions generated by a 2.0L BMW lean-burn turbocharged GDI engine operated under different combustion strategies (lean homogeneous, lean stratified, stoichiometric and fuel rich) before and after a three-way catalyst.

In addition to PM number concentrations and size distributions, we characterized the size, mass, composition and effective density of individual exhaust particles emitted under ~20 engine-operating conditions. These measurements were used to calculate fractal dimension, average diameter of primary spherules, number of spherules, void fraction and dynamic shape factors as function of particle size.

We find that most of the particles produced by the GDI engine are fractal agglomerates containing small amounts of oxygenated organics and PAHs. The fraction of Ca-containing particles, originating from the detergent additives to lubricating oil, varies with operating conditions. These are compact particles with vacuum aerodynamic diameters above 200 nm.

Lean stratified operation yielded the most diesel-like PM. The vast majority of these particles are fractal soot agglomerates with a fractal dimension of 2.18 and are composed of primary spherules with an average diameter of 22 nm. The void fraction of these particles increases from 20% for 50 nm soot particles to nearly 80% for particles larger than 200 nm.

Under stoichiometric operation PM number concentrations decrease by an order of magnitude compared to lean stratified condition. While fractal soot particles emitted under either stoichiometric or lean stratified operations are very similar, the stoichiometric PM contains a higher fraction of Ca-dominated non-fractal particles. Comparison between the characteristics of PM before and after a three-way catalyst provides evidence for the removal of the nuclei mode by the catalyst.

10CO.5

Morphology of Particles Emitted during Cold Start and Hot Start Operating Conditions of a GDI Engine Fuelled on Gasoline and Ethanol Blends. RAMIN DASTANPOUR, Steven Rogak, Phillip Mireault, Manuel Ramos, James S. Wallace, *University of British Columbia*

Although gasoline direct injection engines offer benefits such as high power and low fuel consumption, their emissions are a concern. It has been shown that a large portion of the emissions from an engine over an operating cycle, are produced during the start period (cold start and hot start). There is limited data on particle number and size distribution, and no data available on the morphology of the particles formed during these transient conditions.

Concentration and size distribution of particulate matters produced during cold start (CS) and hot start (HS) were measured with an Engine Exhaust Particle Sizer (EEPS). Using a thermophoretic particle sampler (TPS), soot samples were collected for Transmission Electron Microscope (TEM) analysis from CS and HS operating conditions of a 2.0 litre, direct injection, inline 4 cylinder engine. Variations in the morphology of soot and particulate matter produced during CS and HS periods, and the effects of ethanol on these emissions were investigated using E0 (gasoline) and E30 fuels (gasoline blended with 30% ethanol).

For both fuels, it was found that the concentration and size of the soot aggregates decrease with time over the period of CS and HS. TEM and EEPS results show the presence of two distinct types of particulate matter emissions in CS. At the beginning of CS (~17 s), all emitted particles were fractal-like aggregates. After this period a mixture of small spherical particles (d<4 nm) and reduced concentration of soot was observed. The size of the spherical particles increased over the CS period. In spite of the utilization of hot dilution and a themodenuder, samples taken after the first 17 seconds of HS show the presence of a mixture of soot, volatile cubes, and small spherical particles for E30, while only soot was observed in the E0 samples.

10CO.6

Effect of Drive Cycle and Gasoline Particulate Filter on Size and Morphology of Soot Particles Produced by a Gasoline Direct Injection Vehicle. MEGHDAD SAFFARIPOUR, Fengshan Liu, Kevin Thomson, Tak Chan, Joseph Kubsh, Brezny Rasto, *National Research Council Canada*

To provide a better understanding of soot formation in Gasoline Direct Injection (GDI) engines and the impact of Gasoline Particulate Filters (GPF) on these emissions, a detail characterization of the size and morphology of particulates is performed by Transmission Electron Microscope (TEM) image analysis on a 2013 2.0-liter GDI vehicle at standard temperature on a chassis dynamometer. Particulate samples are collected over the U.S. Federal Test Procedure (FTP-75) and the US06 Supplemental Federal Test Procedure (US06), with and without the use of a catalytic regenerative GPF. In the absence of the GPF, TEM images exhibit fractal-like clusters of spherical primary particles (spherules), with no evidence of volatile material (organic carbon) or collapsed particles. Throughout both drive cycles, spherule size remains unchanged (about 26 nm) with a narrow size distribution. The aggregate fractal dimensions and fractal prefactors are 1.8 and 1.4, respectively, showing that these particles have morphologies similar to diesel particulates. TEM image analysis indicates no statistical difference between the sizes of soot aggregates in different phases of the FTP cycle. However, over the US06 drive cycle, particles are smaller and contain fewer spherules (15 spherules compared to 22). This is because of the higher engine speeds and lower residence times compared to the FTP cycle. When a GPF is installed, the aggregates are slightly larger, confirming that finer particles are more effectively removed by the GPF. On the other hand, the size of spherules and the morphology of aggregates do not change. In contrast to the FTP drive cycle, over the US06 cycle, post-GPF exhaust temperature is hot enough to support soot regeneration during which, additional ultrafine particles are emitted with a volatile nature. TEM images verify the presence of a considerable amount of these ultrafine and volatile particles and show that soot aggregates are coated with these materials.

10IM.1

A Novel Glass Chamber for Studies of Aerosol Dynamics and Interactions. YEVGEN NAZARENKO, Parisa A. Ariya, *McGill University*

Aerosol dynamics and interactions involving (1) airborne particles, including anthropogenic particulate air pollutants, (2) bioaerosols, and (3) gaseous atmospheric constituents and pollutants is of major importance in the context of climate processes and atmospheric air pollution. Important determinants involved are the physico-chemical nature, structure of particles and their surface, atmospheric processing and interfacing with other atmospheric constituents under various environmental conditions influencing particle formation, growth, aging and fate.

Studies of the above-mentioned interactions may be performed in simulated environments inside aerosol chambers. The challenges associated with such experimental setups include (1) minimization of aerosol particles' and volatiles' losses, (2) control of concentrations of aerosol components, (3) control of physical conditions including temperature, humidity and illumination, and (4) flow control into, inside and out of the chamber.

We developed a spherical glass aerosol chamber with single inlet and outlet where the in- and out-flow may be blocked by PTFE valves. Thus, the chamber can be used in static and flow-through modes. Two thin glass wells that house thermocouples are installed in the chamber and allow temperature monitoring in two points within the internal space. A special port with a septum is optionally used to hold a miniature temperature/relative humidity probe exposed to the internal aerosol space. The inside surface of the chamber may be covered with 15% acetone solution of halocarbon wax for minimization of particle and gas phase losses. The chamber setup is equipped with a modular gas/aerosol generation/dilution/mixing/injection system that allows delivery of a specific conditioned aerosol/gas mixture at a precise in-flow rate. The sampling modules connected to the chamber outlet provide for aerosol collection using an electrostatic precipitator for subsequent microscopic analysis, solid phase microextraction for gas chromatography mass spectrometry investigation, on-line mass spectrometry, among others.

The design and example experimental results will be presented to illustrate the applicability and performance of the developed system for research of air pollution, aerosol dynamics and gas/aerosol transformations.

10IM.2

Characterization of the Photochemistry in a Potential Aerosol Mass (PAM) Chamber by Modeling and Measurements: Radical Formation, OH Exposure Quantification and Calibration Equation Derivation. RUI LI, Joost de Gouw, William Brune, Brett Palm, Amber Ortega, Weiwei Hu, Douglas Day, Jose-Luis Jimenez, *NOAA & CIRES & University of Colorado-Boulder*

The Potential Aerosol Mass (PAM) chamber is a highly oxidizing reactor for studying the formation and oxidation of secondary organic aerosols (SOA). The PAM system was designed for a wide range of oxidant exposure times and short experiment duration with reduced wall loss effects, and has been used in many field and laboratory studies on SOA formation. However, the detailed balance of radical formation and destruction under various environmental and input conditions is not completely understood. The uncertainties in radical quantification can significantly affect the interpretation of SOA formation in the reactor. To better characterize the photochemistry and OH radical formation in the PAM chamber, a model has been developed to simulate the formation and evolution of oxidants, which was compared against PAM measurements under a variety of experimental conditions. The PAM experiments were conducted with CO and SO2 as reagents for quantifying OH exposure. The model outputs of OH exposure and ozone concentration were evaluated using measurements and agreed within a factor of 2. A sensitivity study was performed to characterize the dependence of the OH exposure, ozone concentration and HO2/OH radical ratio on photon flux, humidity, temperature, pressure, residence time and external OH reactivity in the PAM chamber. Model results show that OH exposure is strongly suppressed depending on the reactivity of the sampled gases and on the photon flux, and depends more weakly on humidity. An OH exposure calibration equation was derived as a function of ozone, humidity, and external OH reactivity. The OH exposure calculated from the derived calibration equation shows good agreement with those calibrated from several field campaigns, which supports the validity of the model. The quantification of OH exposure and improved understanding of the PAM technique resulting from this work further establishes the viability of this tool for aerosol formation and aging research.

10IM.3

Real-Time Separation and Detailed Characterization of Aspherical Nanoparticles. ALLA ZELENYUK, David Bell, Jacqueline Wilson, Dan Imre, *Pacific Northwest National Laboratory*

Particle shape can play a central role in determining particle properties and behavior. Recently we developed a novel system that makes it possible to identify in real-time the presence of particles of different shapes, separate them based on their shape, and characterize their chemical and physical properties. In this system, a new-generation compact aerosol particle mass analyzer (APM) is used to classify particles with a narrow distribution of masses that are then further classified with a differential mobility analyzer (DMA) to generate an aerosol population with a single charge and narrow distributions of mobility diameters and shapes. Once classified, the compositions, morphologies and vacuum aerodynamic size distributions of these particles are characterized with our single particle mass spectrometer, SPLAT II.

We successfully applied the combined APM/DMA/SPLAT, or ADS, to characterize compact aspherical particles, like ammonium sulfate and NaCl, and fractal soot particles to determine particle mass, mobility and vacuum aerodynamic diameters, composition, morphology, density or effective density, and the dynamic shape factors (DSFs) in the transition and in the free-molecular regimes. In addition, for fractal particles, this approach provides information on particle fractal dimension, number and average diameter of primary spherules that comprise the fractal agglomerate, void fraction and surface area, all as a function of agglomerate size.

We will present the results of a study in which ADS was applied to gold nanospheres, nanorods, and nanowires with different sizes and aspect ratios. We show that it is possible to separate gold nanoparticles with different shapes, characterize their DSFs in the transition and in the free-molecular regimes, and determine intrinsic physical properties (mass, length, and aspect ratios). We also examine the alignment of nanorods and nanowires in the DMA and its effect on the measured mobility diameter that was previously used for separation of particles with high aspect ratios.

10IM.4

Development of Triggering-LIBS for Elemental Analysis of Submicrometer Single Particle in Real Time. Heesung Lee, GIBAEK KIM, Jihyun Kwak, Kihong Park, *GIST*

Atmospheric aerosols play important roles in radiation balance, cloud formation, visibility impairment, and human health. Although PM10 or PM2.5 contain small fractions of heavy metals, the exceeding amounts of toxic heavy metals could cause adverse effects on human health. In order to measure the heavy metal concentration, conventional filter–based techniques have been used, in which the collected ambient particles on a filter for 12 or 24 hours were extracted into a solution with subsequent analysis using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) or Atomic Absorption Spectroscopy (AAS). Nevertheless, the complex preparation steps resulted in various sampling artifacts, and the methods suffered from a low time resolution.

The Laser Induced Breakdown Spectroscopy (LIBS), used to determine elemental composition of particles in real time (Kwak et al., 2012; Kim et al., 2013), employed laser–induced plasma to dissociate and break particles in that plasma volume. The particles were turned into their plasma state and when they came to the ground state, unique lights were produced according to their atomic constituents.

The previous version of our LIBS system employed an aerosol–focusing system to hit particles by laser in a more conditional manner. Due to the free firing laser system, the previous system suffered from low hitting efficiency. In current study, we employed a triggering laser system to hit submicrometer particles with higher efficiency than that of conventional LIBS systems (i.e., free firing LIBS system). The Nd:YAG laser was used as a plasma source. The triggering signal was generated when the particles passed through a continuous wave (CW) laser beam (642 nm, Excelsior Co.), and the signal was sent to an oscilloscope (Lecroy Co.) through photomultiplier tube (PMT) (H10722-20, Hamamatsu Co.). A delay generator (BNC 575, BNC Co.) controlled the firing of flash lamp, Q–switch of pulse laser (1064nm, Surelite II-10, Continuum Co.), and a gate delay of a spectrometer (Applied Spectra Co.). This enabled the pulse laser to fire at the time when the particles arrived at a focal point of the laser beam.

10IM.5

Recent Applications of Single Particle Aerosol Mass Spectrometry (SPAMS). DAVID FERGENSON, Anna Susz, David Kohler, Jia-Yih Feng, Jordon Rose, Maria Balaxi, Bradley D. Morrical, Payam Nahid, Midori Kato-Maeda, Adithya Cattamanchi, *Livermore Instruments Inc.*

Single Particle Aerosol Mass Spectrometry (SPAMS) measures the aerodynamic diameter and chemical composition of individual aerosol particles sampled directly from the environment in real-time. In a SPAMS instrument, individual particles are drawn through several stages of differential pumping after which they cross a square profile, continuous wave laser and an adjacent pulsed, high powered ionization laser. The transit time of the particle across the continuous wave laser is used to compute its velocity and thus its aerodynamic diameter. The pulsed laser generates ions from the chemical constituents of the particle and those ions are analyzed by a dual-polarity time-of-flight mass spectrometer. A Livermore Instruments SPAMS 3.0 analyzes up to 250 particles per second in this manner with the added advantage of being able to analyze particles over a broad range of sizes, ranging from 0.1 micrometers to at least 8 micrometers in aerodynamic diameter.

Two recent applications of the SPAMS 3.0 will be discussed: The analysis of inhaled pharmaceuticals and the real-time detection of mycobacteria. SPAMS analyses performed on a commercial formulation of indacaterol demonstrated analytical consistency in repeated measurements carried out over a 2-week period. The particle size distribution of aerosolized ciprofloxacin determined using SPAMS analysis was compared with cascade impaction data to enable scaling between SPAMS and the standard regulatory and pharmacopeial approach of using Next Generation Impactor analyses coupled with high performance liquid chromatography. In a separate series of experiments, several strains of M. tuberculosis were analyzed, with pathogen-specific marker peaks detected in all.

10IM.6

PAHs Emissions in Diesel and Biodiesel Using LVI-PTV-GC-MS. CAROLINA SOUZA, Sergio Correa, *Rio de Janeiro State University*

This work aims to develop and validate an analytical method to measure the 16 priority polycyclic aromatic hydrocarbons (PAHs) in the gas and stratified aerosol from diesel/biodiesel vehicle exhaust using gas chromatography (GC) with programmed temperature vaporization (PTV) and large volume injection mode (LVI) coupled to mass spectrometry (MS). Five operation parameters of the injection PTV (vent time, valve vent split, initial injector heating time, sample volume and injection speed) were optimized applying factorial and central composite design with response surface. The purposes were evaluate the effect of each variable has on the signal intensity (peak area) of the target PAHs and to find a set of variables values which simultaneously maximize all analytical responses, thus obtaining lower detection limits. Among these variables, vent time showed the highest effect on the signal intensity of the target PAHs. After optimization, the method was validated using extracts of gases (from XAD-2 samples) and stratified aerosol (from 10-stage nano MOUDI) from the exhaust of a engine operating with diesel and biodiesel. Limits of detection in the range of 0.74 to 4.6 µg/L were obtained, values lower than the conventional split/splitless injection. Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Fluoranthene and Pyrene were identified. Concentrations between 0.16 and 14.15 µg/m3 were obtained in the emissions. The PAHs present in aerosol were preferentially associated to particles with a diameter smaller than 0.56 µm.

10SA.1

Indoor PM2.5 in Santiago, Chile, Spring 2012: Source Apportionment and Outdoor Contributions. LUPITA MONTOYA, Francisco Barraza, Hector Jorquera, Gonzalo Valdivia, *University of Colorado Boulder*

A simultaneous indoor and outdoor PM2.5 campaign was carried out at Santiago, Chile (6 million inhabitants) in spring 2012. Paired indoor and outdoor samplers were used to measure total and trace elemental masses and EC/OC composition in Teflon and quartz filters, respectively; 47 households at Downtown Santiago were included in this study. Mean outdoor and indoor PM2.5 concentrations were 19.2 and 21.6 micrograms per cubic meter, respectively. We found no statistical evidence that indoor concentrations of PM2.5 or its species were affected by socioeconomic status ($p>0.01$). Linear regressions of indoor versus outdoor PM concentrations were fitted for each species analyzed and for each household as well. Household averaged species infiltration factors were 0.74 (±0.21), 0.88 (±0.22), 0.83 (±0.12) and 0.83 (±0.03) for PM2.5, organic carbon, elemental carbon and sulfur, respectively. The distribution of species-averaged household infiltration factors had a median value of 0.75, mean = 0.78, std. dev. = 0.18 and IQR = (0.67, 0.86). For the very first time, Positive Matrix Factorization (PMF3) was applied to an indoor PM2.5 chemical composition dataset measured at Santiago. Source identification was carried out by inspection of key species in source profiles and by comparison with published source profiles already found in Santiago. We identified six sources; three of them are outdoor contributions: motor vehicles: 6.6 (±1.4) micrograms per cubic meter, street dust: 1.4 (±0.6) micrograms per cubic meter and secondary sulfates: 3.1 (±0.6) micrograms per cubic meter; the indoor sources are indoor dust: 2.7 (±0.5) micrograms per cubic meter, chlorine based cleaning: 2.8 (±0.4) micrograms per cubic meter and cooking and environmental tobacco smoke: 6.0 (±0.7) micrograms per cubic meter. Outdoor and indoor sources each contribute half of the measured indoor PM2.5; hence, there is potential for reducing PM2.5 population exposure by improving venting and filtration of indoor air.

10SA.2

Characterization of Aral Sea Particulate Matter in Kyrgyzstan. NITIKA DEWAN, Brian Majestic, Martin Shafer, James Schauer, Paul A. Solomon, *University of Denver*

The Aral Sea has receded up to 90% in size. As a result, these sediments are resuspended by the wind and may be a new source of particulate matter (PM) in Central Asia, which could have an impact on human health and climate. In this study, Sr isotopes, along with other elemental compositions, are used as tracers to explore if the Aral Sea sediments are an important source of air pollution to Central Asia. A series of $PM_{2.5}$ and PM_{10} resuspended sediments and atmospheric PM samples were collected at two urban sites (Bishkek and Lidar) in Kyrgyzstan, located ~1,500 km downwind of the Aral Sea. The average $^{87}Sr/^{86}Sr$ ratio for the Aral Sea sediments was found to be 0.70987 (0.70947-0.71064), indicating that exposed sediments are primarily influenced by quickly eroding rocks at high elevations. The ratio in the surface soils in Kyrgyzstan is dominated by the weathering of native rocks and vegetation showing an average $^{87}Sr/^{86}Sr$ ratio of 0.71579 (0.71448-0.71739). $^{87}Sr/^{86}Sr$ of PM_{10} samples (0.70951-0.71387) are slightly more radiogenic than those in the $PM_{2.5}$ samples (0.70947-0.71274). The airborne PM collected in Kyrgyzstan has an average $^{87}Sr/^{86}Sr$ ratio of 0.71177 (0.70948-0.71335), which is in between the two end members, indicating a mixture of Aral Sea sediments and local soils.

10SA.3

Estimating the Impact of Air Pollution Controls on Ambient Concentrations. LUCAS HENNEMAN, David Lavoue, Heather Holmes, James Mulholland, Armistead Russell, *Georgia Institute of Technology*

Air pollution controls are costly. Given such costs, there are concerns as to the efficacy of specific policies and regulations in terms of providing the expected air quality benefits. The air pollution accountability chain is defined by five links: regulations, emissions, air quality, exposure/dose, and human health impacts. This Health Effects Institute-funded research takes advantage of existing long-term air quality, meteorology and acute health effects data to investigate the relationships between past regulatory actions, emissions, and ambient air pollution concentrations in Atlanta.

Meteorological detrending, using nonlinear filtering based on a Taylor Series decomposition and statistical models, is used to account for the variability in measured concentrations associated with meteorology and the seasonality in emissions. Detrended time series of pollutant concentrations and emissions estimates are used to identify techniques that can be used to investigate how changes form a specific regulatory emissions control impact observed pollutant concentrations. The techniques are also used to derive empirical sensitivities of measured ambient concentrations to changes in pollutant emissions. These empirically derived sensitivities of ambient concentrations to changes in emissions are compared to sensitivities calculated using CMAQ-DDM (the Community Multiscale Air Quality Model with the Decoupled Direct Method). These results investigate regulations implemented in the Southeastern United States, specifically the Tier 2 Vehicle and Gasoline Sulfur Program (2004), the 2007 Heavy-Duty Highway Rule, the Acid Rain Program (1995), the Clean Air Interstate Rule (2008).

Outcomes of this study include the development of empirical and model-based approaches to estimate the emissions-air quality and meteorology-air quality relationships, including the associated uncertainties. These results establish a foundation to assess the impacts of regulatory emissions control strategies on human health outcomes.

10SA.4

Receptor Modeling of Near-Real-Time, Ambient PM2.5 and Its Constituents Collected at an Urban-Industrial Site in Toronto, Ontario. UWAYEMI SOFOWOTE, Ankit Rastogi, Jerzy Debosz, Philip Hopke, *AQARU, EMRB, Ontario Ministry of the Environment*

$PM_{2.5}$ and other atmospheric pollutants were continuously monitored at high time resolution for 1 year at an urban–industrial location in Toronto, ON, Canada’s largest city. The data collected for these pollutants were examined to determine seasonal trends and potential sources. Advanced receptor models including residence time weighted concentration (RTWC) and simplified quantitative transport bias analysis (sQTBA) trajectory ensemble models (TEM) and conditional probability function (CPF) were applied to these data to identify potential local and regional sources of pollution impacting this receptor site. Seasonal trends showed that concentrations of $PM_{2.5}$ were more frequently high in winter than in any other season. The black carbon–derived measurement commonly known as Delta C (i.e., BC_{370nm}–BC_{880nm}) had its greatest abundance in winter and lowest levels in summer. The seasonality of Delta C is indicative of the impact of residential wood combustion near the receptor site. CPF indicated that lead and iron had the most unidirectional radial plots with sectors located west–southwest of the receptor being the most likely local source regions. Winter CPF for Delta C is almost of equal strengths in all directions suggestive of near–uniform isotropic local impacts. The sQTBA model provided the most satisfactory spatial representation of impacting sources. The strongest sources of $PM_{2.5}$ identified by the sQTBA model were both local and transboundary in origin. More potential source regions were found in winter and summer than in spring and fall.

10SA.5

Positive Matrix Factorization 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*

Week-long total suspended particle samples collected between 1964 and 2010 from Kevo, Finland were analyzed for trace metals, soluble trace metals, major ions and MSA, and black carbon (BC). Long-term datasets of aerosol chemical composition are very useful key for understanding and explaining past events. Significant changes have occurred in the Arctic in the past half century. In order to better understand these changes the 47-year complete data set was analyzed by Positive Matrix Factorization (EPA PMF5). The dataset was split into three time periods, 1964-1978, 1979-1990, and 1991-2010. Ten factors were determined for the 1964-1978 period, and 9 factors each resolved for the latter periods. All three time periods have two factors representing Cu-Ni-Co smelters, one dominated by Cu, the other by Ni and Co; a factor primarily consisting of Mo and W most likely due to mining, processing, and transportation of alkaline rocks on the Kola Peninsula; a factor of V, BC, and nss-SO4 characterizing residual oil combustion; a biogenic sulfate factor represented by methane sulfonic acid (MSA), a factor dominated by water soluble Fe and some Mn from the nearby iron mines and mills, and a factor consisting primarily of Sn. Similar factors containing the majority of As and some Re and Se were determined for the 1979-1990 and 1991-2010 time periods, while the 1964-1978 run contains additional inputs of Sb, Mo, and Tl. A Mn-Cd factor was found during the 1979-1990 and 1991-2010 period but not for the 1964-1978 time period. Unique factors for Ag, Au, and sea-salt (Na and Mg) were determined for the 1964-1978 time period. The combination of seasonal trend analysis and Potential Source Contribution Function (PSCF) analysis applied to the PMF results will help identify source profiles and their sources locations.

10SA.6

Long-term Source Apportionment of Ambient Fine Particulate Matter (PM2.5) in the Los Angeles Basin: A Focus on Emissions Reduction from Vehicular Sources. SINA HASHEMINASSAB, Nancy Daher, Bart Ostro, Constantinos Sioutas, *University of Southern California*

Positive Matrix Factorization (PMF) was utilized to identify and quantify sources of PM2.5 in central Los Angeles (LA) and Rubidoux, using the Speciation Trends Network (STN) data, collected between 2002 and 2013. Vehicular emissions (including both gasoline and diesel vehicles) were found to be the second major contributor to PM2.5, following secondary aerosols, with a near 20% contribution to total mass in both sites. During 2002 to 2004, the median and annual average values of vehicular emissions were relatively constant at both sites. Their contributions peaked in 2007 and 2005, respectively in LA and Rubidoux, while trended downward afterward until 2013. In 2013, the median values of daily-resolved vehicular emissions source contributions in LA and Rubidoux were respectively 70 and 52% lower than their corresponding values in 2007 and 2005. Starting in 2007, all manufactured diesel trucks must meet the EPA 2007 emission standard, requiring a 90% reduction in their PM emissions. Moreover, after 2007, several major steps were taken by the California Air Resources Board and the ports of LA and Long Beach to reduce emissions from vehicular sources, particularly from diesel trucks. To assess the effect of these regulations, daily-resolved vehicular emissions source contributions from 2002 to 2006 were pooled together and compared to the combination of 2008 to 2012 datasets. Compared to 2002-2006 dataset, the median values of vehicular emissions in 2008-2012 statistically significantly ($p<=0.001$) decreased by 24 and 21% in LA and Rubidoux, respectively. These reductions were noted despite an overall increase (about 5%) in the median value of the daily flow of vehicles in downtown LA after 2007, while the traffic counts were comparable before and after 2007 in Rubidoux. Overall, our findings demonstrate the effectiveness of stringent regulations in reducing PM emissions from vehicular sources in the LA basin over the past decade.

11AC.1

The Effect of Particle Morphology on its Evaporation Kinetics and Rates of Heterogeneous Reactions.

ALLA ZELENYUK, Jacqueline Wilson, David Bell, Dan Imre, *Pacific Northwest National Laboratory*

The properties of mixed particles depend on their shape and morphology. For example, the rates of heterogeneous reactions strongly depend on whether the condensed-phase reacting substances are on the particle surface or inside the particle, behind a protective shield.

We demonstrated the ability to generate size-selected particles with complex shapes and morphologies and to characterize their three-dimensional structures utilizing our “depth-profiling” approach, in which by controlling laser fluence, we control the depth to which the laser penetrates the particle. At low laser fluence, the surface compounds dominate the particle mass-spectra, and at higher fluence, the mass spectra represent the composition of the entire particle. This approach was successfully applied to characterize morphology of NaCl seeds coated with solid pyrene and with liquid dioctyl phthalate (DOP), NaCl particles coated by secondary organic aerosol (SOA), SOA-coated DOP particles, and DOP-coated SOA particles, revealing their complex layered morphologies.

We will present the results of a recent study, in which we characterized the morphology of particles formed by SOA condensation on pre-existing size-selected seed particles with different phase and volatility (DOP, polyaromatic hydrocarbons, oleic acid) and quantified their evaporation kinetics and rates of heterogeneous oxidation as a function of SOA coating thickness. In addition, we examined the stability and characterized the morphology, evaporation kinetics, and reactivity of particles with reverse morphology, i.e. SOA core coated with the corresponding organic.

We find, for example, that the evaporation of SOA-coated DOP particles and DOP-coated SOA particles exhibit very different behavior: The DOP coating on SOA evaporates very fast, while SOA-coated DOP does not evaporate, showing that the highly viscous semi-solid SOA coating prevents DOP core from evaporation. Similarly, our data show that SOA coating of oleic acid particles significantly reduces the rate of their heterogeneous oxidation by ozone.

11AC.2

Gas-Particle Partitioning of Organic Aerosols: Defining the Influence of Surface Interactions on Their Volatility.

RICHARD E. COCHRAN, Alena Kubatova, Evguenii I. Kozliak, *University of North Dakota*

Organic aerosols (OA) and their partitioning into the particle phase has long been a complex problem given the large number of species typically present along the aerosol surface. There has been much agreement that interactions between an organic compound and the aerosol surface decrease the compounds volatility. However, the extent of these “matrix-analyte” interactions is not fully understood, and thus current models may misrepresent the partitioning of OA between the gas and particle phases. In order gain a more accurate representation, experimental values need to be established comparing the thermodynamic influences of the “matrix-analyte” interactions. Therefore in this work vaporization enthalpies of a wide and representative range of OA species were experimentally determined under a variety of conditions. Initial experiments were performed with analytes in the form of neat solutions and analytes spiked to model particles, with vaporization enthalpies determined by using tandem thermogravimetry-differential scanning calorimetry (TGA-DSC). Silica and graphite particles were used to represent polar and non-polar aerosol matrices, respectively. Individual vaporization enthalpies of species in the presence of more complex multi-component matrices (i.e., multi-component model particles and real-world particles) were determined using a thermal desorption/pyrolysis-gas chromatography/mass spectrometry (TD/Py-GC/MS) system.

11AC.3

Effect of Precursor Molecular Structure on the Volatility, Viscosity and Oligomer Content of SOA Particles Formed by Ozonolysis of Cycloalkenes. JACQUELINE WILSON, Alla Zelenyuk, Dan Imre, ManishKumar Shrivastava, *Pacific Northwest National Laboratory*

The formation, properties and temporal evolution of secondary organic aerosol (SOA) particles strongly depend on their phase and volatility. These properties affect the ability of SOA particles to maintain equilibrium with rapidly changing gas phase concentrations and temperature, as experienced in the mixed planetary boundary layer, by internal mixing and evaporation/condensation.

Studies by our group, and others, have shown that 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. We have also shown that when hydrophobic organic vapors, like polycyclic aromatic hydrocarbons (PAHs), are present during SOA formation their presence further reduces SOA volatility. Evaporation kinetics studies reveal that these semi-volatile hydrophobic compounds are trapped within the SOA and that their evaporation rates are determined by their diffusion through the SOA and can therefore be used to obtain the SOA viscosity. Application of this approach to freshly made alpha-pinene SOA doped with various PAHs yielded a viscosity of 10^8 Pa s, and $3 \cdot 10^8$ Pa s for the same particles after aging.

These findings are consistent with the fact that SOA particles contain significant amounts of high molecular weight organic compounds (oligomers), which have the potential to severely retard diffusion, mixing, and thus evaporation of smaller molecules.

We present the results of recent studies that explore the relationship between cycloalkenes with differing molecular weight and ring structure (C_5 – C_8 cycloalkenes, including C_7 isomeric cycloalkene systems (1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, methylenecyclohexane and cycloheptene) used as SOA precursors – in the absence and presence of hydrophobic organics – and SOA volatility and viscosity. We will show that differences are mostly related to differing SOA oligomer content, which depends on the precursor, particle age, and how much, if any, hydrophobic organic vapors are incorporated.

11AC.4

APM Measured Shape Factor Change of α-pinene SOM and Its Dependence on Relative Humidity. YUE ZHANG, Marianna Santos Sanchez, Claire Douet, Yan Wang, Adam Bateman, Zhaoheng Gong, Mikinori Kuwata, Lindsay Renbaum-Wolff, Pengfei Liu, Bruno Bianchi Sato, Allan Bertram, Franz Geiger, Scot Martin, *Harvard University*

A flow tube reactor was used to generate α-pinene secondary organic material. The secondary organic material particles were brought to a 9 L flask to enhance coagulation under different relativity humidity (RH) levels. A DMA-APM system was used to measure particle mobility diameter and particle mass, in order to determine particle shape factors. In this study, the particle shape factor was dependent on the particle number concentration, particle size and RH. An optimal particle number concentration was found, which enhanced coagulation of particles with similar diameters and created non-spherical particles under dry (<5% RH) conditions. These non-spherical particles transformed back to spherical particles between 20%-35% RH. The particle shape transition between low and high RH suggests a possible viscosity change rather than a chemical composition change, based on both the APM shape factor and AMS measurement results. This implies that particle viscosity should be within the solid region under 20% RH and within semi-solid to liquid region for RH above 35%. This method provides a new way to estimate particle viscosity through direct aerosol measurement and is applicable under low RH conditions.

11AC.5

Ultraviolet and Visible Complex Refractive Indices of Brown Carbon Formed via Photooxidation of Aromatic Toluene and m-Xylene. PENGFEI LIU, Scot Martin, *Harvard University*

Recent field and laboratory studies have suggested that the secondary organic materials (SOM) formed from anthropogenic volatile organic compounds act as brown carbon. However, the spectral data of their optical properties are still scarce. In the present study, spectroscopic data of real and imaginary refractive indices (m = n - ik) were obtained in the ultraviolet (UV)-visible region, using the spectroscopic ellipsometry and the UV-visible spectrometry, respectively. The SOMs were produced in an oxidation flow reactor by photooxidation of toluene and m-xylene at various levels of nitrogen oxides (NOx). The results show that k values of the studied anthropogenic SOMs were more than ten times higher than that of the biogenic SOMs reported in our previous study. The presence of NOx can form organo-nitrogenic compounds, such as nitro-aromatics and organic nitrates, further enhancing the light absorption of studied SOMs. Compared with the SOM derived from m-xylene, the SOM derived from toluene had larger k values, as well as a greater NOx-induced enhancement of k, suggesting different brown-carbon-formation potentials of different aromatic precursors. Bulk composition analyses using the infrared spectrometry suggest a major fraction of SOMs formed via particle-phase heterogeneous reactions, which can result in a larger SOM yield than model prediction. Our results imply that fresh anthropogenic SOM formed in urban environments can be a large source of atmospheric brown carbon. This type of brown carbon can potentially play an important role in affecting UV irradiance in the troposphere, which might consequently exert influences on the concentration of tropospheric oxidants and the lifetime of greenhouse gases.

11BA.1

Study of the Aerosolization Mechanisms of Bacteria in Single Particle Using Fluorescence Spectroscopy. NICOLAS GROULX, Nathalie Turgeon, Caroline Duchaine, *Université Laval, Canada*

The study of the aerosolization mechanisms of microorganisms is a novel field of research in which few is being published from a fundamental point of view. For example, the distribution of microorganisms (bacteria, virus, spores) inside a single droplet of bioaerosol as not been precisely determined yet, as well as its infectious potential. Also, the effects of ionic charges of the nebulization media upon viral bioaerosols have not been deeply studied, which leaves numbers of unanswered questions regarding the efficiency of protective masks.

We propose to study the distribution of microorganisms in a single bioaerosol particle. The setup which allows a controlled dilution of bioaerosols is described in order to show how E. coli bacteria are distributed inside aerosols by analysis of single particles impacted on a black filter. The coaerosolization of E. coli and Pseudomas fluorescens has been performed as well. The results show surprisingly that even if P. fluorescens cells are more numerous than E. coli in our experiments, it doesn’t affect the specific distributions of each type of bacteria in aerosol particles. This suggests that in those conditions, E. coli and P. fluorescens are not aerosolyzed the same way and that further investigations with this system will be performed.

11BA.2

Bacterial and Fungal Ecology in Indoor and Outdoor Air. JOANNE B. EMERSON, Patricia Keady, Anne Perring, Jonathan Awerbuch, Joshua P. Schwarz, David Fahey, Shelly Miller, Noah Fierer, *University of Colorado Boulder*

We have a limited understanding of the diversity and abundances of bacteria and fungi in indoor and outdoor air and of the biotic and abiotic factors that influence them. Our group uses molecular methods, including targeted gene sequencing, to characterize bacterial and fungal community composition in air samples from a variety of environments. Sampling sites include the near-surface atmosphere, inside and outside family residences (including homes affected by the September 2013 Boulder County flood), and the atmosphere above the surface (accessed via a 300 m tower). We will present the integration of microbial DNA sequencing data and abundance estimates with measurements of environmental parameters to assess ecological influences on bacterial and fungal community composition and seasonal dynamics in indoor and outdoor air. Results indicate seasonal shifts in air microbial community composition inside and outside family residences, significant differences in bacterial and fungal communities between flooded and non-flooded homes, and temporal influences on atmospheric bacterial and fungal community composition in the near-surface atmosphere and aloft.

11BA.3

Proteomic Analysis of Sphingomonas aerolata Incubated in the Airborne State. Valdis Krumins, Maksim Abadjev, Sjef Boeren, Tomas Kruse, Peter Schaap, Hauke Smidt, Gediminas Mainelis, Lee Kerkhof, DONNA FENNELL, *Rutgers, The State University of New Jersey*

The objective of this study was to analyze the proteomic response of an atmospheric microorganism to aerosolization and the presence of a volatile substrate while airborne.

Sphingomonas aerolata strain NW12 (AJ429240.1), a psychrotolerant bacterium isolated from ambient air and obtained from Leibniz Institute DSMZ-German Collection of Microorganisms and Cell Cultures, was used as a model environmentally significant atmospheric bacterial species. The genome of S. aerolata strain NW12 was sequenced using the Illumina HiSeq2000 platform. The genome was annotated and 3344 predicted protein sequences were identified.

S. aerolata was grown in minimal media containing acetic acid as the sole substrate, and then aerosolized into rotating gas-phase bioreactors, which can maintain bacteria in the airborne state for several days. The bacteria were fed either gaseous ethanol or no substrate and incubated for two days. Cells were collected onto membrane filters (Supor, Pall, Port Washington, NY) and proteins were extracted directly from the membranes. Proteins were cleaved into peptides by in-gel trypsin digestion. Proteins were identified using liquid chromatography-mass spectrometry (LC-MS-MS) by matching accurate peptide masses and the corresponding mass fragmentation spectra to the protein database prepared from the sequenced genome.

The aerosolization system and gas-phase rotating reactors were able to produce and maintain approximately 20 to 80 x 106 total cells in suspension over several days, enough for adequate protein capture. Approximately 400 putative proteins were identified from the aerosolized cells, enough to allow comparison of the different treatments. Comparison of four replicate reactor runs in the fed and unfed state to liquid-grown cells indicated differential expression of several proteins in the aerosolized versus liquid-growth cells. Expression of proteins while aerosolized indicates the S. aerolota are active while suspended in air. Rather than being a passive conduit for bacteria, air may be an environment where bacteria carry out active biological functions.

11BA.4

Characterization of Fungal Fragments. JACOB MENSAH-ATTIPOE, Sampo Saari, Jorma Keskinen, Anniina Salmela, Anna-Maria Veijalainen, Pertti Pasanen, Tiina Reponen, *University of Eastern Finland*

Particles, intact spores and sub-micrometer size fragments, are released from fungal growth during growth and sporulation. Among these particles, fragments stay longer in air, are easily inhaled and penetrate deep into the respiratory tract having the potential for causing serious adverse health effects. It is, however, unclear whether the fragments originate from fungal growth or from growth materials as a result of fungi decomposing the growth surface. In this study, we measured the concentration and elemental composition of fragments and spores released from different materials.

Particles from three fungal species (Aspergillus versicolor, Cladosporium cladosporioides and Penicillium brevicompactum), grown on agar and gypsum board for 1, 4 and 18 weeks were aerosolized using the Fungal Spore Source Strength Tester (FSSST) at three different air velocities (5, 16 and 27 m/s). Released spores (da > 0.8 micro-meters) and fragments (da < 0.8 micro-meters) were detected and counted using Optical Particle Size Spectrometer (0.3 – 10 micro-meter) and LAS-X II (0.1 - 1 micro-meter), respectively. The morphology and elemental composition of the particles were analyzed using a transmission and scanning electron microscopes (TEM, SEM) coupled with an energy dispersive spectrometer (EDS).

Release of spores and fragments from both agar and gypsum board increased with increasing air velocity. When grown on agar, the highest concentration of spores and fragments were obtained from 1 week old cultures of P. brevicompactum at an air velocity of 27 m/s. However, no clear trends were observed for particles released from gypsum board. Similar elemental compositions were observed between the spores and fragments. The main elements detected in both spores and fragments were carbon and oxygen in abundance with minor detection of sodium, potassium, phosphorus, calcium, magnesium and silicon.

Preliminary results indicate that the fragments are of fungal origin. The amount of fragment released is influenced by air velocity, growth substrate and fungal species.

11BA.5

Development of a Laboratory Surrogate for Swine Bioaerosol. CHRISTINE LOZA, John Horns, Brian Mader, Scott Dee, *3M*

Virus-containing bioaerosol is an important component of indirect disease transmission in swine-producing regions. The swine industry has begun to implement filtration systems for air entering swine facilities to reduce the risk of airborne spread of virus. It is necessary to know the size and virus distribution of swine bioaerosol to guide filter testing and selection. We present the size and virus distributions of bioaerosol sampled at swine facilities during porcine epidemic diarrhea virus or porcine reproductive and respiratory syndrome virus outbreaks. Variation of the size distribution in rooms housing different weights of swine will be discussed. Particles were sampled in real-time to characterize the size distribution and collected on impactor substrates for offline viral analysis. From these size and virus distributions, two different laboratory surrogate aerosols were developed using live virus and swine fluids relevant to the mode of virus transmission. A characterization of the laboratory surrogate aerosol size and virus distribution will be presented.

11CO.1

Size Distributions and Volatility of Vehicle PM Emissions Measured in a Traffic Tunnel. ALBERT A. PRESTO, Xiang Li, Timothy Dallmann, *Carnegie Mellon University*

Emissions from motor vehicles are a major source of urban air pollution, including carbonaceous particulate matter (PM) in the form of organic and elemental carbon (OC and EC). Organic PM emissions from both gasoline and diesel vehicles readily evaporate with dilution or mild heating, meaning that populations living near roadways may be exposed to PM with different composition than what is measured in standard dynamometer testing.

This study considers measurements of PM size distributions and PM volatility conducted in a traffic tunnel in Pittsburgh, PA. PM size from 7-400 nm was measured with a pair of scanning mobility particle sizers. PM composition was measured with both filter and continuous measurements of OC and EC, and nonrefractory PM composition was monitored with an Aerosol Chemical Speciation Monitor. PM volatility was investigated using a thermodenuder (TD). The TD operated in two modes: (1) the TD was cycled through low temperature settings between 40-100 C and long residence time (19 sec) to investigate the volatility of organic PM, and (2) the TD was held at high temperature (250 C) and short residence time (3 sec) to quantify the size distribution of nonvolatile PM.

The PM number size distribution peaks at approximately 20-30 nm. Mild heating in the TD causes 10-50% of the organic PM to evaporate. TD modeling using the volatility distributions of May et al (2013) adequately describes the PM evaporation in the TD. High temperature stripping of the PM reveals two nonvolatile modes – one consisting of EC centered at 80-100 nm, and another consisting of particles smaller than 10 nm. The composition of the smaller nonvolatile mode is uncertain, and may contain ash particles resulting from impurities in fuel and lubricating oil.

11CO.2

Pyrolysis Smoke Generated Under Low-Gravity Conditions. GEORGE MULHOLLAND, Marit Meyer, David Urban, Gary Ruff, Zeng-guang Yuan, Victoria Bryg, Thomas Cleary, Jiann Yang, *NASA Glenn Research Center*

A series of smoke experiments were carried out in the Microgravity Science Glovebox on the International Space Station (ISS) Facility to assess the impact of low-gravity conditions on the size distribution and structure of the smoke aerosol. This information will be used in the design of better fire detection for spacecraft. The smokes were generated by heating five different materials (all polymers) commonly used in space vehicles. They were characterized by the measurement of the zeroth, first, and third moments of the size distribution. This study focuses on the effects of flow and heating temperature for both normal and low-gravity conditions on the pyrolysis rate, the smoke plume structure, the smoke yield, the size distribution, and particle structure. Low-gravity conditions allowed a unique opportunity to study the smoke plume for zero external flow without the complication of buoyancy. The diameter of average mass for the smoke increased on average by a factor of 1.7 and the morphology of the smoke changed from agglomerate with flow to spherical at no flow for one material. The no flow case is an important scenario in spacecraft where smoke could be generated by the overheating of electronic components in confined spaces. The low-gravity conditions allowed the study of coagulation without the complication of particle losses due to gravity. From electron microcopy of samples returned to earth, it was found that pyrolysis smoke can form an agglomerate shape as well as a spherical shape, which had previously been the assumed shape. The relationship between the properties of the pyrolysis vapors and the smoke structure will be discussed.

11CO.3

Combining Selective Catalytic Reduction (SCR) System with Biodiesel in Mobile Sources: New Issues Arise. Yara S. Tadano, Guillherme C. Borillo, Thiago O. B. Silva, Fabio B. Valebona, Penteado Neto, Denis Rempel, Lucas Martin, Carlos I. Yamamoto, Sanja Potgieter-Vermaak, Ana Flavia L. Godoi, RICARDO H. M. GODOI, *Federal University of Parana - Curitiba, PR, Brazil*

Due to an urgent and pressing need to better understand the demand for petroleum-based energy, only a few studies have focused on the effects of biodiesel on the emission of unregulated pollutants from vehicles equipped with Selective Catalytic Reduction (urea-SCR) systems. The major goal of this research was to quantify the organic and inorganic gas emissions using a diesel engine equipped with urea-SCR measured by an FTIR system operating with Low-Sulfur Diesel (LSD), Ultra-Low-Sulfur Diesel (ULSD) or with a blend of 20% soybean biodiesel in ULSD (B20). A dynamometer test bench operating the European Steady Cycle (ESC) was used to access the pollutants concentrations. Our NO_x emissions results are in compliance with the European, American and Brazilian regulations to SCR system use. However, biodiesel fuel in combination with SCR system yielded substantial concentrations of NH_3, N_2O, non-methane hydrocarbons (NMHC) and some diesel hydrocarbons (HCD). Formaldehyde (which has a high Photochemical Ozone Creation Potential [POCP]) emissions decrease when using SCR system, though N-octane (which has the higher Photochemical PeroxyAcetylNitrate Creation Potential [PPCP]) increased when combining SCR system with LSD and ULSD fuels. According to our results, we may conclude that the SCR system satisfies its original purpose of reducing NO_x, however, it brings new issues comprising harmful compounds, such as NH_3 and N_2O. Combining biodiesel blend (B20) with the use of SCR system is a suitable strategy, as it reduces hazardous pollutants emissions and also reduces the emission of those compounds with high POCP and PPCP, formaldehyde and n-octane, respectively.

11CO.4

In-Situ Measurements of Contrail Properties Measured during the 2013-2014 ACCESS Project. RICHARD MOORE, Bruce Anderson, Edward Winstead, Kenneth Thornhill, Andreas Beyersdorf, Charles Hudgins, Robert Martin, Michael Shook, Luke Ziemba, ACCESS Science Team, *NASA*

We present measurements of aerosol and cloud contrail microphysics measured in-situ behind the CFM56-2-C1 engines of the NASA DC-8 aircraft during the 2014 Alternative Fuel Effects on Contrails and Cruise Emissions (ACCESS) project. Aircraft engine emissions can have a disproportionately large climatic impact since they are emitted high in the troposphere and in remote regions with otherwise low aerosol concentrations. This has motivated numerous past ground-based studies focused on quantifying the emissions indices of non-volatile and semi-volatile aerosol species, however, it is unclear the extent to which emissions on the ground translate to emissions at cruise conditions. In addition, the ability of engine-emitted aerosols to nucleate ice crystals and form linear contrails or contrail cirrus clouds remains poorly understood.

To better understand these effects, the ACCESS-I project was conducted in 2013 to quantify aerosol emission indices for a number of petroleum-based and bio-based jet fuels at cruise conditions, while the 2014 ACCESS-II project focused on measuring the contrail microphysics. Three different fuel types are discussed: a low-sulfur JP-8 fuel, a 50:50 blend of JP-8 and a camelina-based HEFA fuel, and the JP-8 fuel doped with sulfur. Emissions were sampled using a large number of aerosol and gas instruments integrated on an HU-25 Falcon jet that was positioned in the DC-8 exhaust plume at approximately 50-500 m distance behind the engines. It was found that the biojet fuel blend substantially decreases the aerosol number and mass emissions indices, while the gas phase emission indices were similar across fuels. The effects of these fuel-induced changes of aerosol emissions on contrail properties will be discussed.

11CO.5

The Use of Diesel, Biodiesel Combined and Selective Catalytic Reduction (SCR) After-Treatment System on Particulate Matter Emissions: A Dynamometer Test Bench. GUILLHERME C. BORILLO, Thiago O. B. Silva, Yara S. Tadano, Fabio B. Valebona, Penteado Neto, Denis Rempel, Lucas Martin, Carlos I. Yamamoto, Marcelo Nalin, Jacson Weber de Menezes, Flemming R Cassee, Sanja Potgieter-Vermaak, Ana Flavia L. Godoi, Ricardo H. M. Godoi, *Federal University of Parana - Curitiba, PR, Brazil*

The new emission control systems in combination with the use of biofuels bring new insights to the investigation of unregulated combustion emissions. This study has focused on the distinct particulate matter emission due to the use of Low-Sulfur Diesel (LSD), Ultra-Low-Sulfur Diesel (ULSD) or a blend of 20% soybean-biodiesel in ULSD (B20) on the engine equipped with Selective Catalytic Reduction (SCR) system. A bench dynamometer tests system was used following the European Steady Cycle (ESC) testing cycle. Soluble ions, PAH´s and Nitro-PAH´s, elementary composition, black carbon, the soot molecular reactivity and oxidative stress were analyzed using IC, GC-MS, EDXRF, Aethalometer (optical analysis), Micro-Raman and Electron Spin Resonanse, respectively, for the total particulate fraction. Gravimetric analyses were performed on segregated particulate matter and have shown that the combustion of ULSD generates more fine particles compared to the other fuels. Among all tested combinations, SCR+B20 promote the higher reduction of major ions particles. The results didn’t show significant difference for elemental concentrations and optical properties concerning the fuel and SCR system combinations. The higher and lower reactivity were observed for ULSD exhaust particles and B20 samples, respectively. The PAH’s and Nitro-PAH’s concentration are dependent of fuel composition and after-treatment system. SCR+B20 combination increased fivefold the oxidative stress of PM. Different approaches of the combination SCR-Fuels were discussed, presenting new concerns about the particulate matter and the effects in human health and environment.

11IM.1

A New Method to Measure the Extinction Cross Section Using Digital Holography. MATTHEW BERG, Nava Subedi, *Mississippi State Univeristy*

This work will present a new technique to measure an aerosol particle’s extinction cross section. The concept relies on digital holography, where the interference pattern of a particle’s scattered and incident light is recorded optoelectronically to yield a digital hologram. Much information about a particle’s physical character can be extracted from such holograms. For example, a silhouette-like image of the particle can be obtained via a simple Fourier-transform-based operation. This talk will show how the digital hologram can also yield the value of the extinction cross section for single and multiple nonspherical particles. Given the simplicity of the measurements involved, such capability could have important applications to quantify extinction by complex-shaped aerosol particles, such as mineral dust, and can do so in situ.

11IM.2

Enhanced Thermal/Optical Characterization of Aerosol Elemental, Molecular, and Optical Properties. XIAOLIANG WANG, Xufei Yang, Benjamin Sumlin, Gustavo Riggio, Jerome Robles, L.-W. Antony Chen, LaxmiNarasimha Yatavelli, Judith Chow, John Watson, *Desert Research Institute*

Thermal/optical analyses are widely used to quantify organic and elemental carbon (OC and EC, respectively). This paper presents enhancement to the thermal/optical analysis to characterize aerosol elemental, molecular, and optical properties. Such multi-dimensional analysis provides a new tool to study aerosol source and impact. In the enhanced thermal/optical analyzer, a ~0.5 cm2 punch from a quartz-fiber filter sample is heated in programmed heating steps. Carbonaceous and other materials are volatilized, pyrolyzed, and combusted to gas phase compounds under either an inert ultrapure helium (He) atmosphere at lower temperatures (<= 580 °C) or a mixture of 98% He and 2% O2 atmosphere at higher temperatures (>=580 °C). For analysis of elements of C, H, N, and S, the evolved gaseous species are oxidized in a high temperature (~900 °C) CHNS reactor containing oxidizing agents to convert organic components to CO2, H2O, NOx/N2, and SO2. The oxidation products are measured by a quadrupole mass selective detector (MSD). A stream of evolved gas is sent to an O reactor consisting of a nickel-coated carbon reactant that converts O to CO. CO is then oxidized to CO2 and quantified by a nondispersive infrared (NDIR) sensor. To analyze the mass spectral fingerprints of aerosols, a stream of the evolved gas is sent through an empty quartz tube heated to 650ºC to break low-volatility, large organic molecules into small fragments, which are then analyzed by the MSD. Seven lasers in the wavelength range of 405 nm - 980 nm are used to monitor the optical reflectance and transmittance signals. The spectral signals allow estimation of brown and black carbon, provide insight into the charring process, and improve the charring correction. CHNSO abundance, mass spectra, and optical signature of model compounds and typical source and ambient aerosols will be presented.

11IM.3

Multi-Wavelength Measurements of Soot Optical Properties Using CAPS PMssa and CRD-PAS Instruments. Sara Forestieri, Andrew Lambe, Molly Cummings, James Brogan, Christopher Cappa, Paul Davidovits, ANDREW FREEDMAN, Timothy Onasch, *Aerodyne Research, Inc.*

We have obtained measurements of light absorption, scattering and extinction coefficients and thus single scattering albedo (SSA) of soot particles produced using an inverted diffusion flame and a premixed flat burner flame operating with methane and ethylene fuels, respectively. Extinction and absorption were measured at 405 nm and 532 nm using a dual cavity ringdown photoacoustic spectrometer (CRD-PAS; UC Davis). Scattering and extinction were measured at 630 nm using a CAPS PMssa single scattering albedo monitor (Aerodyne). Soot particle mass was quantified using a centrifugal particle mass analyzer (CPMA; Cambustion), mobility size with a scanning mobility particle sizer (SMPS; TSI) and soot number concentration with a mixing condensational particle counter (MCPC; BMI). The wavelength dependent, mass-specific optical properties were measured for denuded soot particles as a function of particle mobility size and as a function of non-absorbing coatings (dioctyl sebacate and sulfuric acid). The measured mass specific absorption coefficient at 405 nm for denuded soot is substantially higher than that reported by Radney, et al. [Environ. Sci. Tech., 48:3169–3176 (2014)] even after accounting for differences in soot chemical composition.

11IM.4

Cleanable, High-Flow Aerosol Concentrator. STEVEN SPIELMAN, Nathan Kreisberg, Susanne Hering, *Aerosol Dynamics Inc.*

We have developed a device that concentrates the particles from a 15 L/min aerosol flow into a 1.5 L/min output. The device combines a water-based condensational growth tube and an aerodynamic focusing stage. The growth tube uses a parallel plate configuration, with outer dimensions 43 x 90 x 390 mm. Constructed only of stainless steel and PTFE, it allows for aggressive cleaning options necessary in biological applications or in cases where the build-up of organic compounds must be controlled. Heat and moisture are delivered (and removed) by a filtered, recirculating water system, which prevents the accumulation of water soluble compounds on the wetted surfaces. The activated particles form 2- to 3-um droplets, which enter the concentrator (43 x 72 x 50 mm) attached directly to the growth tube housing. The droplets are aerodynamically focused by eight round orifices operating in parallel. Waste flow is extracted from annular slits leaving most of the droplets in the 1.5 L/min concentrated flow. We have demonstrated 7x concentration enhancements of particles as small as 15 nm. The concentration factor was comparable for salt, oil, and ambient particles.

11IM.5

Surface Tension Measurement of Secondary Organic Aerosols Using Atomic Force Microscopy. ANDREW HRITZ, Dabrina Dutcher, Timothy Raymond, *Bucknell University*

Experimental measurements of secondary organic aerosol’s surface tension are needed to better understand these complex systems and to refine computational models that rely on our characterization of these systems. Obtaining direct measurements of surface tensions using traditional methods is challenging due to high sample volume requirements for direct measurement techniques relative to the small volumes of aerosol particles. Recent advances in Atomic Force Microscopy (AFM) tips have allowed direct measurement of the surface tension of small volumes of liquid[1]. In this study, the AFM method was utilized to directly measure the surface tension of liquid aerosols. Aerosols were generated in a small Teflon smog chamber through the oxidation of pure volatile organic compounds by ozone. The aerosols were collected by direct impaction of the liquid phase particles into custom-made impaction wells. The surface tension of the liquid aerosol from the oxidation of alpha-pinene will be presented along with a comparison of these values to values measured indirectly and those used in current models.

[1] Yazdanpanah, Mehdi M., Mahdi Hosseini, Santosh Pabba, Scott M. Berry, Vladimir V. Dobrokhotov, Abdelilah Safir, Robert S. Keynton, and Robert W. Cohn. "Micro-wilhelmy and related liquid property measurements using constant-diameter nanoneedle-tipped atomic force microscope probes." Langmuir 24, no. 23 (2008): 13753-13764.

11RA.1

Atmospheric Monitoring in the Western Mediterranean in Summer 2013: Overview of Physic-chemical Properties and Variability. JORGE PEY, José Carlos Cerro, Stig Hellebust, H. Langley DeWitt, Brice Temime-Roussel, Miriam Elser, N. Pérez, Alexandre Sylvestre, Dalia Salameh, Grisa Mocnik, Andre Prévôt, Yanlin Zhang, Soenke Szidat, Nicolas Marchand, *Aix-Marseille Université, CNRS, LCE FRE 3416*

Despite vast efforts to reduce atmospheric aerosol concentrations, the Mediterranean atmosphere still contains high loadings of aerosols during the warm season, in part due to the poor knowledge about their sources. Mineral dust, sulfate and organic compounds are the most frequent chemical species. While the sources of mineral dust and sulfate are fairly well-characterized, the origin of the organic aerosol is unclear, although it has been found that the organic carbon is mostly from contemporary (non-fossil) sources.

As part of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx), simultaneous field campaigns were conducted in the summer of 2013 in different Mediterranean observatories. Here we focus on Corsica-Ersa and Mallorca-Cap des Pinar supersites. A complete instrumentation set-up to measure the aerosol and gas-phase chemical and physical properties and concentrations in Mallorca was deployed: a HR-ToF-AMS; a PTR-ToF-MS; a SMPS to obtain particle number and size distribution of aerosols in the range 10-700 nm; a LAAPTOF to characterize in real time individual particles in terms of size and chemical composition; an Aethalometer AE31 to monitor the absorption coefficients of aerosols between 370 nm and 950 nm; two high-volume samplers for subsequent chemical determinations, including off-line 14C analysis, of the PM10 and PM1 fractions; a mobile van with air quality surveillance instruments (e.g., CO, SO2, NOx); and a meteorological tower.

During the campaign, Mallorca and Corsica were affected concurrently by common atmospheric events including Saharan dust outbreaks, episodes of new-particle formation and regional recirculation of air masses. In addition, specific characteristics were found to influence Mallorca and Corsica independently. In particular, more Saharan dust episodes and persistent accumulation processes were observed in Mallorca, while outflows from the Po valley were observed at times in Corsica. Thus, the general atmospheric characteristics of the western Mediterranean could be drawn, and the particularities of each region were also investigated.

11RA.2

A Study on Primary Marine Organic Aerosols and Biological Materials in Seawater. JI YEON PARK, Min Soo Kang, Wajih Ur Rehman, Dohyung Kim, Kihong Park, *Gwangju Institute of Science and Technology*

It is important to identify mass spectra of primary biological markers by means of an aerosol mass spectrometer (AMS) to determine their contribution to formation of primary marine organic aerosols (e.g., bubble bursting mechanisms) in real time. In this study, mass spectra of three types of laboratory-generated marine bacteria (e.g., Pseudomonas aeruhlnosa, Vibrio litoralis, and Flavobacterium sp.) and natural seawater aerosolized by a bubble bursting system were investigated by using a quadruple aerosol mass spectrometer (QAMS) for the determination of primary biological markers in the AMS mass spectra of organics. Chemical constituents of non-refractory submicrometer particles in the ambient atmosphere were measured in real time using the QAMS at a coastal site (Boseong, Korea) in the fall (10/29/2012–11/16/2012). Simultaneously, various biological materials (e.g., chlorophyll-a (<700 nm), bacteria (200 nm–1 µm), and virus (20 nm–200 nm)) in seawater sampled from coastal Boseong (e.g., ~1.6 km away from the ambient sampling site) were determined by an UV spectrophotometer and epifluorescence microscopy to find effects of biological materials in seawater on primary marine organic aerosols. In the AMS mass spectra of organics, m/z 54, 95, and 105 were newly found for the laboratory-generated marine bacteria in marine or nutrient broths, which were not observed in organic mass spectra of pure broths. In addition, these fragments were observed in organic mass spectra of sea spray particles produced from natural seawater. This suggests that mass fragments at m/z 54, 95, and 105 could be used as primary biological organic markers for studying formation of primary marine organic aerosols. Further analyses for determining the fraction of primary biological organic aerosols (i.e., the ratio of a sum of the primary biological markers in organic mass spectra to total organic mass spectra) and their correlations with biological materials in seawater are in progress, and will be presented.

11RA.3

Using Ocean Biogeochemistry and Surface Activity to Improve Understanding of Regional Patterns in Sea Spray Chemistry. SUSANNAH BURROWS, Oluwaseun Ogunro, Amanda Frossard, Lynn Russell, Phil Rasch, Scott Elliott, *Pacific Northwest National Laboratory*

Surface-active organic molecules are strongly enriched in primary sea spray aerosol (SSA) as a result of their adsorption onto bubble films, and accumulation in the sea surface microlayer. A new modeling framework is presented that predicts the enrichment of organics in the aerosol on the basis of their surface activity. We utilize output from an ocean biogeochemistry model to describe the geographic distribution of several classes of organic compounds in the ocean. We assign chemical properties to each class based on laboratory measurements, and use the Langmuir adsorption isotherm to predict the organic mass fraction of the generated SSA. Recent observations across several ocean regions have lead to differing conclusions regarding the correlation of chlorophyll-a and SSA organic mass fraction. Our model predicts a strong positive correlation of chlorophyll-a and SSA organic mass fraction in nutrient-rich regions such as the North Atlantic, largely driven by the seasonal cycle, but less variability and a negatively correlated seasonal cycle in nutrient-poor regions such as the southeast Pacific. These results demonstrate that the new model can resolve certain apparent discrepancies between observations, and represents an advance in understanding how the drivers of SSA composition differ between ocean regions.

11RA.4

Characterization of the Springtime Arctic Aerosol. RICHARD LEAITCH, Julia Burkart, Andreas Herber, Shao-Meng Li, John Ogren, Sangeeta Sharma, Jonathan Abbatt, *Environment Canada*

Aerosol measurements were conducted from the Alfred Wegner Institute POLAR 6 DC-3 aircraft on 11 flights during March 22, 2012 to April 6, 2012 between Longyearbyen, Svalbard, Norway and Eureka, Nunavut, Canada. The measurements included particle size distribution (DMT UHSAS), refractory black carbon (rBC) number and mass (DMT SP2), particle light scattering (TSI 3563 Nephelometer) and particle absorption (NOAA CLAP). Our analysis uses the profile data from the flights to study new particle formation (NPF) and factors controlling the aerosol single scatter albedo (SSA). Evidence for NPF formation is found in clean air coming off Greenland in the 2-3 km altitude range. The SSA is examined with respect to the measurements of rBC, particle size distributions and light scattering.

11RA.5

Chemical Characterization of PM2.5 for the Year 2013 for 5 Rural Background Sites in France. ANTOINE WAKED, Jean-Luc Jaffrezo, Jean-Luc Besombes, Emmanuelle Drab-Sommesous, Eve Chretien, Pierre-Yves Robic, Sebastien Conil, Géraldine Guillaud, Jérôme Rangognio, Quentin Poinsignon, *Univ. Grenoble Alpes, CNRS, LGGE, F-38000 Grenoble, France*

The chemical characterization of PM2.5 was conducted at 5 rural background sites in France for the year 2013. Chemical analysis of weekly samples included the measurements of organic carbon (OC), elemental carbon (EC), ionic species, monosaccharide’s anhydrous and polyols. The sampling sites were spatially distributed to cover many parts of the French territory. The results obtained showed well identified temporal variations common to all the 5 sampling sites. During winter, concentrations of biomass burning markers such as levoglucosan, EC, and potassium are significantly increased indicating the strong impact of this source on the large scale. During summer, concentrations of the marine biogenic tracer methane sulfonic acid (MSA) and primary biogenic markers such as arabitol and mannitol were increased due to higher biological activities and photo-oxidation processes. Episodes of high sea salts as well as ammonium nitrate were mostly observed during winter, with variable synchronicity among sites. This study gives for the first time some comprehensive information on the chemical characterization of PM2.5 at rural background sites in France. The use of markers of biogenic aerosols such as MSA in continental areas such as France also brings new insights into the composition and sources influencing the atmospheric background.

11SA.1

Novel Approach for Estimating Light Duty Gasoline and Heavy Duty Diesel Mobile Source Impacts Based on Mobile Source Emissions and Fused Observation-CMAQ Data. XINXIN ZHAI, Mariel Friberg, Heather Holmes, Yongtao Hu, James Mulholland, Armistead Russell, *Georgia Institute of Technology*

The relationship between geo-coded patient information and ambient air quality is being investigated over Georgia in a spatially resolved health study. In Atlanta, epidemiologic results using central monitor data suggest associations of acute health effects and mobile source emissions. Here, we develop a procedure to provide spatially resolved daily light duty gasoline and heavy duty diesel mobile source PM2.5 impact estimates using concentration fields from a data fusion approach that combines observations and chemical transport model (CMAQ, 4 km and 12km resolutions) predictions to yield daily concentration fields of single pollutants for 2002-2010. Daily 24-hr average concentration fields of PM2.5 elemental carbon, CO, and NOx were generated for Georgia using ambient monitor data and CMAQ predictions. The fields were then used as input to an emission-based integrated mobile source indicator method (IMSI) developed by Pachon et al. (2012) to estimate mobile source impact fields at a 4 km resolution for Georgia. The IMSI uses EC, CO, and NOx concentrations and the ratio of spatially resolved mobile emissions to total emissions for each species to estimate mobile source impacts. The IMSI is applied to the Georgia domain by using emissions modeling results based on data from the National Emissions Inventory. The results are scaled using regression relationship of mobile PM2.5 emissions and CMB mobile impact estimates at 11 monitors in Georgia. The spatially-resolved daily source impact estimates across Georgia allow for the spatial analysis of health data to assess pollutant exposure risks of susceptible and vulnerable populations.

11SA.2

Determination of Local and Remote Sources Areas of PM_{10} In Northern France. Aude Pascaud, Esperanza Perdrix, LAURENT ALLEMAN, Stéphane Sauvage, Tiphaine Delaunay, *Mines Douai, SAGE, F-59508 Douai, France*

North-western Europe is submitted to frequent high-pollution PM_{10} episodes. The exceedance of the existing European ambient air quality standards for PM_{10} represents a serious health risk for populations living in such impacted areas. This is particularly the case for more than 4 million inhabitants living in the French Nord-Pas-de-Calais region, recurrently submitted to PM_{10} high concentration episodes. Despite the potential influence of various cofactors, the occurrence rates of respiratory and cardiovascular diseases are more elevated among this population compared to the French averages and suggest a possible link with chronic exposure to elevated atmospheric particulate pollution. In northern France, primary sources of particulate matter are related to a heavily industrial sector, dense urbanization, heavy traffic and intensive agriculture. As atmospheric particles can be transported over long-distances, PM_{10} mass concentrations measured by the Regional Network for Air Quality Monitoring (RNAQM) are due to both local and long-range sources.

In order to help regional policy-makers to take suitable and efficient measures against air pollution to protect public health, the challenging task of our work was to determine whether local sources of atmospheric particles are involved in these frequent exceedances of the PM_{10} daily limit value.

In a first step, we developed a robust methodology based on a hierarchical clustering to select monitoring stations with distinct distributions of the hourly averaged PM_{10} mass concentration measured by a dense continuous monitoring network (27 stations over 5 years, 2009-2012). Secondly, a multi-site concentration field analysis was applied to daily PM_{10} concentrations at selected stations. This statistical method consists in redistributing the concentrations of PM_{10} to air mass back trajectories in order to identify potential source areas influencing the receptor site. Additionally, we investigated the matches and discrepancies between these resulting potential source areas and the regional 3 km^2 grid-based emission inventory.

11SA.3

Influence of Industrial Activities on Concentrations and Chemical Composition of Ambient Aerosol Particles. ALEXANDRE SYLVESTRE, Aurelie Mizzi, Sebastien Mathiot, Boualem Mesbah, Julien Don, Gautier Revenko, Philippe Chamaret, Jean-Luc Jaffrezo, Henri Wortham, Nicolas Marchand, *Aix-Marseille Université, CNRS, LCE FRE 3416*

Located in the South East of France, Fos-sur-Mer is one of the largest industrial harbors in Europe. Multiple industrial activities are implanted; mostly oil refineries and steel plants. Previous studies showed the influence of this industrial area on the air quality over the city of Marseille (El Haddad et al, 2011), but no detailed chemical data of aerosol composition in this area were available so far.

Aerosols (PM2.5) were thus collected on a 24h basis during one year (May 2012 to August 2013) in three residential areas in the vicinity of the main industrial activities: Fos-sur-Mer, Port-St-Louis and Rognac. 432 samples were collected and 82 were selected for an in-deph chemical analysis (OC/EC, major ions, metals and organic markers). The selected samples encompass all the pollution typologies which can be observed in this area. Results show an increase of OC by a factor of 2 during PM10 episodes (daily average over 50µg/m3). High PAH concentrations (up to 100ng/m3) are observed during those episodes but also when daily limit of 50µg/m3 is not reached. High concentrations of trace metals were also observed with total concentration up to 2µg/m3 at Fos-sur-Mer and Port-St-Louis. Total metal concentrations are 5 times lower at Rognac on average. If at Fos-sur-Mer, PAH are associated with some metals like Se, Rb, Pb, Ni, Mo or Cs such correlations are less pronounced at Rognac and Port-St-Louis pointing out the influences of different sources. Furthermore, intense episodes of submicron particles (up to 300 000 cm-3) associated with SO2 are observed, highlighting the impact of industrial activities during days for which the exceedance limit is not reached (Dron et al., 2014). CMB and PMF analysis including both trace metals and organic markers will be presented in order to assess the total impact of industrial emissions in this very sensitive area.

11SA.4

Source Apportionment of PM10 in a North-Western Europe Regional Urban Background Site (Lens, France): Interest of the Use of Organic Tracers in a Positive Matrix Factorization Methodology. ANTOINE WAKED, Benjamin Golly, Olivier Favez, Laurent Alleman, Christine Piot, Tiphaine Delaunay, Emmanuel Verlinden, Jean-Luc Besombes, Jean-Luc Jaffrezo, Eva Léoz-Garziandia, *Univ. Grenoble Alpes, CNRS, LGGE, F-38000 Grenoble, France*

The sources of ambient particulate matter (PM10) collected over a one year period at an urban background site in Lens (France) were determined with Positive Matrix Factorization (US EPA PMF v3.0). Components measured and used in the PMF include the conventional species (soluble ionic species, trace elements, levoglucosan, elemental carbon (EC) and organic carbon (OC)) and also a wide range of organic tracers (sugars alcohols, hopanes, alkanes, sulfur containing PAH, PAH and methylPAH). A selective iteration process was followed for the qualification of the more robust and meaningful PMF solution. The contribution made by organic tracers on the PMF output increases the ability to identify and define some PM sources like primary biogenic emission and combustion source. By using this data set, PMF outputs showed that the main emission sources were (in a decreasing order of contribution): secondary inorganic aerosols, biomass burning, aged marine emissions, with probably predominant contribution of shipping activities, mineral dust, fresh sea salts, primary biogenic emissions, traffic emissions, and coal combustion. Significant temporal variations were observed for most of the identified sources. Biomass burning emissions were weak in summer but responsible for a much larger fraction of total OC in wintertime. In addition, the factor "coal combustion" also presents a very marked seasonal variability since it is negligible in summer and increases in winter. This factor has been identified and quantified using organic markers such as PAHs and sulfur containing PAHs. Conversely, primary biogenic emissions were negligible in winter but represent large fraction in summer. The latter result calls for more investigations of primary biogenic aerosols using source apportionment studies, which quite usually disregards this type of sources.

11SA.5

Comparison of the Sources of Organic Aerosol (OA) Using Aerosol Mass Spectrometry at Two Mediterranean Islands: Corsica and Mallorca. H. LANGLEY DEWITT, Jorge Pey, Stig Hellebust, Brice Temime-Roussel, Aurelie Mizzi, Dalia Salameh, Alexandre Sylvestre, Miriam Elser, N. Pérez, José Carlos Cerro, Jean-Luc Jaffrezo, Grisa Mocnik, Andre Prévôt, Nicolas Marchand, *Aix-Marseille Université, CNRS, LCE FRE 3416*

The atmosphere above the Mediterranean Sea is heavily impacted by a mix of continental aerosol sources as well as primary (e.g., sea salt) and secondary (e.g., sulfate, organic sulfate) marine aerosols. Although the region is typically calm with low surface biological activity, periods of high wind speeds and/or plankton blooms increase marine aerosol; anthropogenic emissions could also affect the formation rate of secondary marine aerosol by increasing available oxidants in the atmosphere. During the summer, the long hours of sunlight and dry weather accelerate the photochemical processing of aerosol and gas-phase species. As part of the Chemistry-Aerosol Mediterranean Experiment (ChArMEx) field campaign, two high-resolution aerosol mass spectrometers (HR-ToF-AMS), co-located with other instrumentation such as a PTR-ToF-MS, an Aethalometer/MAAP, a SMPS, and high-volume samplers (for off-line analysis of organic markers, trace metals, OC/EC, and major ions), were deployed on the islands of Corsica (on an isolated ridge 10 km from the sea) and Mallorca (seaside) to measure the chemical composition, concentration, and size of aerosol in the western Mediterranean basin. Back-trajectories of air masses, pollution outflow forecasts, MODIS satellite chlorophyll data, and dust aerosol maps were used for interpretations of aerosol sources, and the marine aerosol influence at different locations and heights (sea-level and above) was investigated. Higher levels of organic sulfur species, generally used as tracers for secondary marine aerosol, were observed at the Mallorca site compared to concentrations measured at the hilltop Corsica site. Recent improvements in the source apportionment approach based on AMS measurements made it possible to separate and identify different aerosol sources (e.g., SOA, marine aerosol). Separating anthropogenic from natural aerosol influences in this heavily human-impacted environment will increase our understanding of the interaction of anthropogenic aerosol, gases, and oxidants with naturally occurring aerosol and gas-phase emissions in these marine environments.

12BA.1

Exposure of Aerosolized Bacillus Spores to Combustion Products of Novel Reactive Biocidal Materials: Kinetics of Inactivation Process.

SERGEY A. GRINSHPUN, Michael Yermakov, Reshmi Indugula, Atin Adhikari, Tiina Reponen, Edward Dreizin, Mirko Schoenitz, *University of Cincinnati*

Targeting a bio-weapon facility for destruction may cause highly pathogenic bio-agents to release into the atmosphere. Some bio-agents (e.g., Bacillus anthracis spores) can remain viable even after exposure to heat in a combustion/explosion setting. As part of the bio-agent defeat program, novel halogen-containing reactive materials are being developed to inactivate stress-resistant viable microorganisms during their release. In this study, we tested two such materials, $Al{\bullet}I_2$ and $Al{\bullet}B{\bullet}I_2$, with respect to the biocidal capability of their combustion products against two well-established surrogates of Bacillus anthracis: Bacillus subtilis var. niger (aka Bacillus atrophaeus or BG spores) and Bacillus thuringiensis kurstaki (Btk spores). A state-of-the-art experimental facility was used to investigate the survival of aerosolized spores. The spores were dispersed in dry airflow and exposed to the tested combustion products in a temperature-controlled environment during different time periods ranging from ~0.12 to ~2.0 s. For both species and both iodinated materials, the bioaerosol inactivation factor increased exponentially with the exposure time. The inactivation effect was more pronounced for Btk than BG spores suggesting that the former are more sensitive to the stress produced by the release of iodine during combustion of $Al{\bullet}I_2$ and $Al{\bullet}B{\bullet}I_2$. It was demonstrated that the main reason of inactivation of aerosolized spores observed in our tests was their interaction with iodine in the air flow rather than exposure to heat. The data generated in this study help understand the kinetics of the spore inactivation occurring due to exposure to combustion products of halogen-containing reactive materials.

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12BA.2

An Aerosol Dry Deposition System for Quantifying the Retention of Bacillus Spores on HVAC Filters.

ANNE MARIE ERLER, Staci Kane, Matthias Frank, George R. Farquar, Lewis Wogan, *Lawrence Livermore National Laboratory*

Following a biological incident, surface samples will be taken to characterize the scope of the public health risk. Although many strategies exist for sample collection, interest has grown to utilize Heating Ventilation and Air Conditioning (HVAC) filters as a sample type due to the filter's ability to concentrate aerosolized particles on its impact surface. Typical HVAC filter media installed in public ventilation systems are rated by the American Society of Heating, Refrigeration, and Air Conditioning Engineers (ASHRAE) for the capture of only crude debris greater than 3 microns in diameter. Little testing has occurred on this filter media to confirm whether it could be utilized to recover smaller particles that may be present after a biological event. The initial physical state of a surface-deposited material (e.g. wet vs. dry) will impact the surface adhesion and re-aerosolization properties of the materials. To more accurately simulate real-world deposition for spore-forming agents, Lawrence Livermore National Laboratory (LLNL) has developed a flow-through Dry Deposition System (DDS) that was used to deposit aerosolized spores onto sectioned HVAC filters. One of the advantages of the LLNL DDS is the ability to provide highly accurate, absolute numbers for spore deposition since quantitative particle measurements are taken upstream and downstream of the filter using two cross-calibrated Aerodynamic Particle Sizer (APS) instruments. Additionally, the LLNL DDS utilizes low aerosol flow rate to deposit spores on the filter's impact surface and can produce aerosolized spores at a wide range of desired concentrations. Low-level spore deposition was tested by depositing Bacillus spores on two different types of HVAC filters. The spores were directly extracted from the HVAC materials and recoveries were determined by culture analyses. Recoveries were also compared to filters inoculated by air-dried liquid deposition in order to determine if differences existed between the two deposition methods.

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12BA.3

Resuspension of Spores from Urban Surfaces. JEROME GILBERRY, Jonathan Thornburg, Laurie Brixey, Alfred Eisner, Russell Wiener, Marshall Gray, *RTI International*

The SPORE program is developing a quantitative assessment of the risk of public health exposure from the resuspension of B. anthracis spores in an outdoor, urban environment. One aim is to determine the suitability of the biological simulant Btk as a surrogate for BaA in terms of resuspension from surfaces, represented in this research by coupons made of a variety of outdoor materials. The end goal is to statistically compare the two sets of data and develop a model to predict resuspension.

Coupons of outdoor surfaces were loaded with spores using custom-built deposition chambers. The dosed coupons were inserted into a small resuspension wind tunnel where a slotted nozzle generated the force required to resuspend the spores. Aerosolized spores were collected on filters that were extracted, plated, and cultured for enumeration. The experimental variables were spore type, spore preparation, jet velocity, surface type, and roughness level of each surface type. Detailed characterization of the test surfaces enabled development of a non-dimensional resuspension model.

The fraction of spores resuspended in this study agrees with previous data. Resuspension fractions varied from 1E-07 to 1E-01, depending on the spore preparation, jet velocity, and test surface characteristics. Measured Btk and BaA resuspension fractions for each spore preparation were statistically similar ($p\text{-value} > 0.4$). This finding allowed the Btk and BaA data to be combined for the development of the non-dimensional model. The surface energy of adhesion, the air jet velocity, and the coupon features that determined the total surface area and surface roughness were statistically significant model parameters. The modeled and experimental resuspension fractions were statistically similar, with an overall R^2 greater than 0.75.

The experimental methods and modeling approach developed in this effort can be extended to additional outdoor and indoor surfaces to further our understanding of the potential public health risks from anthrax resuspension.

12BA.4

Improved Threat Characterization Using Next Generation Sequencing. ZAHRA CHAUDHRY, Peter Thielen, Verratti Kathleen, Christopher Bradburne, *JHU APL*

Most biosurveillance strategies and programs use PCR to detect threat agents. This technology is hampered by false positives and false negatives. Additionally, a positive hit provides no additional information such as whether or not the hit is actually a threat or within the noise of the background, if the threat is synthetic, or if it is a new or emerging pathogen. This study seeks to address these questions beyond the basic confirmation given by PCR, by collecting environmental aerosols and interrogating them using next generation sequencing, sensitive sample preparation techniques, and focused database development in order to fully characterize an aerosol sample.

Atmospheric aerosol samples were collected on the JHU/APL campus in Laurel, MD for 14 consecutive days to mimic a biosurvellance program. One sample day was spiked with a biosimulant to simulate a hypothetical threat event. The DNA was extracted from all the samples and purified using several methods: Powersoil, Boreal Aurora, LifeTech silica bead kit, and the Ampure bead kit. Two methods were used to aid in threat characterization: a hybridization-based background subtraction, and an informatics-based background subtraction. In the first method, the spiked sample is enriched with the background biome from a sample day with a similar back-trajectory and the combined sample is sequenced. In the second method, the spiked sample and background sample are sequenced separately, and the background data is informatically subtracted from the hypothetical data set. Results of the multiple purification methods and the characterization methods will be presented.

This study culminates in the creation of four databases: one for environmental background sequences, one for select agent reference strains, one for more focused threat sequences that are found in select agents, and one for synthetic sequences and commercial components that may indicate an engineered organism.

12BA.5

DHS Biological Hazard Assessment Research: Characterizing Agents to Inform Risk: A Focus on Aerosols. MATTHEW MOE, Lloyd Hough, Scott White, *Department of Homeland Security*

The 2007 National Strategy for Homeland Security notes that the nation must apply a risk-based framework across all homeland security efforts to identify and assess potential hazards, determine what levels of relative risk are acceptable, and prioritize and allocate resources among homeland security partners to, among other things, respond to and recover from Chemical, Biological, Radiological, or Nuclear (CBRN) incidents. To accomplish this, the U.S. Department of Homeland Security (DHS) employs a suite of risk assessments based on computational models to evaluate a myriad of CBRN scenarios, the results of which inform the allocation of resources to prepare for and respond to such an event. The fidelity of the computational models depend significantly on the quantitative values that are used to describe the characteristics considered. While the majority of these values are derived from published scientific literature, quantitative values describing essential and impactful characteristics of many biological agents such as source terms, decay rates, and infectious doses, remain elusive. The DHS Biological Threat Characterization Program (BTCP) supports these modeling efforts by performing research to allow better models to be developed, and provide more accurate estimates for these and other parameters. An overview of processes used by DHS to identify opportunities for refinement through research, the review and selection process for individual projects, and the strategic research directions anticipated for the aerobiology portfolio will be provided.

12CA.1

Experimental Studies of Particle Bounce: Comparison of Secondary Organic Material (SOM) from Harvard Environmental Chamber and Field Studies in Amazonia. ADAM BATEMAN, Pengfei Liu, Yue Zhang, Zhaoheng Gong, Bruno Bianchi Sato, Glauber Cirino, Joel Brito, Rodrigo A. F. Souza, Antonio O. Manzi, Paulo Artaxo, 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 and material properties. It has been suggested that particulate material 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 particulate matter as a function of RH.

12CA.2

Interpretation of Regression Parameters for Quantification of Organic Aerosol Mass Components with Infrared Transmission Spectra. SATOSHI TAKAHAMA, Ann Dillner, *Ecole Polytechnique Federale de Lausanne, Switzerland*

In this work, we present a comparison of two regression approaches for quantitative analysis of vibrational spectra for laboratory-generated aerosols and particulate matter collected on IMPROVE network filters. Infrared spectroscopy provides a method for non-destructively analyzing the organic functional group abundance and total organic aerosol mass (OM) on off-line filters with high mass recovery (Russell, 2003).

The first method for quantification considered, explicit band-fitting (Takahama et al., 2013), proceeds by sequential application of non-linear least squares regression to apportion spectrum extinction to substrate (PTFE) interference and molecular bond absorption according to separate constraints provided by laboratory standards. The second method, partial least squares regression (Coury and Dillner, 2008; Ruthenburg et al., 2014), trains a set of regression parameters on laboratory standard mixtures by projection to and rotation of latent factors to maximize predictive power. We will discuss the relative merits each method and also present a mechanistic interpretation of regression parameters generated mathematically from the partial least squares calibration, and use this interpretation to additionally assess our capability for prediction of thermal optical reflectance OC, EC, and TC from infrared absorption spectra.

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12CA.3

Atmospheric Aging of Fullerene Nanoparticles. DHRUV MITROO, Peter Colletti, Michael Walker, Jiewei Wu, John Fortner, Brent Williams, *Washington University in St. Louis*

Rapid growth of industrial scale nanomaterial production underpins rising concerns regarding the eventual fate and possible inadvertent impacts of these materials on the health and function of natural systems. While there have been a number of studies regarding the environmental chemistry of engineered nanomaterials in water and soils, the role of atmospheric processes and chemistries of such materials has not been thoroughly investigated. Carbon based nanoscale materials, in particular fullerenes and carbon nanotubes, have been widely proposed for a variety of applications and are now being produced at the industrial scale. An understanding of how such materials behave once released in the atmosphere (or exposed to atmospheric processes) is critical for accurate risk assessments and effective management of waste disposal practices and release scenarios. To date, studies regarding fullerene environmental fate, transport, and effects have centered on aqueous available forms, either as aqueous stabilized nanoscale colloids (termed nC_{60} or $nanoC_{60}$) or with pre-characterized, water-soluble derivatives (such as hydroxylated fullerenes or other commercially available materials). While insightful, the vast majority of these studies fail to incorporate the significant potential for a number of naturally occurring atmospheric-based (photo)reaction scenarios, which could fundamentally change fullerene physicochemical behavior and environmental impact (i.e. altering aggregate stability, monomer solubility, and effective toxicity).

To systematically evaluate atmospheric nC_{60} (photo)reactions, we developed a setup for introducing an aerosol stream of pure nC_{60} into the Potential Aerosol Mass (PAM) reactor for oxidative aging studies ranging from OH-dominated to O_3-dominated regimes under UV irradiation. Chemical and physical identification of nC_{60} and its oxidation reaction products, as well as preliminary kinetics, are presented for various model atmospheric aging conditions.

12CA.4

Phase Separation Effects on the Optical Properties of Mixed Brown Carbon/Ammonium Sulfate Aerosol. JAMES RADNEY, Christopher Zangmeister, *National Institute of Standards and Technology*

The role of brown carbon aerosols (BrC) in the atmosphere has been a subject of strong interest in recent years. In the atmosphere, BrC is rarely pure but instead exists as a complex mixture of multiple species; the most common of which is ammonium sulfate (AS). Here, we demonstrate that the mass mixing ratio of BrC and AS significantly affects the optical properties of the resultant particle compared to what would be predicted through simple mixing or core-shell models. Relative to pure AS, small additions of BrC decrease the observed extinction cross section (Cext) by up to 20%. Above a critical mass ratio of BrC, Cext spikes to be higher than that of pure AS; further increases in BrC content further increase Cext. This decrease and subsequent increase in extinction with BrC is a direct result of changes in scattering as absorption increases monotonically with BrC content. We posit that air inclusions and are present at the phase interface of BrC and AS, in a manner similar to mixed crystals of different lattice structures, and are responsible for the observed trends.

12CA.5

Soot Aggregate Restructuring due to Coatings of Secondary Organic Aerosol from Aromatic Precursors. ELIJAH G. SCHNITZLER, Jason S. Olfert, Wolfgang Jaeger, *University of Alberta*

Soot aggregates are emitted from many sources, such as biomass burning and diesel engines, and have a significant warming effect on climate. The extent of this effect depends on the optical and morphological properties of the aggregates, and these properties evolve during the lifetime of the aggregates. For example, aggregates can be coated by neat liquids, such as sulfuric acid, or complex mixtures of compounds, such as the array of semi-volatile oxidation products present in secondary organic aerosol (SOA). Such coatings, through surface tension effects, tend to restructure and, more specifically, compact the aggregates. Past studies have characterized aggregate restructuring due to neat liquids, including sulfuric acid and oleic acid, and mixtures, including SOA derived from alpha-pinene, toluene, and isoprene. In this study, we further characterized aggregate restructuring due to SOA derived from aromatic precursors, including benzene, toluene, para-xylene, and ethylbenzene. Two sets of experiments were carried out. In the first set, the maximum change in aggregate diameter due to SOA coatings was measured for initially 100, 150, 200, and 250 nm aggregates, using a tandem differential mobility analyzer. Briefly, soot aggregates were dried, denuded, neutralized, classified, and injected into a smog chamber; an aromatic SOA precursor and hydrogen peroxide were injected into the chamber; and the chamber was irradiated with black lights. In the second set of experiments, the coating mass was measured using a centrifugal particle mass analyzer, and the coating mass dependence of aggregate restructuring was determined for coatings derived from each SOA precursor.

12CO.1
Emissions of Intermediate-volatility Organic Compounds from On-road Vehicles. YUNLIANG ZHAO, Ngoc Nguyen, Albert A. Presto, Andrew May, Christopher Hennigan, Allen Robinson, *Carnegie Mellon University*

Intermediate-volatility organic compounds (IVOCs) emitted from primary sources have been indicated to contribute significantly to secondary organic aerosol formation by chamber experiments, field measurements and SOA models. However, the importance of IVOCs in the atmosphere is poorly understood due to the lack of measurements of IVOCs in both the atmosphere and emissions. In this study, emission factors and volatility distribution of IVOCs were characterized in tailpipe emissions from in-use, on-road vehicles at the California Air Resources Board Haag-Smit and Heavy-Duty Engine Testing Laboratories. The test fleet was composed of 47 light duty gasoline vehicles, 5 diesel trucks. Control technologies can significantly reduce emissions of IVOCs. The emission factors of IVOCs are found to strongly correlated to emissions factors of non-methane organic gases (NMOG) and primary organic aerosol (POA). The strong correlation indicates that IVOC emissions can be well predicted based data of NMOG and POA in the emission inventory. The volatility distributions of IVOCs emitted from on-road gasoline vehicles are different from those from diesel vehicles, but they exhibit a consistent profile for both on-road gasoline and diesel vehicles, respectively. Based on on-road fuel usage, diesel trucks dominate the IVOC emissions from on-road vehicles. These laboratory measurements are also compared with the measurements made in a traffic tunnel, and strong consistency is found between them.

12CO.2
An Investigation of Soot Oxidation-Induced Fragmentation in a Two-Stage Burner. HOSSEIN GHIASSI, Isabel C. Jaramillo, JoAnn S. Lighty, *University of Utah*

Soot particles are destroyed in flames through oxidation by OH and O2. Under high O2 conditions, our results suggest that fragmentation of soot aggregates occurs. Due to an increase in surface area, this would result in an increase of oxidation. Soot fragmentation studies were carried out experimentally in a two-stage burner, where soot was produced in a first-stage premixed burner, while in a second stage, the soot was oxidized under slightly-rich conditions. Temperature, particle size distributions (PSD), and measurements of specific gas-phase compounds were performed to characterize the flame. Fragmentation was reflected by an observable increase in the number concentration of ultrafine particles. Different oxidizer gas mixture, oxygen/helium, oxygen/argon, and oxygen/nitrogen, were used to investigate how these gas environments affect the fragmentation. Fragmentation has been hypothesized to be caused by oxygen diffusion into the particle or bridges between particles, causing it to break apart. The diffusion of oxygen varies in these different binary mixtures. It was observed that soot fragmentation occurred in the oxidation region to differing extents related to the gas mixture. The results confirmed the importance of oxygen diffusion in the particle breakup.

12CO.3

Aerosol Measurements in Solid Rocket Propellant Fire Plumes. FRED GELBARD, Daniel Lucero, Brandon Servantes, Andrew Lennon, Karen Siegrist, Mike Thomas, Adam Willitsford, *Sandia National Laboratories*

Much aerosol is generated by a burning solid rocket propellant that is released into the atmosphere. Under accident conditions in which the rocket fails, the burning propellant may land on top of hazardous materials. The heat from the burning propellant may then vaporize the hazardous material which can subsequently homogenously nucleate and/or condense on the propellant aerosol. Because aerosol particle size greatly influences risk assessment of the hazardous material, data on the size distribution of the resulting aerosol are essential.

In this work we report aerosol data for large blocks of burning solid rocket propellant. Measurements of aerosol generated by the burning propellant suspended 2.5 to 3.8 cm. above concrete and coated steel are presented. By combining cascade impactor particle collection and scanning electron micrographs we find that the data are explained by aluminum from the propellant burning to produce mostly 50 nm diameter alumina primary particles, with a smaller mass fraction of the aerosol consisting of micrometer size particles. The 50 nm diameter alumina particles provide most of the surface area for vapor condensation, and these particles agglomerate rapidly to form particles 0.4 – 1.2 µm in aerodynamic diameter within 2.5 meters from the bottom surface.

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12CO.4

Measurements of High Spatial Resolution of Ultrafine and Coarse Aerosol Particles in Industrial Plume. JAN HOVORKA, Veronika Docekalova, Miroslav Klán, Filip Kobrzek, Petr Marecek, *Charles University in Prague*

Industrial plumes pose critical parameter to the air quality of surrounding environment. However, dispersion of industrial plume is rather modeled than measured at nowadays, which limits air pollution source apportionment based on earth-bound measurements at single receptor. To partially overcome such limitation, we conducted measurements of highly resolved horizontal and vertical profiling of aerosol particles in an industrial plume evolved in proximity to residential area.

Unmanned, remotely controlled airship with GPS 10Hz position tracking, electrically powered with propulsion vectoring which allows average cruising airspeed of 4 ms^{-1}, was used. The airship was equipped with specially designed gondola carrying temperature/relative humidity sensor and three aerosol monitors connected to 50 cm long pre-heated inlet. The monitors acquired 1Hz data on TSP of PM_{10}, $PM_{2.5}$ and PM_1 and number concentration of fine and ultrafine particles. Two overnight and one early morning flights were conducted above large heavy-industry complex and residential area nearby. Airborne measurements revealed limited horizontal and upward vertical dispersion but efficient downward vertical plume dispersion. Results of airborne measurements concur with ground-based measurements at the air monitoring station situated in residential area nearby. There were recorded several episodes of remarkably elevated SO_2 and CO concentrations concurrently with particle number size distribution with count median diameter at about 40 nm and particle number concentration reaching 10^5 cm^{-3}. Bearing on mind absence of strong local heating source or dense traffic near the station, industrial plume hitting the ground is relevant explanation of such elevated pollutant levels.

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12CO.5

Filtration of Ultrafine Dust Emitted by Biomass Combustion with a Baghouse Filter Using Precoat Materials. SASCHA SCHILLER, Hans-Joachim Schmid, *University of Paderborn, Germany*

To comply with the legal requirements in Germany a baghouse filter has been developed. It combines excellent separation efficiency with convenience in operation for wood-fired heaters (e.g. pellet heaters). In order to prevent clogging of the filter cloth by sticky and ultrafine particles, it is necessary to use a precoat. For this purpose different precoat materials have been analyzed (e.g. limestone powder). With this very efficient technology, extremely high separation efficiencies > 99 % could be reached in a long-term stable process. The costs of the material are negligible when it comes to the calculation of the needed mass of a private household. However, due to the large-scale quantities in the industrial sector the reuse of the precoat material can generate significant savings. Therefor, different tests were performed to reuse and mix the precoat materials several times. During these tests the filtration behavior was detected by measuring the total collection efficiency, the grade efficiency, and the pressure drop curve of the filter. In addition to that different characteristics (porosity, bulk flow properties, particle size distribution) of the precoat materials have been analyzed after every step of reusing or mixing to detect the influence of the reuse. After that the experiences made with the laboratory build-up (pellet heater, nominal output: 15kW) were used to do a scale-up for a real application (pellet heater, nominal output: 320kW). Because of the operating method of the two plants (single-line-dedusting-mode) the resulting pressure drop curves show an inhomogeneous filtration behavior. This behavior can be described with a known model from the literature. To get a better understanding of the agglomeration and the adhesion of the ultrafine dust particles and the precoat particles optical test were made with a scanning electron microscope (SEM) after separating single particles.

12IM.1

Design, Testing, and Validation of a Calibration Chamber for Particles. Wendy Merkley, KORI MOORE, Randy Martin, Michael Wojcik, *Utah State University*

A multi-port fixture has been developed to provide a controlled, uniform measurement environment for the cross calibration of particle point sensors. The system includes an inlet HEPA filter, a port for test particle introduction, four sampling ports in a plane perpendicular to the flow, an exhaust HEPA filter, and a vacuum system. The chamber consists of 10 cm diameter stainless steel tubing sections with custom ports for aerosol introduction, aerosol sampling, and flow measurement. Flow disturbances upstream of the sampling plane were designed to be sufficiently distant to achieve laminar flow before reaching the sampling plane. Flow uniformity across the plenum cross section just upstream of the sampling plane was verified using a hot wire anemometer prior to each sample period. Isokinetic sampling over a range of common flow rates was achieved through design of dedicated sampling nozzles. The uniformity of particle distribution across the sampling plane was assessed through measurements at multiple positions on the sampling plane using optical particle counters (OPCs). A powder with a polydisperse size distribution was utilized in all particle uniformity tests. Inter-OPC calibrations were derived using collocated ambient samples and applied to all measurements to minimize instrument bias. The results of this test demonstrated no apparent bias in particle distribution. Therefore, this plenum system may be used to inter-compare and calibrate aerosol sensing instrumentation and/or to characterize the microphysical properties of a test aerosol using various measurement techniques.

12IM.2

A Novel Instrument for Measuring Broadband Optical Properties of PM Deposited on Filters. KEITH BEIN, Charles McDade, *UC Davis*

A new instrument called BITS (Broadband Integrating Transmittance/Reflectance Spectrophotometer) has been designed and constructed to allow light absorption and fluorescence measurements to be made using broadband radiation spanning the ultraviolet to near-infrared spectral range. The broadband light source has an output spanning 190 to 1700 nm, which is accomplished by the combination of a deuterium and tungsten halogen lamp. Light from the source is directed through a collimating, filtering and focusing assembly and then onto the PM deposit. An integrating sphere captures light reflected, or back emitted, from the deposit, and both the reflected light and the light transmitted through the deposit, or forward emitted, are measured by a single CCD detector via novel collection optics assemblies and a custom bifurcated fiber optics bundle. Absorbance is determined from the reflected and transmitted measurements. Fluorescence is measured by filtering the visible and near IR radiation from the incident light beam and using the CCD detector to measure any emitted visible radiation. Theoretical considerations and the design of BITS, as well as calibration procedures and first results from measurements on filters collected by the IMPROVE network, will be presented.

12IM.3

Measuring PM and Related Air Pollutants Using Low-Cost Sensors. KAROLINE JOHNSON, Michael Bergin, Armistead Russell, Gayle Hagler, *Georgia Institute of Technology*

Emerging air quality sensors may play a key role in better characterizing levels of air pollution in a variety of settings including near sources and in communities. There are a wide range of low-cost (< $500 US) sensors on the market, but few have been characterized. This new generation of inexpensive sensors would allow larger fleets of monitors to be deployed to better study the spatial and temporal variability of pollutant concentrations if they prove to be accurate and durable. The small size and light weight of these sensors provides the opportunity for wearable applications that could play a key role in future estimates of human health impacts of PM and other pollutants. The sensors can also be deployed on various mobile and stationary measurement platforms to better characterize pollutant sources and source regions.

We will present measurements from an assortment of sensors, costing $20-$700, that have been used to measure air pollution in the US, India, and China with a focus on estimating PM concentrations. The pollutant levels in these three countries ranges from low concentrations seen in the US (up to approximately 20 ug m-3) to much higher concentrations measured in India and China (up to approximately 300 ug m-3). Based on the evaluations in these very different pollutant settings, the optimal concentration ranges of these sensors have been determined. Used in conjunction with data from a carbon dioxide sensor, emissions factors were estimated in some of the locations. In addition, temperature and humidity sensors can be used to calculate corrections for the sensors. These sensors have been evaluated against reference methods with promising results.

12IM.4

Performance Evaluation of a Low-Cost, Real-Time Community Air Monitoring Station. WAN JIAO, Gayle Hagler, Ron Williams, Bobby Sharpe, Joann Rice, Lewis Weinstock, *ORD-US EPA, RTP, NC*

The US EPA's Village Green Project (VGP) is an example of using innovative technology to enable community-level low-cost real-time air pollution measurements. The VGP is an air monitoring system configured as a park bench located outside of a public library in Durham, NC. It contains air monitoring and meteorological instruments that measure PM2.5 (Thermo pDR-1500), ozone (2B Technologies), temperature, relative humidity, wind speed, and direction. These instruments are integrated together using an Arduino microcontroller with real-time data streamed wirelessly using an Ethernet gateway to a cloud database once every minute. The data are then made available online to the public after automated quality checks. The entire station utilizes solar energy with battery backup to be self-powered and totally off the grid. In the first six months of field sampling since June 2013, the station has successfully collected over 3600 hours of PM2.5 concentration data, with fewer than 10 days of down time due to power loss. To evaluate the VGP sensor system performance, data collected were summarized and compared with measurements made at nearby air monitoring stations operating federal equivalent methods (FEM) for PM2.5 and ozone, with comparisons at hourly and 5-minute average time resolutions. In addition, the use of solar energy to support VGP operation was also assessed. The hourly average VGP PM2.5 concentrations generally co-varied with the nearest benchmark FEM site during sampling period, with a slope of the regression line of 0.96 and r2 of 0.74. Comparison results indicated that design features incorporated in the VGP are promising to enhance air quality and exposure monitoring capacities in community settings, which provide additional air quality data to supplement regulatory monitoring.

12IM.5

Measurement System for the Simultaneous and Continuous Determination of PM-fractions 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. Numerous other articles in the press recently underline that air pollution is one of the major dangers to human health worldwide.

We will present a new measurement system that can measure the number concentration and size distribution of airborne particles from 8 nanometer to 40 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 facilitates source apportionment.

12RA.1

Livestock Ammonia Emissions: From Process-based Farm Emissions Models to a New National Inventory for Beef, Swine, and Poultry in the United States. ALYSSA MCQUILLING, Peter Adams, *Carnegie Mellon University*

Ammonia is a critical air pollutant, and its emissions from livestock production have been largely exempt from regulation (Centner et al. 2010; Smith et al. 2013). Before regulations can be imposed, ammonia emissions from livestock, which depend on manure management, nutrition, and meteorology, must be better understood. Based on the earlier work of Pinder et al. (2004), process-based farm emission models (FEMs) have been developed for beef, swine, and poultry emissions, and constrained by literature data. The FEMs allow us to capture seasonal and regional variability in ammonia emissions due to varying climate and manure management practices. The FEM performance was better for emissions sources with better input information and for enclosed sources, compared to open sources like feedlots or lagoons (r-squared value for swine housing is 0.67, while feedlot r-squared is 0.21-0.36). Recent data from the National Air Emissions Monitoring study (NAEMS) offers independent data to help evaluate and improve farm-level models. Comparison of emissions predictions from FEM models versus the NAEMS measurements show that the FEMs often under-predict emissions at colder temperatures, but in some cases, NAEMS measurements are noticeably different than prior measurements in the literature (NAEMS emissions are up to 10-15x higher than literature for swine lagoons). Model re-tuning is ongoing to improve agreement among the literature, NAEMS and model results. The next step toward producing a process-based ammonia emission inventory is to use a statistical model to predict the distribution of manure management practices for each county in the country and for each animal type—beef, swine, and poultry. By combining the results from the FEMs and the national practices, we produce inventories for major livestock types that capture seasonal and regional variability in ammonia emissions. Data regarding national practices are from the National Animal Health Monitoring Survey and the USDA National Agricultural Census.

12RA.2

Response of Total NH_3 to Reductions in Atmospheric Levels of SO_2 and NO_x: An Analysis of Data from SEARCH. RICK SAYLOR, LaToya Myles, Eric Edgerton, *NOAA Air Resources Laboratory*

Ammonia (NH_3) emissions constitute a major source of reactive nitrogen to the atmosphere and NH_3 is recognized as an important link in the global nitrogen cycle. Neutralization of sulfuric (H_2SO_4) and nitric (HNO_3) acids in the atmosphere by NH_3 forms ammonium (NH_4^+) salts that comprise a significant fraction of the total mass of fine particles in many areas. Due to the rapid equilibration of NH_3 with ambient ammonium nitrate (NH_4NO_3) aerosol particles measurements of gas-phase NH_3 alone are not sufficient to fully characterize its nature. To do so requires simultaneous measurements of both gas-phase NH_3 and particle-phase NH_4^+, preferably at similar temporal resolutions. Nine years (2004-2012) of 24-hr-integrated total NH_3 (gaseous NH_3 + $PM_{2.5}$ NH_4^+) data from the Southeastern Aerosol Research and Characterization study (SEARCH) network are analyzed and presented in this work and trends in total NH_3, the ratio of gas-phase to particle-phase NH_3 and particle acidity are examined in light of the implementation of air quality regulations over recent decades which have reduced concentrations of SO_2 and NO_x, precursors to H_2SO_4 and HNO_3 respectively, in the southeast U. S. atmosphere. Implications of the trend findings are explored.

12RA.3

Trends in Concentrations of Atmospheric Gaseous and Particulate Species at Look Rock as Related to Primary Emissions Reductions.

STEPHANIE SHAW, Roger Tanner, Solomon Bairai, Stephen Mueller, *Tennessee Valley Authority*

Air quality measurements at Look Rock, TN, (LR) begun in 1980, were later expanded to an NPS-operated IMPROVE network station, and expanded again by TVA (1999-2007) to examine the effects of EGU emissions reductions of SO2 and NOx on air quality at the station. LR was designated a non-urban NCORE site in 2010, and continuous monitoring of aerosol mass, sulfate, black carbon and primary and secondary gases, supplemented by enhanced measurements during a series of intensive research studies, have produced a uniquely comprehensive air quality database on background levels of species relevant to NAAQS for ozone and particulate matter for a high-altitude site in the southeastern USA. Analysis of temporal trends (1999-2013) has been conducted at the site in collaboration with SAS activities at LR and other southeastern U.S. locations.

Key findings from these trend studies include the observation that primary pollutant levels have consistently tracked emissions reductions from EGUs and other primary sources in the region, but reductions in secondary pollutants such as particulate sulfate and, specifically, ozone have been less than proportional. Organic carbonaceous material (OM) remains a major contributor to fine particulate mass at the site, as confirmed by ACMS measurements at the site in 2013. A large portion (65-85%) of OM derives from modern carbon, based on 14C measurements. Important parameters affecting ozone levels, fine mass, and visibility also include the specific diurnal meteorology at this ridge-top site, its location in a largely mixed-deciduous forest, and the presence of primary sources of precursors at distances of 50-500 km from the site in all directions.

12RA.4

The Role of Nucleation in Controlling Aerosol Size Distributions: Analysis of 10 Months of Recent Aerosol Size Distributions at a Non-Forested Agricultural Location.

ROBERT BULLARD, Ashish Singh, Charles Stanier, *University of Iowa*

The formation and growth of new particles in the atmosphere are important phenomena that have an impact on global climate. Long-term records of aerosol size distributions are used to understand nucleation and its precursors. Urban environments and forested rural environments are well studied compared to rural agricultural environments. This study examines 10 months of aerosol size distribution measurements at the Bondville environmental and atmospheric research site (BEARS) in Bondville, IL. BEARS is located within a non-forested rural continental environment. Potential precursors to nucleation include locally emitted and regional sulfur dioxide, as well as ammonia emissions from agricultural operations.

Past work on long-term and seasonal analysis of particle number concentrations at BEARS revealed the highest average number concentrations in the spring and fall. Long-term decreases in SO_2 concentration (1988 – 2012) in all seasons can account for decreases in particle number concentrations (1994 – 2012) in most seasons, but particle number concentrations are increasing or constant in the late spring, where particle concentrations are higher than all other seasons.

These past results are combined with aerosol size distribution data from July 2013 – May 2014 are used to a) identify relationships between elevated number concentrations and nucleation, b) identify nucleation event frequency and intensity for all seasons, and c) utilize available gas-phase precursor (sulfates, nitrates, and ammonium) data and solar intensity (UV-B) and cloud cover data at BEARS to determine factors contributing to nucleation and growth. This will provide information on nucleation in this agricultural setting, which may be typical of other agricultural locations in the Midwest.

Preliminary data shows frequency and intensity of nucleation events decreasing with colder temperatures. Peak diurnal patterns are well correlated with existing ground-based CPC, with peak number concentrations occurring in the mid morning and extending to the late afternoon.

12RA.5

Volatility Measurement of Ultrafine Particles in the Midwestern United States: Field Measurement from Bondville, IL. ASHISH SINGH, Robert Bullard, Matthew Johnson, Charles Stanier, *University of Iowa*

Volatility measurement of ultrafine particles (10-100 nm) provides important information about particle growth pathways and thermodynamic properties, and can assist in constraining chemical composition. Bondville, Illinois is a Midwestern United States site where particle nucleation and extensive secondary sulfate and organic aerosol formation has been reported. Furthermore, the volatility of UFPs using V-TDMA has not been reported for many sites in the Midwestern U.S. Consequently, the relative contributions of organic and inorganic constituents to particle growth in the UFP size ranges, and the presence or absence of low-volatile particle cores in 10-100 nm particles, has not been determined.

This study will present results for UFP volatility from preliminary measurements during summer 2013 and spring 2014 sampling campaign in Bondville, IL. Analysis of sub-sample of days showed that nuclei mode particles were mainly from two sources: regional nucleation and localized plume enhanced in SO2. Comparison of volatility across these two conditions indicated similar volume fraction profiles from 100 to 2500 C, with the presence of low-volatile cores during regional nucleation only. These results will be extended to include all sampled data, diurnal, and seasonal variability. Data analysis will be conducted fitting the volatility profile to dynamic and equilibrium volatility basis set profiles for comparison to other studies and to model input profiles. The presence of low volatile particle cores will be determined as a function of co-pollutants and air mass history. Additionally, the mixing state of nuclei and Aitken mode aerosol will be investigated using size resolved volatility at 80-250 0 C. V-TDMA results will be interpreted with respect to pollutant trace gases and particulate times series (e.g. CO, SO2 and NOX, NH3, and BC).

12SA.1

Quantifying Variability in Molecular Markers Used for Vehicle Source Profiles: Effects on PM Source Apportionment Results. ALBERT A. PRESTO, Andrew Hix, Christopher Hennigan, Allen Robinson, *Carnegie Mellon University*

PM source apportionment results obtained with the chemical mass balance (CMB) model can be highly sensitive to the choice of source profiles. Source profiles for gasoline and diesel vehicle emissions have often been constructed from relatively small vehicle fleets (N<10), and in some cases published source profiles represent the emissions of a single vehicle. Source apportionment studies cope with the variety of available source profiles by considering averages of published profiles, or by using graphical tools such as ratio/ratio plots to select source profiles that bound ambient data. Additionally, many published source profiles are dated, and may not be representative of emissions from modern vehicles. For example, the majority of the vehicles tested in the large Kansas City Vehicle Emissions Study and Gasoline/Diesel split study were produced >10 years ago.

This study addresses source profiles for gasoline vehicle emissions in two ways. First, we present emissions measurements of molecular markers such as hopanes and polycyclic aromatic hydrocarbons (PAHs) for a fleet of 65 in-use vehicles spanning model years 1987-2012. This dataset represents the first large-scale measurements of molecular marker emissions and marker/OC ratios from Tier 2/LEV-2 (e.g., model years 2003-2013) vehicles for use in source apportionment.

While the vehicle fleet tested here is larger than many previous studies, it is still insufficient to describe the variability of molecular marker emissions across the entire on-road vehicle fleet in the U.S. We therefore used bootstrap resampling to generate probability distributions of marker/OC ratios. These probability distributions are used as inputs to a Monte Carlo implementation of CMB in order to determine the impact of gasoline source profile variability on CMB predictions.

12SA.2

Analysis of Polar Organic Compounds by TAG-AMS: Case Study of an Alpine Valley in France. AMELIE BERTRAND, H. Langley DeWitt, Brice Temime-Roussel, Thorsten Hohaus, Donna Sueper, Florie Chevrier, Jean-Luc Besombes, Jean-Luc Jaffrezo, Grisa Mocnik, Nathan Kreisberg, Gabriel Isaacman, Susanne Hering, Allen H. Goldstein, John Jayne, Henri Wortham, Nicolas Marchand, *Aix-Marseille Université, CNRS, LCE FRE 3416*

Highly time-resolved measurements of organic markers in ambient aerosol represent a keystone for our understanding of the evolution and the source of the Organic Aerosol (OA) in the atmosphere. A new in situ Thermal Desorption Aerosol Gas Chromatograph (TAG) coupled with an Aerosol Mass Spectrometer (TAG-AMS) has thus been developed to bridge the gap between classical offline organic markers analysis and online bulk OA analysis (William et al, 2014). The TAG system as described by Williams et al. (2006) allows for the online analysis of non or moderate polar organic markers, such as PAHs, alkanes, or hopanes, but is limited at measuring very polar organic markers such as levoglucosan. An in situ derivatization step has then been developed by flushing MSTFA saturated helium through the system during thermo-desorption (Isaacman et al., 2014). Thus the combined TAG-AMS system with in-situ derivatization provides real-time detection by AMS offering quantitative mass loadings data while simultaneously contributing molecular scale information at a high time resolution for detailed organic speciation of polar and unpolar SOA compounds.

The TAG-AMS was deployed on site in the Arve Valley (France) in February 2014 for an intensive two-week campaign co-located with a set of instrumentation such as PTR-ToF-MS, Aethalometer AE33, SMPS and HV samplers. The system was operated in AMS mode for 60 minutes during which aerosols were sampled in the TAG collection cell at 6.7 L/min. TAG was operated for desorption and subsequent analysis during 40 minutes. In addition an extra HV sampler was operated on the same schedule as the TAG.

Direct comparisons of online data are made to offline techniques. Source apportionment for both data sets (AMS and TAG) was performed using a PMF model and is compared to the Aethalometer results. Finally challenges with the derivatization step and ensued optimisations made are presented.

12SA.3

Performance Evaluation of Three Co-Located Ultrafine Particle Monitors Near the 710 in California. Ahmed Mehadi, Donald Hammond, Jeff Wright, Andrea Polidori, Timothy Morphy, ROBERT ANDERSON, *CARB Monitoring and Laboratory Division*

Ultrafine particles (UFP) are important indicators of many nearby pollution sources, including combustion sources, motor vehicle traffic, and others. New regulations and health studies have increased the importance of accurate and widespread measurements of these particles. Specifically, while methods for measurement of UFP are well-established, the instrumentation is often complex and not suitable for routine measurement without significant time commitment from a skilled technician or scientist.

This study evaluated the durability and precision of the upgraded TSI CPC Model 3783 or the same instrument labeled as the Teledyne ultrafine particle monitor model 651 for potential network use (ambient or near-roadway). Durability will be measured by the continued operation of the instruments over a four-month period without requiring major repairs. Instrument precision was also assessed by calculating intra-model variability.

In addition, one meteorological instrument was used to measure wind speed and direction to verify when the CPCs are downwind of the freeway. SCAQMD also obtained weigh-in-motion (WIM) data from the California Department of Transportation’s on-road sensors located near the study site. WIM data will be used to determine the type and number of vehicles passing by the study site during the study period.

Data from the collocated instruments were analyzed for precision. The precision of the instruments were found to be well within +/- 10 percent with R2 > 0.98 for all three monitors and calculated based on U.S. EPA’s requirement of calculating precision for continuous PM2.5 (40 CFR Part 58 Appendix A 4.3.1).

References

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12SA.4

Selenium in Ambient Fine Particulate Matter: Measurement and Trend Analysis. LI DU, Jay Turner, *Washington University in St. Louis*

Selenium compounds in ambient particulate matter (PM) have been categorized as hazardous air pollutants by the US Environmental Protection Agency (EPA) due to their toxic effects on human health. In addition, selenium often serves as one of the primary tracers for coal and oil combustion emissions in air quality studies. However, the presently low selenium mass loadings at most sites in the Chemical Speciation Network (CSN) pose challenges to detection by X-Ray Fluorescence (XRF) as implemented for the CSN. For example, the detectability of selenium (percentage of samples above the method detection limit, MDL) at a site in St. Louis decreased by more than 50% during the past decade because of the reduction in ambient selenium levels. In this study, a selenium measurement methodology based on Inductively Coupled Plasma/Mass Spectrometry (ICP-MS) that was originally developed to measure selenium in aquatic organisms was adopted. Spiking the digested sample solution with 3% (v/v) of methanol improved the sensitivity of the selenium signal using the standard mode of ICP-MS and lowered the MDL by about 65% compared to XRF analysis as routinely implemented for the CSN. The adopted method was optimized and applied to CSN protocol PM2.5 samples collected as part of the Roxana Air Quality Study (RAQS) which is being conducted in Roxana (IL) and as of July 2014 will include two years of 24-hour integrated 1-in-6 day sampling for PM2.5 mass and speciation. For the 90 samples collected and analyzed to date, the detectability was 9% for XRF analysis as implemented for the CSN, 0% for ICP-MS without methanol addition, and 47% for ICP-MS with methanol addition. The extent to which selenium appears to be a suitable tracer for coal combustion was examined using various tools such as potential source contribution function (PSCF) and will also be presented.

12SA.5

Temporal and Regional Analysis of Spatially-Resolved PM2.5 Source Apportionment Results over Continental US. CESUNICA IVEY, Heather Holmes, Yongtao Hu, James Mulholland, Armistead Russell, *Georgia Institute of Technology*

In recent investigations, human exposure to particulate matter with an aerodynamic diameter of 2.5 microns or less (PM2.5) was found to be correlated with adverse health impacts such as low birth weight, increased mortality rate, and exacerbation of existing cardiovascular and respiratory illness. Consequently, it is of interest to determine the sources of PM2.5 and how ambient concentrations attributed to those sources correlate with negative health impacts. Determining these associations is challenging due to spatially and temporally limited ground measurements of PM2.5 and PM species concentrations, uncertainty in PM2.5 emissions inventories, and source impact modeling limitations. Epidemiological studies that investigate these relationships are limited by spatially and temporally sparse source impact data.

In this work, a novel hybrid source apportionment method is employed that addresses these challenges. First, the Community Multi-scale Air Quality Model (CMAQ), equipped with the decoupled direct method for analysis of PM2.5 sensitivities to emissions, is used to produce daily, 36-km resolution source impacts over continental U.S. Then the hybrid method uses nonlinear optimization to minimize the discrepancies between ground observations of speciated PM2.5 and source impact results from CMAQ. Observations are available every third day from the Chemical Speciation Network. Finally, spatiotemporal kriging is applied to spatially interpolate adjustments, and the adjustments are implemented to compute daily, spatial source impact results for the entire year 2006. Source impacts are estimated for 20 source categories including, fossil fuel combustion, biogenics, livestock operations, aircraft, diesel and gasoline vehicles, metals processing, sea salt, and dust. Spatial trends are analyzed for 10 regions, which are chosen based on the Environmental Protection Agency region classification. Seasonal trends are determined by performing time series analyses. The results of this work provide spatially and temporally complete source impact data for use in studies seeking to evaluate the relationship of PM2.5 sources to adverse human health impacts.