Plenary I (Friedlander Lecture)

Nucleation of Clusters Bridging the Scale from Molecules to Nanoparticles. PAUL E. WAGNER, Paul M Winkler, *Fakultaet fuer Physik, Universitaet Wien, Vienna, Austria*

Gas to liquid phase transitions are important processes in materials science, aerosol physics and atmospheric science. The recent decade of atmospheric observations has demonstrated particle formation by nucleation to be a frequent phenomenon in the global atmosphere. The underlying activation mechanisms of small molecular clusters are thus of vital importance. However, homogeneous as well as heterogeneous nucleation are still among the least understood phenomena in aerosol science.

New particle formation by homogeneous or heterogeneous nucleation generally proceeds via critical molecular clusters, whose sizes can be directly determined from experimental observables using the nucleation theorem. Homogeneous nucleation rate data provide information on the sizes of critical clusters down to diameters of 2 nm in satisfactory agreement with the Kelvin relation [1]. Experiments on heterogeneous nucleation in n-propanol vapour allowed for the first time to bridge the scale from molecular clusters to nanoparticles [2]. For charged seed particles an enhancement of heterogeneous nucleation and a significant charge sign preference were observed.

Recently we have activated single seed ion molecules at sizes far below the Kelvin-Thomson prediction. This unexpected behaviour has now been explained by quantitative determination of the molecular content of critical clusters [3]. We found these clusters to be significantly larger than the seed particles and in fact fairly well predicted by the Kelvin-Thomson relation. Consequently the fundamental detection limit of Condensation Particle Counters is now considerably extended down to particle diameters of about 1 nm. We have designed a new expansion type measurement system (vSANC), which will be used in joint nucleation experiments at CERN, Geneva [4].

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Plenary II (AEESP Lecture)

Embracing Complexity: Deciphering Origins and Transformations of Atmospheric Organics through Speciated Measurements. Allen Goldstein, *University of California, Berkeley*

Organic material accounts for a large fraction of atmospheric aerosol, with the majority being secondary organic aerosol (SOA) formed through oxidation processes. Primary emissions leading to SOA include thousands of chemicals from a variety of natural and anthropogenic sources ranging over approximately 15 orders of magnitude of volatility. As organics are oxidized they fragment to form smaller volatiles or add functionality leading to SOA formation, dramatically increasing the complexity of compounds present. A continuing challenge in aerosol research is to elucidate the sources, structure, chemistry, fate, climate and health impacts of these organic atmospheric constituents.

The complex chemical composition of organic aerosols presents unique measurement challenges. Dr. Goldstein’s group and close collaborators have developed the Thermal Desorption Aerosol Gas chromatograph (TAG) system for hourly in-situ speciation of a wide range of primary and secondary organic compounds in aerosols. This instrument combines a particle collector with thermal desorption followed by GCMS detection to provide hourly separation, identification, and quantification of organic constituents at the molecular level. We incorporated two-dimensional chromatography (GCxGC), providing dramatically enhanced speciation. We developed a semivolatile collection and analysis system that allows simultaneous measurement of specific organics in the gas and particle phases, enabling analysis of their partitioning. We also developed a combined TAG-AMS (Aerosol Mass Spectrometer) instrument for simultaneous measurements of the total and speciated aerosol composition. We are currently exploring soft ionization with vacuum ultraviolet radiation using a high resolution time of flight mass spectrometer (GCxGC/VUV-HRTOFMS) to more fully separate and identify compounds in complex mixtures such as diesel fuel, motor oil, fire emissions, in controlled oxidation studies, and in ambient samples. This talk will review recent developments (TAG, 2DTAG, SVTAG, TAG-AMS, GCxGC/VUV-HRTOFMS), and present new atmospheric observations, source characterizations, and controlled oxidation studies to more fully characterize atmospheric organic sources and transformation processes.

Plenary III
A Tangled Web: Occupants, Squames, Ozone, SOA and SVOCs in Indoor Environments.

Charles Weschler, *UMDNJ-Robert Wood Johnson Medical School*

By their very presence and independent of their activities, humans influence the environments they occupy. The outer layer of human skin — the stratum corneum — is covered by lipids including squalene and unsaturated fatty acids. These compounds react readily with ozone, significantly reducing its indoor concentration and generating oxidized byproducts. From first principles, one expects that some byproducts of ozone-lipid chemistry partition between the gas phase and airborne particles, contributing to secondary organic aerosols (SOA) in occupied rooms. Conversely, the lower indoor ozone levels as a consequence of titration by the exposed skin, hair and clothing of occupants means less generation of SOA from ozone-initiated reactions with terpenoids and other unsaturated organic compounds that can serve as SOA precursors indoors. Occupants also inadvertently transfer their skin oils to exposed indoor surfaces and continuously shed their skin as small flakes, known as “squames.” A typical adult sloughs 200,000 - 600,000 squames per minute, equivalent to 30 - 90 mg per hour. Consistent with their origin, these squames contain squalene (~1% by weight) and unsaturated fatty acids. By transferring their oils and depositing their skin flakes onto indoor surfaces, occupants alter indoor environments even when they are no longer present. Evidence for what humans leave behind includes measured levels of squalene in airborne particles and settled dust, as well as human skin microbiota found in airborne particles and on indoor surfaces as determined by rDNA gene-sequence analysis. The squalene and unsaturated fatty acids in settled dust and on indoor surfaces further impact the levels of ozone and, indirectly, SOA. In turn, indoor particles, including squames, their fragments and ozone-derived SOA, can alter the concentrations and fates of co-occurring SVOCs. All else being equal, as particle concentrations increase, gas-phase concentrations of SVOCs decrease, and emission rates of SVOCs from indoor surfaces increase. For any given SVOC, the larger the ratio of its particle- to gas-phase concentration, the larger the influence of particles on its overall dynamics. Additionally, it has been argued recently that airborne particles might enhance the net flux of SVOCs to human surfaces by as much as a factor of five for realistic indoor conditions. In summary, dynamic physical and chemical processes involving people and particles can markedly influence pollutant exposures that humans experience in indoor environments.

Plenary IV
Multiphase Oxidation Chemistry: Impacts on Both the Gas Phase and Aerosol.

Jonathan Abbatt, *University of Toronto, Canada*

Whereas gas phase oxidation mechanisms are comparatively well understood, considerable uncertainties remain with respect to the nature and potential importance of multiphase oxidation processes in which oxidative reactions occur either within a condensed phase or at a gas-particle interface. While such chemistry has long been recognized to be important in the oxidation of sulfur(IV) to sulfur(VI) in cloudwater and for promoting the Ozone Hole, its prevalence with tropospheric aerosol and at the Earth’s surface remains poorly quantified. As well, such reactions are likely to occur indoors, given the relatively slow gas-phase chemistry that prevails in these environments. In part, these uncertainties arise because of the complexity of the chemistry: oxidants may either form in-situ or be delivered from the gas phase, chemistry can occur at interfaces or in the bulk, and mass transport limitations can be important in both the gas and condensed phases. After an introduction to the general issues involved in multiphase oxidation chemistry, this talk will illustrate the complexity of the field by focusing on specific examples from across the realm of aerosol and atmospheric chemistry. Attention will be given to: i) organic aerosol oxidation, whereby the overall oxidation state and hygroscopicity of the particle may change, ii) transformations of trace, toxic species (such as polycyclic aromatic hydrocarbons) within particles, and iii) oxidation processes that occur within cloudwater. In addition, the potential for multiphase chemistry occurring at the Earth’s surface, such as at high latitudes with salty substrates or with the marine surface microlayer, will also be discussed.

1AC.1

Modeling of Solute Activities and Relative Humidity in Atmospheric Aerosols. CARI DUTCHER, Ge Xinlei, Anthony Wexler, Simon Clegg, *University of California, Davis*

Accurate predictions of water and solute activities in atmospheric aerosols to very low equilibrium relative humidities (RH) are central to predications of aerosol size, optical properties and cloud formation. A powerful method has been recently developed (Dutcher et al. JPC C, 2011, 2012) for capturing the thermodynamic properties of multicomponent aerosols at low and intermediate levels of RH (< 90%RH) by applying the principles of multilayer adsorption to ion hydration found in solutions. In these works, statistical mechanics is used to model adsorption of a solvent on to n energetically distinct layers in the hydration shell surrounding the solute molecule in aqueous mixtures.

Here, we extend the model to the 100% RH limit and reduce the number of adjustable model parameters, allowing for a unified thermodynamic treatment for a wider range of atmospheric systems. The long-range interactions due to electrostatic screenings of ions in solution are included through a mole fraction based Pitzer-Debye-Huckel (PDH) term. Equations for the Gibbs free energy, solvent and solute activity, and solute concentration are derived, yielding remarkable agreement of the solute concentration and osmotic coefficients for solutions over the entire 0 to 100% RH range. The number of adjustable model parameters is reduced by relating the values of the energy of adsorption to each hydration layer to known short-range Coulombic electrostatic relationships. The effect of the PDH long-range and Coulombic short-range electrostatics on the mixing relationship is explored and new insights into the molecular relationships within atmospheric aerosols is discussed.

1AC.2

Model for Acid-Base Chemistry in Nanoparticle Growth. TAINA YLI-JUUTI, Kelley C. Barsanti, Lea Hildebrandt Ruiz, Antti-Jussi Kieloaho, Theo Kurten, Ulla Makkonen, Tuukka Petäjä, Mikko Äijälä, Markku Kulmala, Ilona Riipinen, *University of Helsinki*

The climatic effects of particles formed in gas-to-particle phase transformation depend on how fast they grow relative to how quickly they are scavenged by larger particles. Sulphuric acid is found to be the key compound in atmospheric nucleation but its contribution to nanoparticle growth is estimated to be small in many environments. The observations on atmospheric nanoparticle growth suggest that a large fraction of the growth is due to condensation of organic vapors, although the exact identification of these vapors as well as the mechanisms related to the growth are still unknown. To condense on atmospheric nanoparticles organic vapors must have very low-volatility. While reversible condensation requires a very low saturation vapor pressure, particle phase processes like salt formation may also enable compounds with higher saturation vapor pressures to contribute to particle growth. Recently, evidence for the presence of organic salts in atmospheric nanoparticles has been observed.

We studied the potential contribution of organic and inorganic salt formation on particle growth rates using our newly developed model for acid-base chemistry in nanoparticle growth. This single particle model combines a dynamical condensation model for calculating the mass fluxes of vapors to a particle and an equilibrium thermodynamic model (Extended Aerosol Inorganic Model, E-AIM) for calculating the particle phase dissociation of acids and bases, including calculation of activity coefficients. We applied the model for an atmospherically relevant system consisting of two acids (sulphuric acid and an organic acid), two bases (ammonia and an amine) and water. Using the model we studied the potential effect of particle phase salt formation on the growth rates of individual particles in various ambient conditions, as well as the relative contributions of chemically distinct acids and bases. We will discuss the results in the context of atmospheric particle growth rates and their observed size dependence.

1AC.3

Modeling the Formation and Evolution of Secondary Organic Aerosol in a Potential Aerosol Mass (PAM) Chamber. Shuang Chen, WILLIAM BRUNE, Paul Davidovits, Andrew Lambe, Timothy Onasch, *Pennsylvania State University*

A model was set up to simulate the formation and evolution of secondary organic aerosol (SOA) in a Potential Aerosol Mass (PAM) chamber, a small flow-through 15L cylinder containing ultraviolet lights that produce a highly oxidizing environment. The hydroxyl (OH) levels are high enough that a few minutes in the chamber is equivalent to 0.6 to 15 days in the atmosphere. The model framework was based on the two-dimensional volatility basis set approach (2D-VBS), in which all organic oxidized products in the model were distributed on the 2D space of volatility and oxygen-to-carbon (O:C) ratio. First-generation organic products from the oxidation of a precursor were modeled with the use of the VBS parameters from previous experimental studies. The O:C ratios of these products were assigned based on the measurements at low OH exposure. Further homogeneous and heterogeneous oxidation was assumed for all organic products. Both functionalization and fragmentation processes were included in the model. The model predictions of SOA yields and O:C ratios were compared with the experimental data of the PAM chamber. The results showed that at the same levels of OH exposure, the predicted SOA concentrations generally agree well with the measurements. Sensitivity analysis indicated that the model predictions of O:C ratio and SOA concentrations were most sensitive to the fragmentation branching ratio of the products and the rate coefficient of the reactions of semi-volatile products with OH.

1AC.4

Modification of the CMAQ Secondary Organic Aerosol (SOA) Module to Allow Consideration of Activity Coefficients and Water Uptake. MARGUERITE C. MARKS, Abdullah Mahmud, Kelley C. Barsanti, William E. Asher, James F. Pankow, *Portland State University*

Current regional air quality models such as CMAQ (Community Multiscale Air Quality model) consider that the formation of secondary organic aerosol (SOA) can be calculated by assuming thermodynamic ideality in the organic particulate matter (OPM) phase as well as negligible uptake of water into the OPM phase. Theoretical predictions and model simulations considering non-ideality and water uptake show that the standard model assumptions can lead to large errors in predicted SOA mass, and that the magnitude of these errors is sensitive to the composition of the OPM phase. The SOA module in CMAQ v4.7.1 has been revised in this work to allow consideration of the effects of both non-ideality and water uptake. First, a reasonable specific surrogate structure was assigned to each of the lumped products assumed to be produced by reaction of the different precursor hydrocarbons considered in CMAQ (e.g., isoprene, benzene, and toluene). Second, the CMAQ code was modified to allow iterative calculation (at each point in space and time) of the gas/particle partitioning coefficient for each of the SOA-forming products and for water. Third, model simulations were performed for the Eastern US at a resolution of 12-km x 12-km for three summer months in 2010, under a range of relative humidity conditions. Results will include a comparison of the simulated base-case SOA mass concentrations with those utilizing the updated SOA module, and will be discussed in terms of overall implications for predicted levels of ambient SOA and fine particulate matter.

1AC.5

Impact of Meteorology and Aerosol Composition on Heterogeneous N2O5 Hydrolysis and Chlorine Activation during CalNex 2010. WAYNE CHANG, Steven Brown, Nicole Riemer, *University of Illinois at Urbana-Champaign*

The heterogeneous hydrolysis of dinitrogen pentoxide (N_2O_5) on atmospheric particles is an integral part of nighttime chemistry in the troposphere. In particular, recent measurement campaigns have shown that the activation of chlorine by heterogeneous N_2O_5 reactions on chloride-containing aerosol is an important source of chlorine atoms in the troposphere, even in regions away from continental coasts. The reaction rate of the hydrolysis is highly dependent on meteorological conditions and aerosol composition. Based on chamber measurements, several parameterizations suitable for air quality models have been developed for the treatment of N_2O_5 uptake probability on available aerosol surfaces. Key governing variables for these parameterized functions include temperature, relative humidity, and particulate nitrates, chloride and organics contents. We implemented these parameterized treatments of heterogeneous N_2O_5 hydrolysis in the WRF/Chem modeling system, under both the idealized 1-D and full 3-D framework. In addition, we expanded the gas-phase chemical mechanism with inorganic and organic chlorine species, and corresponding chemical reactions. This newly augmented mechanism is coupled with the parameterization method that accounts for the presence of particulate chloride through the inclusion of the heterogeneous production of nitryl chloride ($ClNO_2$) by N_2O_5 hydrolysis. Under the idealized 1-D framework, we investigated the response of nighttime vertical gradients of N_2O_5 and related products of hydrolysis to seasonal variations and emission compositions. The domain of the full 3-D model is the South Coast Air Basin of California. Through evaluations against measurements made during the CalNex 2010 campaign, the performance of the different uptake parameterization techniques and heterogeneous chlorine activation reactions is assessed, and the resulting impact on the tropospheric pollutant dynamics is quantified in this study.

1AC.6

Improvement of Simulation of Fine Inorganic PM Levels through Better Descriptions of Coarse Particle Chemistry. ERICA TRUMP, Christos Fountoukis, Neil Donahue, Spyros Pandis, *Carnegie Mellon University*

Three-dimensional chemical transport model PMCAMx is updated to improve predictions for the mass and chemical composition of both fine- (PM1) and coarse- (PM10-1) mode particles. ISORROPIA II is used in the new model to extend the inorganic thermodynamic system to the reactive dust constituents Ca2+, K+, Mg2+. The hybrid mass transfer method is used allowing for the dynamic calculation of mass transfer to coarse-mode particles while maintaining computational efficiency by assuming that the fine-mode particles are in equilibrium. The resulting model is applied to Europe and evaluated for the period of May 2008 against ground-based and airborne Aerosol Mass Spectrometer measurements from the EUCAARI campaign.

Earlier implementations of PMCAMx for Europe used a bulk-equilibrium approach to calculate mass transfer to all particles. This approach was able to predict PM1 OA and sulfate concentrations quite well [Fountoukis et al., 2011]. However, the simulations had difficulties in reproducing the observed PM1 nitrate concentrations for locations in which there were relatively high coarse-mode particle concentrations (significant sea-salt or dust concentrations). This shortcoming was apparent for the Mace Head site in Ireland, where a large amount of nitrate is associated with sea-salt, as well as for sites in the Eastern Mediterranean where Saharan dust has a strong presence. The improved simulation of the coarse-mode particle chemistry and dynamics results in significant improvement of the predictions of PM1 nitrate and ammonium, particularly in locations having significant amounts of sea-salt or dust.

References

Fountoukis et al., Atmospheric Chemistry and Physics 2011, 11, 10331-10347

1AC.7

Effect of Criegee Biradical Reactions on Regional Secondary Inorganic and Organic Aerosol. JINGYI LI, Qi Ying, *Texas A&M University*

Recent studies show that reactions rates of criegee biradicals, generated from ozonolysis of alkenes, with SO2 and NO2 are much faster than previously estimated. This leads to speculations that the criegee radicals may play a more significant role in regional and global budgets of sulfate and potentially indirectly affect other secondary pollutants such as secondary organic aerosol (SOA). In this study, the Community Multiscale Air Quality (CMAQ) model with Master Chemical Mechanism version 3.2 (MCM v3.2) is applied to evaluate the effect of faster criegee biradical reaction rates with SO2 and NO2 on regional concentrations of sulfate and SOA. The secondary organic aerosol concentrations are predicted by directly partitioning thousands of semivolatile volatile organic compounds predicted by the gas phase MCM mechanism into the organic phase of the aerosols. The CMAQ-MCM-SOA model will be applied to study regional sulfate and SOA in southeast US and in the Mexico City. While southeast US represents an area with significant biogenic emissions with influence from anthropogenic emissions, Mexico City represents an area with significant anthropogenic alkene emissions and high SO2 concentrations from fossil fuel combustion and natural sources. Difference between the base case simulation with original criegee radical reaction rate coefficients and the sensitivity case with recent estimated faster reaction rate coefficients will be used to quantify the impact of the proposed new reaction kinetics data on regional secondary aerosol concentrations. Effect of these changes on direct radiative forcing will be estimated.

1AE.1

Inhalation Intake Fractions of Vehicle-Attributable Organic PM2.5. JOSHUA APTE, Julian Marshall, William Nazaroff,*University of California, Berkeley*

Fine particulate matter ($PM_{2.5}$) attributable to light-duty vehicles is substantially comprised of semivolatile organic material. The composition and phase partitioning of primary organic aerosol (POA) is understood to be influenced by background organic aerosol (OA) concentrations and evolve in response to changing temperature, dilution processes, and photochemical aging. Although such dynamic processes may substantially influence population exposure to vehicle-emitted $PM_{2.5}$, these phenomena are typically not incorporated into source-oriented exposure models. Here, we present preliminary estimates of the intake fraction (iF) of OA attributable to emissions from urban vehicles.

To make the assessment, we employ a novel fate and transport model to characterize population exposure to vehicle-attributable OA. Dynamic phase partitioning of primary organic emissions owing to dilution and aging is simulated using a volatility basis set (VBS) framework. Exposures are evaluated at multiple spatial scales: in the on-road microenvironment, at urban-ambient conditions, and at the regional scale. The contribution to overall intake is estimated for each microenvironment and summed to determine the total intake fraction of vehicle-attributable OA. Likewise, iF is estimated separately for OA exposures attributable to gas- and particle-phase primary emissions.

Owing to dilution-induced shifts in gas-particle partitioning, the intake fraction for POA may be substantially lower than for vehicle emissions of conserved pollutants. Preliminary results suggest that most population intake of vehicle-attributable OA takes place at the urban scale, with smaller contributions from on-road and regional-scale exposures. Interestingly, regional-scale photochemistry produces large quantities of oxidized POA on a mass basis, but may result in only modest population exposures, since production is spatially dispersed and has relatively low proximity to populations. A consequence of these results is that population intake of vehicle-attributable $PM_{2.5}$ may be more strongly influenced by primary species than would be indicated by regional-scale models or measurements.

1AE.2

Personal, Indoor, and Outdoor Exposure Assessment of Particulate Matter and Their Associations with Respiratory Symptoms in Children. SEUNG-HYUN CHO, Jonathan Thornburg, Charles Rodes, Diane Wagener, *RTI International*

Exposure to particulate matter (PM) has been linked to various adverse health effects. However, assessing the level of exposure is a challenging task due to high cost and varying wearing compliance for personal monitors, and exposure misclassification from stationary monitoring. A comparative PM measurement study has been planned to investigate the difference between personal and stationary air monitoring, and the impact of measures implemented to minimize exposure misclassification. Five to nine days of integrated PM samples of 10 micrometer or smaller will be collected using personal, indoor, and outdoor monitors for 100 children live in Louisiana and Mississippi who are a subset of Children's Health after the Storm (CHATS) cohort. Daily sample will be also collected from a central-site monitor in Louisiana. RTI's MicroPEM equipped with a nephelometer and an accelerometer in addition to particle filter will be used to collect real-time PM concentration and activity level data for personal monitoring. Monitor wearing compliance and an estimated inhalation dose will be calculated from those data. Children will be asked to complete a time-location diary that identifies children's location between indoor/outdoor home, indoors/outdoors other than home, and transportation for four 6-hour integrated time periods. Exhaled nitric oxide, a marker of airway inflammation, will be measured at the end of the air sampling, and respiratory symptoms experienced during the sampling period will be asked. The PM concentrations measured by various monitors will be compared. The difference in associations between health measurements and each type of PM measurement with and without information on monitor wearing compliance and time-location diary will give insight on the best approach and limitations in PM exposure assessment at various monitoring settings. The inhalation dose will provide valuable information that external exposure measurement cannot address on health effects.

1AE.3

Refined Estimates of Ambient PM2.5 Exposure: Validation and Refinement of a Mechanistic Indoor Transport Model.NATASHA HODAS, Qing Yu Meng, Melissa M. Lunden, Barbara Turpin, *Rutgers University*

Use of central-site concentrations to estimate ambient $PM_{2.5}$ exposure is a source of error in air-pollution epidemiology. To reduce this error, computationally inexpensive methods to model indoor concentrations of ambient $PM_{2.5}$ are needed, since people spend most of their time indoors. We validated a method to predict indoor concentrations of ambient $PM_{2.5}$ using measurements from the Relationships of Indoor, Outdoor, and Personal Air (RIOPA) study. A mass balance model was used to calculate indoor concentrations of sulfate and elemental carbon (EC) for homes in California, Texas, and New Jersey using measured outdoor $PM_{2.5}$ species concentrations and air exchange rates. Depositional losses were estimated using published particle-size-resolved deposition rate measurements and species size distributions. We performed a multiple linear regression analysis (MLR) to determine if human activity variables, which were recorded with questionnaires, explained the variance in the difference between modeled and measured indoor $PM_{2.5}$ concentrations. We then refined the model to account for the factors selected by the MLR analysis. Generalizations about species-resolved size distributions based on knowledge of particle sources/formation mechanisms provided reasonable estimates of indoor particle losses, regardless of geographic region. Opening windows and using central air conditioning or heating explained 30% of the variance in the difference between measured and modeled indoor concentrations. Both the initial and refined models captured the distribution of measured indoor sulfate, suggesting either could be applied to estimate exposure at the population level. Only the refined model, which accounts for human activities, captured indoor sulfate at the individual-home level. Modeled indoor concentrations of EC from both models were similar, suggesting that these human activities minimally impact the penetration and persistence of EC. Based on these results, we provide guidance regarding measurements and human activity data most critically needed to facilitate the prediction of refined exposure surrogates in large, prospective epidemiological studies.

1AE.4

Enhanced Air Pollution Epidemiology Using a 3D Source Oriented Air Quality Model in California. JIANLIN HU, Christina Zapata, Bart Ostro, Michael Kleeman, *UC Davis*

Airborne particulate matter (PM) is known to cause a range of adverse health effects but it has proven difficult to isolate a PM chemical component, size fraction, or source that is primarily responsible for the observed mortality. A major problem preventing further progress is lack of high temporal and spatial resolution data in central monitor measurements which are typically employed in epidemiology studies as estimates of exposure. The current generation of source-oriented air quality models can provide much of the information missing from the central site monitoring database. In the present study, the UCD/CIT_Primary source-oriented air quality model has been developed and applied to estimate population weighted primary particulate matter concentrations from ~900 sources in California for a 7-year period (2000-2006) with 4km spatial resolution and 1 day time resolution. Model results have been comprehensively evaluated against monitoring data and receptor model results to verify accuracy and precision for known sites. Excellent agreement was found between the predicted and measured PM2.5 elemental carbon (EC) concentrations; general agreement was also found between model predictions and ambient measurements for 9 trace elements (K, Zn, Mn, Fe, Ti, As, Si, Cr, and Al) in the PM2.5 size fraction. Predicted PM0.1 mass and EC concentrations agreed well with the observed concentrations. Source contributions to PM2.5 and PM0.1 estimated by the UCD/CIT_Primary model generally agreed with the receptor-based model results. The model predictions for 7-years of PM2.5 and PM0.1 concentrations provide a unique dataset for epidemiological analyses. In the present study, source contributions to primary PM mass, EC, trace elements in multiple size fractions (PM0.1, PM2.5, PM10, PM10-2.5) are correlated against life expectancy data in all 28 metropolitan statistical areas (MSA) in California. Relationships between life expectancy and various dimensions of the airborne particle complex will be discussed.

1AE.5

In-Cabin Ultrafine Particle Concentration Inside Passenger Car Fleet on Several Los Angeles Roadways. NEELAKSHI HUDDA, Constantinos Sioutas, Ralph Delfino, Scott Fruin, *University of Southern California*

For large sections of the population, the highest pollutant concentration is encountered during travel where close proximity to relatively undiluted fuel combustion emissions occurs. In order to accurately assess exposure to travel related pollutants like ultrafine particles, this micro-environment needs to be correctly accounted. However, since particulate pollutant species are lost to surfaces or filtered by vehicle’s ventilation system, in-cabin concentrations can vary from nearly zero to nearly equal to roadway concentrations. The objectives of this study were to characterize in-cabin-to-roadway (I/O) ratios for ultrafine particles (UFP) through extensive measurements and modeling, and to generate realistic fleet-wide in-vehicle concentration distributions. Results for the US passenger car fleet incorporated vehicle age, manufacturer, and cabin volume distributions were used to generate fleet wide I/O distributions, which were then linked to particle concentrations observed on seven Los Angeles freeways and over 50 mile of arterial roadways. Each roadway route was sampled for a full spread of traffic and meteorological conditions to capture the full range of expected real world concentrations. In-cabin exposures varied by over a magnitude, due to inter vehicle variability and ventilation choice (in-cabin air recirculation or continuous fresh outside air intake), and inter-vehicle variation in I/O ratios was often more important than differences in on-road concentrations at different locations or on different roadway types. In general, exposure concentrations increased two to four fold when ventilation mode is switched from recirculation to outside air intake, despite air filtration during outside air intake.

1AE.6

Spatiotemporal Assessment of Fine Particle Exposures During Commuting Activities. KIRSTEN KOEHLER, Jennifer Peel, Maggie Clark, Stuart Amy, John Volckens, *Colorado State University*

Commuting generally accounts for a small fraction of an individual's daily time, yet it can represent a large fraction of daily exposure to air pollutants, due to the high concentrations of traffic-related pollutants found near roadways. We developed a multi-pollutant, spatiotemporal exposure assessment method to provide continuous (10-second resolution) estimation of personal exposure. A lightweight backpack contained direct-reading monitors for airborne PM2.5 particle mass, PM2.5 black carbon, and carbon monoxide concentrations. By pairing the exposure monitors with a GPS receiver to track location, we were able to determine when and where exposure takes place. Fifty participants carried the backpack for 24 hours during their daily activities, including commuting. This study was the first to allow participants to choose their mode of commute (bicycle or car) and their route. Participants wore data-logging, personal heart rate monitors to estimate their respiration rate. Pollutant data and GPS coordinates were downloaded into a geographic information system and processed to define a personal exposure track, from which the commutes were extracted. A spatiotemporal exposure map showing "hot spots" for air pollution was developed. Bicyclists often spend a longer time commuting, are in closer proximity to vehicle exhaust, and have a higher respiration rate than drivers, leading to increased cumulative intake of traffic-related air pollutants. Our results suggest that this method can be used to assess short duration, but high intensity exposures experienced during commuting.

1AE.7

Nanoparticle Emission from Engineered Nanostructured Materials Leading to Exposure and Risk. HEINZ FISSAN, Burkhard Stahlmecke, Christof Asbach, Thomas Kuhlbusch, *Institute of Energy and Environmental Technology*

Nanostructured materials are increasingly incorporated in new products. They may release nanostructured materials into the environment during synthesis of nanostructured materials, product manufacturing and use as well as waste. Engineered nanoobjects are discussed to potentially cause adverse (health) effects, especially if they are released into the air and cause exposure of humans. Inhalation is seen as the major uptake route.

The starting point for balancing of released material flows is the amount of released nanoparticles per mass unit of nanostructured material. It can be considered to be a material property. Techniques with the capability of being standardized, based on different stress (energy input) situations have to be developed in order to reduce the tremendous variability of material stress cases. Besides defined stress cases, measurement techniques allowing for quantitative determination of nanoparticle release have to be used. The measures of interest (number, surface area, volume (mass)) depend on the physical and chemical processes occurring during the transport of the nanoparticles in the environment and in the effect system, and the kind of effect considered to be risky. Release is followed by the changes occurring during transport to the exposure point, described by the nanoparticle release-exposure relationship. This relationship can be modeled taking into account different exposure scenarios. Modeled material balances can be evaluated or controlled by measurements at different points of the material pathway.

We will report about a strategy towards measuring nanoparticle release properties of nanostructured materials to derive nanoparticle emission as a starting point for environmental material balancing towards exposure and dose. The measurement of the different needed concentration measures (number, surface area, volume(mass)) in form of size distributions will be critically considered.

1CC.1

Ice Nuclei Production from Sea Spray. PAUL DEMOTT, Ryan Sullivan, Kimberly Prather, Thomas C. Hill, Gary D. Franc, Allan Bertram, Ryan Mason, Timothy Guasco, Douglas Collins, Luis Cuadra-Rodriguez, Andrew Ault, Vicki Grassian, *Colorado State University*

The sources, abundance, nature of atmospheric particles that serve as ice nuclei (IN) are not well characterized, leading to uncertain impacts on clouds, precipitation and climate. Oceanic IN sources are less well defined than known terrestrial sources, yet their potential importance is large due to the occurrence of cold cloud systems over vast oceanic regions of the Northern and Southern Hemisphere (SH). Past research suggests modest oceanic sources of IN to the atmosphere on average, but with strong heterogeneity and episodic IN production associated with marine biological processes.

In this study, we present measurements on aerosols produced from sea spray, isolated from actual seawater via breaking wave action in a laboratory wave channel facility. The temperature spectrum of freezing nuclei was determined from -10 to -35C using multiple methods. Small fractions of the generated particles were active as IN, decreasing roughly an order of magnitude per 5 degree increase in temperature, with a characteristic value of 3 per liter of air at -30C. Lower numbers of IN active at modest supercooling is consistent with past measurements over SH oceans, and appears consistent with reports of more persistent supercooled clouds at SH higher latitudes, and the difficulty that global climate models have in reproducing the energy balance related to clouds in this region.

The composition of IN produced from sea spray is still under investigation. Collected IN residuals examined by SEM were conspicuous in the absence of recognizable bacterial cells, but included certain types of sea salt particles with inclusions, as well as unidentified submicron particles containing elements of Ca, Mg, P, S, and C. Lowest IN concentrations were measured during periods of high organic aerosol loading, measured by single particle mass spectrometry, following additions of bacteria and nutrients to sea water. IN concentrations recovered as cells fed on these nutrients.

1CC.2

Measurements of Ice Nucleation in the Contact Mode by Mineral Dusts. Kristopher Bunker, Swarup China, Claudio Mazzoleni, Alexander Kostinski, WILL CANTRELL, *Michigan Technological University*

What initiates ice formation in the atmosphere for temperatures greater than ~ -20 C? Mineral dusts are known to be the most prevalent ice nuclei, but recent laboratory studies have shown that they are not effective in the immersion/condensation mode for temperatures above approximately -25 C (see e.g. Niedermeier et al., 2010). Ice nucleation in the contact mode, where the aerosol particle initiates freezing at the air-water interface, has been suggested as a possible candidate for nucleation at high temperatures, as previous work has suggested that the contact mode is active at temperatures as much as five degrees higher than the immersion/condensation mode.

We will discuss measurements of ice nucleation in the contact mode by mineral dusts of selected electrical mobility diameters, which cast doubt upon contact nucleation as a pathway to primary ice production in the atmosphere at high temperatures. Specifically, our measurements show that less than one in a hundred Arizona Test Dust particles with a diameter of 1 micron catalyzes freezing of water in the contact mode at -18 C. By comparison, less than one in a thousand kaolinite particles of the same size catalyzes freezing at that temperature. Arizona Test Dust was active in the contact mode at -15 C, though the fraction of particles active at that temperature was almost a factor of 10 smaller than those active at -18 C. Kaolinite was not active at -15 C.

Our measurements also suggest that the smallest Arizona Test Dust particles we investigated (electrical mobility diameter of 62.5 nm) are more effective as contact nuclei. Differences in the morphology of the dust as a function of size may be responsible for the difference.

1CC.3

The Role of Temperature in Cloud Droplet Activation. Sara Christensen, MARKUS PETTERS, Paul Ziemann, Sonia Kreidenweis,*North Carolina State University*

Organic aerosols in the atmosphere are composed of a wide variety of species, reflecting the multitude of sources and growth processes of these particles. Especially challenging is predicting how these particles may act as cloud condensation nuclei (CCN). Köhler theory relates the particle’s dry diameter to its critical supersaturation. A hygroscopicity parameter, kappa, parameterizes this relationship in terms of the particle’s chemical composition. Previous studies have characterized kappa values for pure and mixed compounds at laboratory temperatures, but did not measure its potential dependence on temperature. Here we characterize the temperature dependence of kappa derived from CCN measurements for a variety of organic compounds in the laboratory. Single compound organic aerosol and secondary organic aerosol from the reaction of alpha-pinene and ozone were generated in the laboratory and activation properties were analyzed using size-resolved CCN analysis. The CCN instrument was placed inside a temperature-controlled enclosure. During the experiment the temperature inside the enclosure was ramped down from approximately 40 degree to 0 degree C over a period of approximately six hours. Activation data were collected by alternating diameter scans between organic aerosol and ammonium sulfate aerosol for calibration. The organic aerosol kappa values remained constant or decreased as temperature decreased. These observations can be explained by a weak dependence of water activity on temperature and a moderate dependence of solubility in water on temperature. As a case study, we demonstrate that Köhler theory valid for sparingly soluble compounds can quantitatively explain the temperature dependent activation properties of adipic acid aerosol. We anticipate that our results will help to guide input and parameterization choices in models that rely on theory to extrapolate laboratory and ambient data to temperatures that are different than those during data collection.

1CC.4

The Role of Time in Heterogeneous Freezing Nucleation. TIMOTHY WRIGHT, Markus Petters, *North Carolina State University*

A small fraction of particles in the atmosphere can catalyze ice formation in cloud water drops through heterogeneous freezing nucleation at temperatures warmer than the homogeneous freezing temperature of approximately -38 degree C. The rate for heterogeneous freezing nucleation is dependent on several factors including the type and surface area of dust that is immersed inside the drop. Although nucleation is an inherently stochastic process resulting from size fluctuations of the incipient ice germ, there is a growing body of literature that suggests that quasi-deterministic models of ice nucleation can describe laboratory experiments. Because laboratory data can be fit equally well to different and sometimes contradictory models, agreement between model and data does not uniquely constrain the underlying physics. Here we present new experiments and simulations that aim to better constrain the truth value of theoretical models fitted to laboratory data. We collected ice nucleation data for Arizona Test Dust aerosol immersed in water using a droplet freezing assay setup that allows for the cooling rates to be changed between 10 and 0.01 K per minute. Discrete event simulations based on a variant of the multiple-component stochastic model of heterogeneous freezing nucleation were used to simulate different experimental procedures. The nucleation properties of the dust are specified by four material-dependent parameters. We find that these four parameters can quantitatively explain ice nucleation data from a broad spectrum of experiments. This includes data from published studies using different sizes and methodologies, thus giving credence to the multiple-component stochastic model’s ability to correctly describe ice nucleation physics for dust aerosols. We anticipate that the combination of discrete event simulations and a spectrum of experimental procedures described here can be used to design more meaningful laboratory experiments probing ice nucleation and will aid the development of better parameterizations for use in models.

1CC.5

Aerosol-Clouds-Precipitation: Aircraft Measurements on the East Coast of Canada. STÉPHANIE GAGNÉ, Richard Leaitch, Jeffrey Pierce, *Dalhousie University*

The aerosol indirect effects on clouds are a major source of uncertainty in climate models and predictions. Among the reasons for the large uncertainty are the complexity of understanding cloud microphysics and the controls on precipitation. Further, cloud measurements are typically difficult and costly, and, as a consequence, uncommon.

Environment Canada has conducted over 30 years of in-cloud aircraft measurements using a National Research Council of Canada Convair 580 and DHC-6 Twin Otter. Measurements of aerosol size distributions, cloud droplets and precipitation-sized particles were made along with measurement of the meteorological data along the flight path. We are using this dataset to investigate the links between aerosol, clouds and precipitation. With this purpose in mind, we are building a database of all the clouds measured during these 30 years. We compare the clouds based on their liquid water content, depth, droplet number concentration, aerosol size distribution at the base, precipitation size distribution, etc.

We start by studying one of the campaigns that took place in the Canadian Atlantic area, measured with the Convair 580: Canadian-SOLAS 2003. All the clouds during this campaign were stratiform warm clouds, most of which were measured over water. Clouds from other campaigns will gradually be added to the database, including over-land clouds and ice clouds. At this conference, we will present our latest results from the analysis of this database.

1CC.6

Effect of Rain on the Evolution of Aerosol Concentration Distribution in the Atmosphere. BORIS KRASOVITOV, Tov Elperin, Andrew Fominykh, *Ben-Gurion University of the Negev*

Concentration measurements of aerosols in the atmospheric boundary layer revealed vertical (altitudinal) dependence of the aerosol concentration. Scavenging of aerosols by rains contributes to the evolution of vertical distribution of aerosols. At the same time the existence of vertical gradients of the aerosols in the atmosphere affects the rate of aerosols scavenging by rain droplets. In the present study we suggest a model of scavenging of aerosol particles by rain in the atmosphere with the nonhomogeneous initial distribution of aerosols. It is showed that dynamics of below-cloud scavenging of aerosols is described by an explicit analytical expression. Using the developed model we calculated temporal evolution of vertical concentration distribution of aerosols in the atmosphere. Calculations were performed for different measured vertical aerosol profiles available in the literature. Also it is shown that for the homogeneous initial distribution of aerosols in the atmosphere the obtained analytical expression recovers the well-known exponential dependence of the aerosol concentration on time. It is demonstrated that aerosols are washed down by rain to a zero concentration whereby the aerosol concentration distributions are calculated for the different values of rain intensity. The developed model can be used for the analysis of scavenging of aerosols in the atmosphere by rain and for validating the advanced models for predicting scavenging of aerosols by rain.

1CC.7

Biological Particles in Rain Events. J. ALEX HUFFMAN, Christopher Pöhlker, Ryan Mason, Anthony J. Prenni, Paul DeMott, Niall Robinson, David Gochis, Douglas Day, Viviane Després, Janine Fröhlich-Nowoisky, Eliza Harris, Isabell Müller-Germann, Beatrice Schmer, Bärbel Sinha, Anita Sun, Yukata Tobo, Meinrat O Andreae, James N. Smith, Jose-Luis Jimenez, Martin Gallagher, Sonia Kreidenweis, Allan Bertram, Ulrich Pöschl, *University of Denver, CO*

The content of the abstract has been embargoed.

1CO.1

Understanding the Role of a Nano Ce Additive in the Size Distribution and Organic Composition of the Particulate Phase of Diesel Emissions. DAVID NASH, Jason Weinstein, William Roberts, Tiffany Yelverton, Jost Wendt, Robert Willis, Gary Norris, William Linak, *U.S. EPA*

A number of alkali, alkaline earth, transition, and metalloid elements are known to act as fuel catalysts to limit the formation of soot precursors or promote its oxidation. These have been used with varying success on a variety of stationary and mobile combustion sources. Iron, cerium, and platinum additives have demonstrated abilities to reduce carbon monoxide and visible emissions of soot from diesel engines, so that there are now commercial products containing these elements being offered for this application. While the use of these additives may be effective in reducing particle mass emissions, and are reported to improve engine performance, their use without the accompanying use of diesel particle traps may result in increases in particle number emissions. Further, in addition to the emissions of the metals themselves, these catalysts may affect the composition and emissions of organic species. This study examines the use of nano cerium as a diesel fuel additive. Particle mass emissions, size distributions, morphology, and chemical composition are being characterized and compared to previous results using ferrocene. Dependent variables include fuel metal concentration and engine load. A Yanmar Powersystem YDG-5500E diesel generator is being used to produce representative diesel emissions. Particle mass measurements indicate that cerium is a more effective oxidation catalyst than iron. Particle size distributions indicate a decreasing accumulation mode and a growing ultrafine mode with increasing fuel cerium content. GC/MS analysis of filter samples show a significant increase in particle phase polycyclic aromatic hydrocarbons (PAHs), nitro PAHs (nPAHs), organic acids (OAs) and alkanes (ALs) per volume of exhaust, when cerium is added. Our current efforts employ electron microscopy to indicate where on or within particulate emissions cerium resides and how that might correlate to the relative abundance of each class of organics. Aerosol time-of-flight mass spectrometry (ATOF-MS) methods are being developed and compared with particle size classified inductively coupled plasma – atomic emission spectroscopy (ICP-AES) results to determine cerium’s relative abundance as a function of additive concentration and engine load, yielding information about particle formation mechanisms.

1CO.2

Characterization of Emissions Due to Internal Combustion of Nano-CeO_2 Doped Diesel Fuel. YEVGEN NAZARENKO, Leonardo Calderon, Lin Zhang, Jim Zhang, Paul Lioy, Kian Fan Chung, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

CeO_2 nanoparticles are increasingly being used as a fuel-borne catalyst to improve diesel combustion efficiency. It is unknown whether the addition of nano CeO_2 into diesel fuel alters physicochemical and toxicological properties of diesel exhaust particles. Here we characterized exhaust emissions resulting from combustion of nano-CeO_2 doped diesel fuel in a one-cylinder electrical generator (Yanmar) under 100% load. Envirox^{TM} CeO_2 additive (Energenics Ltd., UK) was mixed with regular ultra-low sulfur diesel fuel at 0 ppm (0X of CeO_2), 5 ppm (0.1X), 50ppm (1X – manufacturer's recommendation), and 500 ppm (10X). A portion of the exhaust was directed into a 25 m^3 stainless steel testing chamber where the exhaust mass concentration during characterization was maintained at approximately 300 $\mu g/m^3$. A Scanning Mobility Particle Sizer and an Aerodynamic Particle Sizer were used to measure aerosol number concentrations. Gas monitors were used to analyze concentrations of CO, CO_2, and NO_x.

We observed that the total aerosol number concentration increased with increasing CeO_2 concentration in the fuel: from 1.5×10^5 cm^-3 for diesel only (0X) to 3.6×10^5 cm^3 for 10X CeO_2. Concurrently, the mean particle diameter by number decreased with increasing CeO_2 concentration: from approximately 160 nm for diesel only (0X) to 100 nm for 10X CeO_2 and the decrease was statistically significant. At the same time, CO_2 concentration increased with moving from 0X to 10X of CeO_2: from approximately 1300 ppm to approximately 2250 ppm. Increasing CeO_2 concentration in the fuel also increased concentrations of NO_x (from 4500 ppb to 10200 ppb) and CO (~4 to ~6.4 ppm) in the exhaust.

The results show that per mass basis the use of CeO_2 additive leads to a reduced size of exhaust particles but might result in an increased concentration of ozone forming gases such as NO_x. The results will be verified for total emissions basis.

1CO.3

Physicochemical Characterization of Cerium Particles Generated by Combustion of Ce-Doped Diesel Fuel. ROBERT WILLIS, Kristin Bunker, Traci Lersch, Gary Casuccio, Eric Grulke, Natalia Mandzy, Joseph Conny, Michael Lewandowski, Jason Weinstein, Jonathan Krug, Kasey Kovalcik, *U.S. EPA*

Diesel engines emit large amounts of soot which degrades air quality and harms public health. Nanoscale metal-oxide fuel-borne catalysts (FBCs) have been shown to reduce soot emissions and improve fuel efficiency. FBCs utilizing nano-sized cerium oxide (ceria) particles are used in other countries, but are not currently approved for on-road use in the US. The EPA's Nanomaterial Research Strategy has targeted ceria as a nanomaterial of concern due to the potential for human and ecosystem exposure to nanoceria particles released to the atmosphere.

In order to understand the exposure potential and environmental fate of nanoceria particles from the use of FBCs, the EPA is conducting research to characterize the morphology, composition, and size distribution of cerium-rich particles generated by combustion of ceria-doped fuel. We will discuss results obtained using a nano-MOUDI™ cascade impactor to collect size-resolved particulate samples on filters (analyzed by ICP-MS) and TEM grids (analyzed with high-resolution electron microscopy).

Analyses of "aged" diesel exhaust showed Ce-rich particles ranging in size from ~12-80 nm, some enclosed within a Ca-rich shell, embedded in or decorating soot particles; no isolated ceria particles were observed. The smooth, rounded morphologies of most of the Ce-rich nanoparticles combined with their sizes, suggest a two-step process during combustion, in which the catalyst ceria particles quickly form aggregates which then fuse together or melt during high-temperature combustion. Experiments are underway to characterize fresh diesel emissions using a dilution manifold to simulate real-world tailpipe emissions. Size distribution data show that, compared to fresh undoped emissions, the nanoceria FBC results in the appearance of a nuclei mode dominated by ceria particles < 30nm in size accompanied by a decrease in accumulation mode soot particles. Results of the characterization of the Ce-rich particles emitted from fresh diesel exhaust generated by combustion of ceria-doped diesel fuel will be presented.

1CO.4

Exhaust PM Measurement Using Low Cost Monitors: What They Measure and How Well. MATTI MARICQ, *Ford Motor Company*

With world wide tightening of engine exhaust PM emissions standards, PM measurement is becoming pervasive throughout the development, testing, and certification phases of motor vehicle production, and is extending as well to on-board diagnostics. At the same time we have seen considerable growth in the variety of instruments and methods to measure PM emissions. Well known devices, such as the scanning mobility particle sizer, electrical low pressure impactor, and aerosol particle mass analyzer are beneficial in the research phase to provide detailed characterization of exhaust PM. But they are less suited for routine test cell operation where simpler less costly devices are needed for long uninterrupted operation harsh environments. High end instruments, such as the Dekati Mass Monitor and Photoacoustic Soot Sensor are available for test cell environments, but their cost and size limits their widespread use.

This work examines three particle monitors: Dust Trak, Pegasor PPS, and DiSC. The intent is not to be comprehensive, but rather to contrast three different strategies aimed at quantifying PM emissions: light scattering, escaping charge, and diffusion size classification. We compare these monitors using both vehicle emissions tests and controlled laboratory aerosols. These monitors show good correlations with the transient changes in PM along a drive cycle, as also previously observed for the Dust Trak in EPA's Kansas City study. However, closer examination with laboratory aerosols reveals significant differences in how these monitors respond to the size and composition of the particles. These responses in turn tell us how robust the PM monitors are to changes in the nature of exhaust PM across different fuels and engine technologies.

1CO.5

Comparison of PM Emissions in Expanding Exhaust Plumes from Gas Turbine Engines burning Conventional and Alternative Fuels. PREM LOBO, Donald Hagen, Max Trueblood, Philip Whitefield, *Missouri University of Science and Technology*

Concern is growing about the emissions from aircraft operations and their impact on local air quality and health effects. The primary products of aviation fuel combustion are gas phase species such as NOx, UHC, CO, SOx, CO2, H2O, and Particulate Matter (PM). As the exhaust plume expands, mixes with ambient air, and cools, volatile compounds present in the gas phase at the engine exit plane, begin to condense on existing particles and form new particles. The nature of these secondary particles depends fuel composition, ambient meteorological conditions, and plume age. Recent studies focusing on the use of alternative fuels in gas turbine engines have shown that alternative fuels significantly reduce primary PM emissions. However, the impact of the emissions from aircraft engines burning these alternative fuels on the environment as the emissions evolve post combustion has not been fully explored.

The comparison of PM Emissions in an expanding exhaust plume from gas turbine engines burning conventional, Fischer-Tropsch (FT) and Hydroprocessed Esters and Fatty Acids (HEFA) fuels is presented here. The emissions data was acquired during two major field campaigns: the Sheffield APU Study conducted in Sheffield, UK in September 2009, and the Alternative Aviation Fuels EXperiment (AAFEX) II conducted in Palmdale, CA in March 2011. For the Sheffield APU Study, emissions were sampled 10m downstream of an auxiliary power unit where the total PM number and mass emissions were found to increase relative exit plane measurements and were attributed to gas-to-particle conversion in the exhaust plume. For the AAFEX II study, PM size, using a differential mobility spectrometer and soluble mass fraction (SMF), using a hygroscopic-tandem differential mobility analyzer were measured 143m downstream of a CFM56-2C1 gas turbine engine. SMF was found to increase with fuel sulfur content and engine power condition, and decrease with particle diameter.

1CO.6

Evaluation of Uncertainties in Aircraft Engine Soot Emissions Derived from Engine Smoke Number. MARC STETTLER, Adam M Boies, *University of Cambridge*

Aircraft gas turbine engines emit particles with a geometric mean particle diameter less than 100 nm consisting of non-volatile and volatile particles. The non-volatile component is primarily black carbon soot (BC). Current regulation is concerned with the visibility of aircraft exhaust, quantified via the engine smoke number (SN) and each engine type is measured before entering service. However, impact assessment of BC on climate and air quality requires mass based emissions estimates. As a result, a method called the First Order Approximation v3.0 (FOA3) is currently endorsed by the US Federal Aviation Administration and the International Civil Aviation Organization to estimate mass emissions of BC. This method relies on an empirical relationship between BC mass concentration in an exhaust sample and resultant SN. We describe how this method, relying on SN, shows a factor of ten or more discrepancy with recently published measurement data for 40% of cases compared. Flexibility within the SN measurement standard procedure is potentially a significant contributing factor. We describe results from a recent experimental study to examine the influence of changing incident flow velocity (a function of filter diameter), sampling line temperature and sample line length within the prescribed ranges. These results are important to quantify the error associated with current estimation methods used in airport emissions inventories and motivate the development of alternative methods independent of SN.

1CO.7

The Investigation of Water-Insoluble Particle Emissions of Butanol and Ethanol Gasoline Mixtures. DANIEL SHORT, Diep Vu, Maryam Hajbabaei, Georgios Karavalakis, Thomas D. Durbin, Akua Asa-Awuku, *University of California, Riverside*

Particle number and size information is important for anthropogenic combustion effects on air quality, climate, and health. The composition of particles from vehicular fuel combustion, may contain water insoluble black carbon (BC) and other insoluble material that modify particle nucleating properties. Conversely, the soluble fraction is important for particle water–uptake and wet deposition processes. Changes in fuel composition will modify the emissions of insoluble materials. Fuel mixtures of ethanol or butanol in gasoline are likely to decrease water-insoluble particle fractions. Compared to ethanol, butanol exhibits high energy content, better fuel economy, and more efficient combustion characteristics. The introduction of new engine technologies may also affect emissions and ultimately air quality. The penetration of gasoline direct injection (GDI) vehicles is expected to rapidly grow in the near future in both the US and European markets. However there are concerns that their elevated particulate emissions may adversely affect air quality, as they emit 3 to 4 times more particles than port fuel injection (PFI) counterparts.

In our study, ultrafine particle size and number concentrations are measured from a combination of conventional, flexible fuel, and GDI vehicles of leading automobile manufacturers. The particle emissions from different ethanol butanol blends in gasoline are compared. A water-based condensation particle counter (CPC) and a butanol-based CPC measure tail-pipe particle number concentrations from each fuel. Both instruments are coupled with a Scanning Mobility Particle Sizer (SMPS). Our measurement and analysis technique exploits the differences in particle distributions from the CPCs to infer insoluble particle mass fractions from real-time emissions. The data is correlated with BC measurements obtained with a Multi-Angle Absorption Photometer (MAAP). The contribution of insoluble mass from insoluble BC is determined. The results of this study will improve our understanding of alternative fuel mixture emissions for particle effects on air quality and climate.

1IM.1
Importance of Temperature Calibration for the Sunset Laboratory Carbon Analyzer: NIOSH and IMPROVE Temperature Protocols. JELICA PAVLOVIC, John Kinsey, *ORISE U.S.EPA*

The Sunset Laboratory Dual-Optical Carbon Analyzer, which simultaneously measures transmission and reflectance signals, is widely used in thermal-optical analysis of particulate matter samples. Most often, it is used to measure total carbon (TC), organic carbon (OC), and elemental carbon (EC) fractions, but also the thermal sub-fractions of OC and EC for source identification purposes. Previous studies (1, 2) have showed that the sample (filter) temperature and front oven temperature measured by the thermocouple (setpoint temperature) can differ by 10 to 50^{o}C. Hence, that temperature disagreement can substantially affect the OC/EC split and further influence the OC and EC concentrations. Since temperature precision in thermal-optical analysis is highly desired, Sunset Laboratory developed a temperature calibration procedure for the temperature sensor built into the front oven of the instrument. That procedure significantly reduced the temperature differences between the setpoint and the sample (filter) temperature, thus providing more confidence in the results. In addition, this method also improves inter-laboratory comparisons. Our experiments thoroughly investigated and clearly showed the need for temperature calibration of each Sunset Carbon Analyzer to obtain more accurate filter temperatures, improve comparability of OC and EC fractions and sub-fractions, and make the method more reliable in source apportionment studies.

Temperature calibrations were performed at NIOSH 5040 and IMPROVE operating conditions to determine the filter/setpoint temperature relationships for both methods. The measured temperatures and the differences between the setpoint and filter temperatures for both methods were investigated. Along with those results, the differences between TC, OC, and EC fractions, as well as OC and EC sub-fractions, before and after temperature calibration for both analysis protocols were also investigated.

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1IM.2
Development of an In Situ Thermal Desorption Gas Chromatograph for Intermediate-Volatility and Semi-volatile Organic Compounds. YUNLIANG ZHAO, Nathan Kreisberg, Susanne Hering, Allen H. Goldstein, *University of California, Berkeley*

Intermediate-volatility and semi-volatile organic compounds (I/SVOCs) have been shown to play a significant role in the formation of secondary organic aerosol; however, the abundance and composition of I/SVOCs in the atmosphere is poorly understood partly due to the lack of instrumentation capable of in-situ measurements of these compounds. In response to this need, we have developed a new sampling inlet and a new collection and thermal desorption system for the Thermal desorption Aerosol Gas chromatography instrument (TAG) to extend its capability to speciated analysis of I/SVOCs. The new sampling inlet consists of two parallel sampling lines, a bypass line and an activated carbon denuder line. The new collection and thermal desorption system consists of a metal fiber filter collection cell and a cold trap made of a section of metal capillary column. Gases and particles are collected by the metal fiber filter with phase partitioning determined by periodic sampling through the denuder. Organics thermally desorbed from the filter are refocused onto the cold trap followed by thermal transfer into a gas chromatograph/mass spectrometer (GC/MS) for analysis. Extensive laboratory tests were made to develop the operating method and to evaluate the performance of these new components. Results demonstrate that the combination of the new collection and thermal desorption system and GC/MS is able to quantitatively measure organic compounds with vapor pressures lower than n-tetradecane (C14). The revised instrument was used to measure speciated I/SVOCs in Berkeley, CA in a fully automated, continuous mode of operation. These measurements not only provide the direct examination of gas/particle partitioning of organic compounds, but also provide source markers for gas-phase organics that serve to constrain the abundance of primary I/SVOCs in the atmosphere. Additionally, these measurements show that many of the organic markers for organic aerosol are actually present as SVOCs.

1IM.3

Development of a Highly Specific and Sensitive Technique to Measure Organic Nitrogen in Atmospheric Aerosols.

JACQUELINE HAMILTON, Mustafa Ozel, Lewis Alastair, *University of York*

Atmospheric particles typically have high concentrations of nitrogen and are a significant source of fixed nitrogen to the environment. While the sources, formation and composition of oxygenated organics in the atmosphere have been extensively studied in recent years, organic nitrogen (ON) has not received the same attention, in part due to a lack of suitable analytical techniques. We have developed a sensitive and quantitative method for the speciation of ON within atmospheric aerosol. Aerosol filter samples were extracted into water followed by solid phase extraction, before analysis by comprehensive gas chromatography with a nitrogen chemiluminescence detection system (GCxGC-NCD). The GCXGC-NCD instrument shows high selectivity, only giving a response for ON compounds and thus removing the complex aerosol matrix. In addition, it gave an equimolar response for most organic nitrogen species, which allowed quantification of total ON content in aerosol samples even when the exact molecular structure was unknown or where standards were not available. It shows high sensitivity, with limits of detection determined to be in the range of 0.16-0.27 pgN. A range of organic aerosol compositions have been analysed including urban aerosol, household dust and secondary organic aerosol formed in simulation chamber experiments. For example, a total of 57 ON compounds were found in urban aerosol collected in Birmingham, UK, (including 10 nitriles, 9 alkyl nitro compounds, 4 nitro-phenols, 4 amides, 3 nitrosamines and 2 nitro-PAHs). The average mass loading of the total identified ON was 532 ngON m_{-3}. The average ON:OC (in terms of ngN:ngC) was 0.022:1 which equates to a C:N ratio of 53. The high sensitivity and selectivity demonstrated by the GCXGC-NCD, makes the technique a significant improvement over previous laboratory methods for ON analysis and it shows promise as a technique to study ON throughout the atmosphere.

1IM.4

Infrared Spectroscopic Determination of Aerosol Organic Mass using Partial Least Squares Regression.

TRAVIS RUTHENBURG, Ann Dillner, *University of California, Davis*

The organic fraction of aerosols is known to affect visibility, climate and health. The Interagency Monitoring of Protected Visual Environments (IMPROVE), established in 1985, operates a long term particulate matter monitoring network primarily in National Parks and Wilderness Areas. Laboratory standards comprising pure and mixed organic compounds with and without absorbing inorganic species are collected on polytetrafluoroethylene (PTFE) filters. Individual compound masses are determined gravimetrically and used to calculate organic functional group masses. Standards are analyzed using Fourier transform infrared (FT-IR) spectroscopy. Functional group masses and infrared absorbance spectra are used to create a multivariate calibration for organic mass using partial least squares regression (PLSR). Validation of the calibration and its use in the analysis of IMPROVE samples is discussed.

1IM.5

Semi-continuous Online Measurements of Reactive Oxygen Species in the Particle and Gas Phase. LAURA KING, Vishal Verma, Rodney Weber, *Georgia Institute of Technology*

Reactive oxygen species (ROS) have been linked to oxidative stress and acute inflammatory responses in the lungs; however, due to limitations in current monitoring capabilities the concentrations, sources or links to other gas and aerosol components of particle-bound ROS are not well known. Traditional particulate filter assessments are also limited due to potential sampling artifacts, highlighting the need for a continuous or semi-continuous method for quantifying ROS concentrations.

Two analytically similar semi-continuous online instruments have been developed to measure ROS. The first instrument uses a mist chamber to alternately collect ROS as a total gas and particle sample, and as a gas fraction. The second instrument uses the particle into liquid sampler (PILS) to collect ROS in the particle phase alone. Each instrument uses 2’,7’ dichlorofluorescin (DCFH) premixed with peroxidase from horseradish (HRP), combined with an fraction of the liquid sample to determine ROS concentration using a continuous flow through cell and spectrometer. The mist chamber system operates on a 10.5 minute cycle, analyzing a 5 minute sample, while the PILS system analyzes collected particles on a near-continuous basis, on a 5 minute cycle. The analytical systems have limits of detection of 2 nmol H2O2/L.

Results from ambient measurements of total ROS, gaseous ROS and particle ROS at contrasting sites will be presented along with ROS phase correlations with other gas and particle phase air quality parameters.

1IM.6

A Long Path Absorbance Photometer for the Determination of Peroxide Content and Brown Carbon in Organic Aerosol.JOSEF DOMMEN, Peter Mertes, Stephen Platt, Imad El Haddad, Lisa Pfaffenberger, Andre Prévôt, Markus Kalberer, Urs Baltensperger, *Paul Scherrer Instiute*

Organic aerosols are composed of thousands of different organic molecules. These compounds have low vapour pressures and must therefore contain many functional groups, e.g. alcohols, carbonyls, carboxylic acids and peroxides. Of these groups, organic peroxides are the least understood. They are difficult to measure and they have been quantified in only few studies. Furthermore it is assumed that they contribute to adverse health effects because of their high reactivity and high oxidation potential.

Not only black carbon but also many organic compounds are light absorbing. The occurrence of such compounds in organic aerosols has been referred to as brown carbon. Incomplete combustion, especially associated with biomass burning has been shown to produce particulate brown carbon. However, brown carbon formation and its removal by photochemical oxidation is not well understood.

Here we present an instrument for the quantification of peroxides in aerosol particles based on iodometry and long path absorption photometry (Peroxide-LOPAP). Extraction, chemical conversion and subsequent measurement of the aerosol samples are performed in a closed, oxygen-free environment. The limit of detection is 0.1 micromolar peroxide, which is orders of magnitude lower than previously obtained.

The method measures quantitatively all peroxides except for very stable compounds like tert-butyl hydroperoxide. Thus, with this instrument the total concentration of peroxides in the aerosol is effectively measured. Since the measurement technique relies on absorption we also measured the light absorbance of other species extracted from the aerosols.

Primary and secondary organic aerosols (POA, SOA) from the following sources were investigated for peroxides and absorbance: SOA from ozonolysis and photooxidation of alpha-pinene, POA and SOA of emissions from wood burning, a diesel car, a two-stroke scooter and cooking.

The highest amount of peroxides with 34% (assuming a molecular weight MW of 300 g/mol) was found in freshly generated SOA from alpha-pinene ozonolysis.

1IM.7

Extractive Electrospray Ionisation (EESI): A Novel Mass Spectrometry Technique for the Online Characterization of Organic Aerosol. PETER GALLIMORE, Markus Kalberer, *University of Cambridge*

Organic compounds are often the dominant fraction of tropospheric aerosol. Despite this, our understanding of the composition of organic aerosol is limited. A lack of detailed knowledge of the chemical composition of aerosols limits our understanding of their effect on climate and air quality.

We present a new technique for online measurement of the compounds present in organic aerosol: Extractive Electrospray Ionization (EESI) coupled to Mass Spectrometry (MS). In this method, a plume of charged solvent droplets is generated using an Electrospray Ionisation (ESI) source. Aerosol particles are directed into this spray and particle-into-droplet extraction occurs, dissolving the soluble aerosol components. The volatile solvent evaporates and gas-phase aerosol analyte ions are formed and sampled at the MS inlet. We present here a custom-designed EESI source which has been designed and optimized to interface with a commercial Ultra-High Resolution Mass Spectrometer.

EESI-MS offers a number of advantages: The online ionization mechanism provides composition information on aerosols in flow-tube and chamber studies with a time resolution of seconds, without the potentially large sampling artefacts introduced by collecting aerosols onto substrates for offline analysis. The ionization process produces molecular ions with minimal fragmentation, which greatly aids the interpretation of spectra for complex mixtures.

We have demonstrated high sensitivity for aerosols composed of oxidized organic compounds. For example, tartaric acid aerosol can be detected at mass concentrations below 0.1 micrograms per cubic meter, with a dynamic range of about 3.5 orders of magnitude, using tandem MS experiments.

EESI can be used for detailed aerosol composition studies and elucidation of particle-phase reaction kinetics. Time-resolved measurements of ozonolysis reaction products of oleic acid aerosol show the formation of oligomers. The average length and oxygen:carbon ratio of these oligomers increase with reaction time, which has implications for particle viscosity, hygroscopicity and phase.

1UA.1

Organic Aerosol Composition, Sources, and Modeling for Los Angeles during the 2010 CalNex Campaign. Patrick Hayes, JOSE-LUIS JIMENEZ, Michael Cubison, Amber Ortega, James Allan, Jessica Gilman, William C. Kuster, Joost de Gouw, Gabriel Isaacman, David Worton, Nathan Kreisberg, Susanne Hering, Allen H. Goldstein, Rebecca Washenfelder, Jonathan Taylor, Rainer Volkamer, Eleanor Waxman, Ryan Thalman, Rodney Weber, Xiaolu Zhang, et al., *University of Colorado*

Data from an HR-ToF-AMS and complementary instrumentation are used to characterize organic aerosol (OA) during the CalNex-Los Angeles campaign. Positive matrix factorization (PMF) identifies hydrocarbon-like OA (HOA), cooking-influenced OA (CIOA), semi-volatile oxygenated OA (SV-OOA), low-volatility oxygenated OA (LV-OOA), and local OA (LOA), which contains prominent amine fragments. The correlations of the PMF components with tracers and photochemical age indicate that, similar to previous work, HOA is a surrogate for primary organic aerosol from combustion sources, and the OOA components are dominated by secondary organic aerosols (SOA). The HOA and BC concentrations exhibit weekly cycles with substantially lower concentrations on Sundays versus weekdays that are quantitatively consistent with the reductions in diesel emissions during weekends, while OOA does not appear to vary, consistent with recent results indicating the dominance of gasoline emissions on SOA formation. The OOA to odd-oxygen (O3 + NO2) ratios for Pasadena are similar to those observed in Riverside and Mexico City, which suggests that the relative SOA vs. odd-oxygen formation efficiencies are similar at the different sites. In addition, the dilution-corrected OA enhancements for the Pasadena ground site increase with photochemical age and are similar to or slightly higher than analogous data from Mexico City and northeastern United States. The OA elemental composition evolves in a Van Krevelen diagram (H:C vs. O:C) with a slope of -0.6, which confirms that the aging of ambient OOA follows a slope considerably shallower than -1, and near -0.5. A box model of SOA formation along in-basin trajectories is implemented following Washenfelder et al. (JGR 2011), and constrained with VOC and oxidant measurements. SOA formation is an order of magnitude larger than can be explained with aromatic precursors, as observed in many other urban areas. Results for other sets of precursors such as S/IVOCs will also be presented.

1UA.2

Organic Aerosol Characterization of the Los Angeles Basin from Aircraft Measurements during CalNex. JILL CRAVEN, Andrew Metcalf, Richard Flagan, John Seinfeld, *Caltech*

An Aerodyne C-ToF Aerosol Mass Spectrometer was deployed on the CIRPAS Twin Otter in May 2010 during the CalNex field campaign. The organic aerosol, composing just above 40 % of the total aerosol mass for the Basin on average, is decomposed into HOA and OOA-like factors with PMF analysis. High organic aerosol loadings were measured downwind of downtown Los Angeles resembling HOA-like aerosol, whereas the Northeastern region of the Basin with similar load- ings was richer in OOA-like aerosol. The O:C ratio of the aerosol in the Basin, was lower than that measured in the Basin outflow. PMF results are supported with AMS inorganic mass time traces, SP2 measurements of black carbon mass loading and coating thickness, and compared to previous field campaign organic mass spectra.

1UA.3

Comparison of Estimates of Airmass Aging Using Particle and Other Measurements near Fort Worth, TX. BASAK KARAKURT CEVIK, Robert Griffin, Andrew Rutter, Barry Lefer, James Flynn, Saewung Kim, *Rice University*

The composition, concentration, and size of submicron aerosols were measured by an Aerodyne high-resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) at a rural location northwest of the Dallas-Fort Worth, TX, area for the month of June 2011 with a time resolution of five minutes. A TSI, Inc., Model AE51 aethalometer using an optical absorption technique also was deployed measure black carbon (BC) concentrations. The total PM_1 mass concentration ranged between 1.01 micro-gram/m^3 and 17.92 micro-gram/m^3, and the mean mass concentration was 4.92 micro-gram/m^3.Significant variability is observed in the time series of total PM_1 and of all four HR-ToF-AMS species, particularly between 21st and 25th of June. The average aerosol composition was dominated by organic matter (54%) and sulfate (24%).Organic aerosol concentrations were highly correlated with carbon monoxide (CO) (R^2=0.64) and BC (R^2=0.48), which are anthropogenic tracers.

Because of the large influence of organics on total aerosol concentration, various techniques associated with organic material are used to estimate the extent of aerosol aging. For example, the average DOA/DCO at this field site during this time was 81.97 ± 34.78 micro-gram/ (m^3 ppmv), which is a typical value for an aged air mass. Other metrics of age include the ratio of OOA2 to OOA1 (more oxidized to less oxidized material), the ratio of sulfate to sulfur dioxide, the ratio of isoprene to its oxidation products, and the ratio of NO_x to NO_y. All metrics point to an aged air mass, but variations in these age matrices help determine the relative contributions of biogenic versus anthropogenic precursors to organic aerosols at the site.

1UA.4

Source Apportionment of Organic Aerosols and VOCs Near Fort Worth, TX. ANDREW RUTTER, Basak Karakurt Cevik, Longwen Gong, Kabin Shakya, Caroline Gutierrez, Melanie Calzada, Saewung Kim, Robert Griffin, James Flynn, Barry Lefer, *Rice University*

An air quality study of the outflow from the Dallas-Fort Worth, TX, metropolitan area was conducted in June of 2011 at a downwind, rural location northwest of Fort-Worth. Measurements of the composition of organic aerosols and volatile organic compounds were made between June 4 and June 30, 2011. Organic aerosol composition was determined using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer. Positive Matrix Factorization (PMF) was used to separate the organic aerosols measured into hydrocarbon-like organic aerosols (HOA) and two classes of oxidized organic aerosols (OOA 1 and 2), where OOA2 was the more oxidized of the two classes. HOA constituted 12% of measured OA mass on average, while the oxidized classes OOA1 and 2 constituted 43% and 41%, respectively.

Volatile organic compounds were measured using an Auto Gas Chromatograph operated by the Texas Commission for Environmental Quality (TCEQ) and a proton-transfer reaction mass spectrometer operated by our research team. The VOC measurements were combined with measurements of ozone, carbon monoxide, and nitrogen oxides, and were entered into a PMF model separate from that used for the organic aerosols. This PMF model identified six source categories: Natural Gas, Fuel Evaporation, Motor Vehicles, Biogenics, and two oxidation factors.

Relationships between the organic aerosol and VOC source factors were observed, allowing a qualitative assessment of whether the organic aerosols measured originated from anthropogenic or biogenic sources.

1UA.5

Understanding Intra-Neighborhood Patterns in Fine Particulate Air Pollution Using Mobile Monitoring in Braddock, PA. Brett Tunno, Kyra Shields, Paul Lioy, Nanjun Chu, Joseph Kadane, Bambang Parmanto, Gede Pramana, Jennifer Zora, CLIFF DAVIDSON, Fernando Holguin, Jane Clougherty, Daniel S. Tkacik, Andrew A. May, *Syracuse University*

Braddock, Pennsylvania is home to the Edgar Thomson Steel Works (ETSW), one of the few remaining active steel mills in the Pittsburgh region. An economically distressed area, Braddock exceeds average annual (15 micrograms/m3) and daily (35 micrograms/m3) National Ambient Air Quality Standards (NAAQS) for particulate matter (PM2.5). A mobile air monitoring study was designed and implemented in morning and afternoon hours in the summer and winter (2010-2011) to explore the within-neighborhood spatial and temporal (within-day and between-day) variability in PM2.5 and PM10. Both pollutants displayed spatial variation between stops, and substantial temporal variation within and across study days. For summer morning sampling runs, site-specific mean PM2.5 ranged from 30.0 (SD = 3.3) to 55.1 (SD = 13.0) micrograms/m3. Mean PM10 ranged from 30.4 (SD = 2.5) to 69.7 (SD = 51.2) micrograms/m3, respectively. During summer months, afternoon concentrations were significantly lower than morning for both PM2.5 and PM10, potentially owing to morning subsidence inversions. Winter concentrations were lower than summer, on average, and showed lesser diurnal variation. Temperature, wind speed, and wind direction predicted significant variability in PM2.5 and PM10 in multiple linear regression models. Information obtained on peak concentration periods, and the combined effects of industry, traffic, and elevation in this region informed the design of a larger stationary monitoring network.

1UA.6

Factors and Particle Dynamics Controlling Pollutant Plume Length Downwind of Major Roadways in Nocturnal Surface Inversions. WONSIK CHOI, Meilu He, Vincent Barbesant, Kathleen Kozawa, Steve Mara, Arthur Winer, Suzanne Paulson,*University of California Los Angeles*

Recent epidemiological and toxicological studies have shown evidence for significant impacts on human health from exposure to fresh vehicular emissions. The pollutant plumes from major roadways generally can impact near roadway neighborhoods over a much wider area under stable atmospheric conditions (> 2 km) than unstable convective boundary layers (< 300 – 500 m). However, factors controlling pollutant plume length downwind of line sources still need to be quantitatively understood for the precise prediction of plume impacts. This study focuses on understanding (1) what are the major contributors to the extent of freeway plumes for the pre-sunrise periods, and (2) how freshly-emitted ultrafine particles (UFP) evolve in their characteristics during downwind transport periods.

We have measured spatial concentration profiles of pollutants emitted from major roadways for stable pre-sunrise periods (4:00 – 6:30 A.M.) using an electric vehicle mobile monitoring platform with no emissions of its own in the California's South Coast Air Basin (SoCAB). Curve fits using a Gaussian dispersion model solution were successfully applied to obtain both the dispersion coefficients and particle number emission factor (PNEF) directly from the observed UFP concentration profiles. The dispersion coefficients ranged more widely than conventionally used Briggs' values with strong correlations with meteorological parameters as well as with differences between the background and plume peak concentrations. These relationships were applied to predict freeway plume transport using a multivariate regression method. The mean PNEF for a mixed vehicle fleet on the four freeways studied here was estimated as 1.2×10^{14} particles·mi^{-1}·vehicle^{-1}, which is 15% of a previously estimated value for the I-405 freeway in 2001, implying significant reductions in UFP emissions over the past decade in the SoCAB.

Preliminary results of observed particle dynamics from size-segregated UFP concentration profiles, including dilution, evaporation/condensation, coagulation, and production rates with distance downwind of the freeways, are also presented.

1UA.7

Ultrafine Particle Infiltration to Passenger Vehicle Cabins: the Effects of Driving Speed and Ventilation Setting. EON LEE, Yifang Zhu, *University of California, Los Angeles*

Previous studies have found motor vehicle emissions leaking into vehicle cabins. However, few studies characterized location-specific infiltration and its contributions to in-cabin air quality. The present study examined ultrafine particle (UFP) infiltration in five passenger vehicles including a minivan and four sedans under different ventilation modes (i.e., off, outside air intake (OA), and recirculation (RC)) on both local and freeway routes. We observed high variability in mechanical ventilation fan settings among tested vehicles (i.e., 4 to 12 steps) and applied an equal measure of quartile fan settings to all the vehicles. This study first distinguished in-cabin UFP penetration by incursion routes: mechanical ventilation and infiltration through leakages. The primary leakage locations were identified at side-doors and rear-trunk by measuring UFP concentration gradients and differential pressure between in-cabin and across potential leakage areas. We found the infiltration amount through the leaks were different by leakage location, driving speed, ventilation modes, and fan settings. Increases in driving speed created differential pressure up to 300 Pa for passenger cars and 100 Pa for the minivan primarily because of aerodynamic changes on the moving vehicle. In contrast, the differential pressure between in-cabin and rear-trunk remained positive in the range of 10 to 60 Pa with respect to driving speeds. It suggests that no leakage would occur through side-doors and rear-trunk as a result of cabin pressurization driven by mechanical ventilation under OA mode. Under RC mode, however, we consistently observed a negative differential pressure between in-cabin and rear-trunk suggesting that on-road pollutants could infiltrate through rear-trunk in RC mode regardless of vehicle type or driving speed. Under RC mode, depending upon vehicle envelope aerodynamics, infiltration through side-doors was inconsistent in terms of leakage flow direction (i.e., into or out of the cabin) and the amount of infiltration.

2AC.1

Secondary Organic Aerosol Formation from the Isoprene Ozonolysis: Effect of OH Radical Scavenger on the Radical Chemistry. KEI SATO, Satoshi Inomata, Risa Uchida, Takashi Imamura, Jun Hirokawa, Motonori Okumura, Susumu Tohno,*National Institute for Environmental Studies*

In laboratory experiments of ozone-alkene reactions, radical scavengers are used to suppress reactions with OH radicals produced. The secondary organic aerosol (SOA) yields from the ozone-cyloalkene reactions are known to be dependent on the scavenger compound. In this study, we conducted ozone-isoprene reaction experiments using (1) no scavenger, (2) cyclohexane as the scavenger, or (3) carbon monoxide as the scavenger. A 6-m3 evacuable chamber was used. The concentrations of ozone and isoprene were monitored by FT-IR. The size-distribution of SOA was monitored by SMPS. The SOA yields of experiments 1, 2, and 3 were determined to be 1.2%, 1.3% and 0.3%, respectively. The rate constant determined for the ozone-isoprene reaction from reactant time profile data of experiments 2 and 3 agreed with the literature values. The fraction of 2-methyltetrols to total SOA mass measured by derivatization-GC/MS analysis in experiment 1 was much higher than those measured in experiments 2 and 3. These results suggest that the OH + isoprene reaction is successfully suppressed in the experiments conducted using the scavenger. Only in the SOA offline sample obtained in experiment 2, adipic acid and C6 hydroxycarboxylic acid were detected. On the other hand, ozone/propylene/cyclohexane system experiment was conducted to study SOA formation from the OH + cyclohexane reaction; however, the concentration of SOA produced was very low; and the C6 products were not detected in the offline sample. The C6 products detected in experiment 2 will be produced as a result of coexistence of RO2 radicals from the OH + cylcohexane reaction and products from the ozone-isoprene reaction. The SOA yield measured using CO represents a value which is not affected by reactions with RO2 radicals originated from radical scavengers. The SOA yield measured in this study using CO was about one third of those measured in the previous study using n-hexane.

2AC.2

Investigation of SOA Composition from the Photolysis of 1-Nitronaphthalene using Single Particle Mass Spectrometry.ROBERT HEALY, Yang Chen, Ivan Kourtchev, Markus Kalberer, John Wenger, *University College Cork*

Nitro-substituted polycyclic aromatic hydrocarbons are of interest due to their associated mutagenic and carcinogenic effects. 1-nitronaphthalene is emitted directly from combustion processes such as vehicle exhaust, but is also formed through the reaction of naphthalene with the hydroxyl or nitrate radical in the presence of NOx. Photolysis has previously been demonstrated to be the major degradation pathway for 1-nitronaphthalene in the troposphere. A series of simulation chamber experiments has been performed to investigate the chemical composition of SOA formed through the direct photolysis of 1-nitronaphthalene using an Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS, TSI). SOA forms rapidly with a yield of up to 50% depending on precursor concentration and photolysis rate. Along with expected products such as naphthoquinone and nitronaphthol, condensed species exhibiting mass spectra consistent with the presence of four aromatic rings were also observed. It is proposed that these species may be formed through dimerization of naphthoxy radicals generated during the photolysis process. Further evidence to support this mechanism was obtained when 1-nitronaphthalene was photolyzed in the presence of excess nitrobenzene. Dimers were then formed containing three aromatic rings, consistent with the reaction of phenoxy and naphthoxy radicals. The molecular formulae of the dimers were also confirmed by collecting SOA on filters and analysing the extracts off-line using an LTQ Orbitrap Velos mass spectrometer (Thermo-Fisher Scientific), fitted with a TriVersa NanoMate chip-based electrospray ionization source (Advion Biosystems). These findings demonstrate the advantages of single particle mass spectrometry as a tool for the investigation of SOA products in simulation chamber studies.

2AC.3

Displacement of Ammonium from Aerosol Particles by Uptake of Triethylamine. Lap P. Chan, CHAK K. CHAN, *Hong Kong University of Science and Technology*

The displacement of ammonium by triethylammonium (TEAH) in aerosol particles of about 15–35 μm in diameter was investigated using an electrodynamic balance (EDB) coupled with in situ Raman spectroscopy. The phase state of particles played a crucial role in the extent of triethylamine (TEA) uptake. At 50 or 75% relative humidity (RH), the heterogeneous uptake of about 40-ppm TEA by aqueous ammonium salts of sulfate [(NH4)2SO4], bisulfate (NH4HSO4), nitrate (NH4NO3), chloride (NH4Cl), and oxalate [(NH4)2C2O4] led to increases in particle mass of over 90%. A complete displacement of ammonium by TEAH was confirmed by direct EDB mass measurements and the Raman spectra obtained. TEAH sulfate was formed during the exposure of aqueous droplets of (NH4)2SO4 and NH4HSO4 to TEA vapor at 50% RH; but a fraction of it decomposed to TEAH bisulfate when the TEA supply was removed. Crystalline solid particles of (NH4)2SO4 and (NH4)2C2O4 experienced small mass increases of <5%, both of which were attributed to the hindered mass transfer of TEA in crystalline solids. However, TEA reacted with the amorphous solid NH4NO3 particle at <3% RH as effectively as if it was in the aqueous NH4NO3 droplet (50% RH) and formed TEAH nitrate. On the other hand, the amorphous NH4HSO4 solid particle reacted with TEA at <3% RH to form crystalline (NH4)2SO4 and liquid TEAH bisulfate and sulfate. The formation of rather inert crystalline (NH4)2SO4 suppressed the ammonium exchange.

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2AC.4

Gas-Particle Partitioning of Ammonia in the Fort Worth, TX Area. LONGWEN GONG, Rafal Lewichi, Robert Griffin, Andrew Rutter, Frank Tittel, Barry Lefer, James Flynn, Jack Dibb, Eric Scheuer, *Rice University*

In order to investigate the dynamics of ammonia in a suburban area expected by urban, industrial, and biogenic sources, intensive measurements of atmospheric ammonia were made northwest of Fort Worth, TX. The mixing ratio of ammonia ranged from 0.1 to 10.1 ppb with a mean of 2.7+/-1.7 ppb. A daytime increase was found, likely due to increasing ambient temperatures affecting temperature-dependent sources such as volatilization of animal waste and vegetation. Ammonia mixing ratios reached maximum values in the early afternoon, after which they decreased and remained relatively low during nighttime. Simultaneous measurements of aerosol and other gaseous species also were conducted. Particulate ammonium concentrations varied from 0.1 to 2.5 microgram/m^3 with a mean of 0.5+/-0.2 microgram/m^3, nitrate concentrations varied from 0.1 to 1.1 microgram/m^3 with a mean of 0.2+/-0.1 microgram/m^3, and sulfate concentrations varied from 0.2 to 6.0 microgram/m^3 with a mean of 1.2+/-0.6 microgram/m^3, respectively. Gaseous nitric acid levels ranged from 0.05 to 5.0 ppb with an average of 0.5+/-0.5 ppb and hydrochloric acid levels ranged from 0.03 to 2.0 ppb with an average of 0.4+/-0.3 ppb. The diurnal profile of the ratio of ammonia to total ammonia (=ammonia+ammonium) exhibited a similar trend to gaseous ammonia, and was anti-correlated with sulfate. Ammonia was present predominantly in the gas phase. The formation of ammonium nitrate and ammonium chloride was not observed; ammonium mainly existed in the form of ammonium sulfate. In addition, ambient aerosols were nearly neutral, indicating that sufficient ammonia was available to neutralize sulfuric acid in the atmosphere.

2AC.5

Chamber Simulation of Photooxidation of Dimethyl Sulfide and Isoprene in the Presence of NOx. Tianyi Chen, MYOSEON JANG, *University of Florida*

In the kinetic model of this study, to advance the photooxidation of DMS in the gas phase, the most recently reported reactions with their rate constants have been included. To improve the model predictability for the formation of sulfuric acid and MSA, heterogeneous reactions of gaseous DMS products [e.g., dimethyl sulfoxide (DMSO)] on the surface of aerosol have also been newly included in the kinetic model. DMS was photoirradiated in the presence of NO_x using a 2 m^3 Teflon film chamber. The resulting chamber data was simulated using the new kinetic model. The model predicted that concentrations of both MSA and H2SO4 would significantly increase due to heterogeneous chemistry included in this study and this was well substantiated with experimental data. The model used in this study also well predicted the decay of DMS, the formation of other gaseous products such as SO_2 dimethyl sulfone ($DMSO_2$), and the ozone formation linked to NO_x cycle. To study the effect of coexisting volatile organic compounds, the photooxidation of DMS in the presence of isoprene and NO_x has been simulated using the new kinetic model integrated with the Master Chemical Mechanism (MCM) for isoprene oxidation, and compared to chamber data. Both the model simulation and the experimental data showed an increase in the yields of MSA and H_2SO_4 as the isoprene concentration increased.

2AC.6

Characterization of Oligomers Products from Heterogeneous Acid-Catalyzed Reaction of Methyl Vinyl Ketone and Their Formation Reaction Mechanisms. Ka M. Chan, Dan D. Huang, Yong J. Li, Man N. Chan, John Seinfeld, CHAK K. CHAN, *Hong Kong University of Science and Technology*

Secondary organic aerosols (SOA) formation involves complex chemical processes in atmosphere. In this work, the heterogeneous acid-catalyzed reactions of gas-phase methyl vinyl ketone (MVK) with inorganic particles were investigated in a flow reaction system. MVK is one of the most important products from isoprene oxidation. The effects of particle composition and relative humidity (RH) on product formation were explored. Reactions on ammonium sulfate, ammonium bisulfate and sulfuric acid particles were studied. The experiments were conducted at RH40% and RH80%. Ultra-performance liquid chromatograph equipped with an electrospray ionization time-of-flight mass spectrometry (UPLC/ESI-TOFMS) and gas chromatography-mass spectrometry (GC-MS) were utilized to identify particle phase products for developing the reaction mechanisms.

Products in particle phase were detected when ammonium bisulfate and sulfuric acid particles were used. However no product was found when ammonium sulfate particles were used. Oligomeric products formed by i) acid-catalyzed hydration followed by oligomerization or ii) acid-catalyzed aldol reaction. Sulfuric acid particles yielded more and higher order oligomers up to hexamers than ammonium bisulfate did. Moreover, the acid-catalyzed aldol reaction occurred only in sulfuric acid particles but acid-catalyzed hydration followed by oligomerization occurred in both ammonium bisulfate and sulfuric acid particles. High relative humidity was found to favor hydration and facilitate the subsequent acid-catalyzed oligomerization. The formation of higher order oligomers suggests that reactive uptake of MVK could contribute significantly to SOA.

Acknowledgement: This work was supported by the Research Grants Council of Hong Kong (Project No. 610909).

2AC.7

Organic Hydroperoxides (ROOH) Photolysis as a Source of Hydroxyl Radicals (OH) in Aqueous SOA. DANA ALJAWHARY, Alex K. Y. Lee, Ran Zhao, Jonathan Abbatt, *University of Toronto*

Atmospheric particulate matter provides a medium into which gaseous organics can condense and further oxidize. While much is known about gas phase oxidation of organics in the atmosphere, there remains a large uncertainty associated with understanding the chemical processing of organics in the condensed phase. Measurements of the oxidants driving the chemical processing in the aqueous phase of organic aerosols are scarce. In addition, the sources of aqueous phase oxidants are not well characterized. Here, we propose that highly reactive OH radicals are recycled in the aqueous phase by the photolysis of organic hydroperoxides (ROOH). For this purpose, two sets of experiments were carried out: the photolysis of 1) a surrogate ROOH (t-butyl hydroperoxide) and 2) a chamber generated SOA, both in solution. The photolysis experiments were simulated under conditions mimicking those of ambient aerosols. OH radicals were measured indirectly by introducing an OH trap to the ROOH and SOA solutions. The OH probe, which is formed from the OH oxidation of the radical trap, was quantified and enabled OH production rate measurement. Photolysis products, precursor ROOH and OH probe concentrations were simultaneously detected using on-line ARI-ToF-CIMS. Intercomparison with off-line ROOH detection using the dichlorofluorescein (DCF) assay was also employed. The kinetics, products and OH yield from the photolysis experiments will be presented.

2AC.8

Photolysis of Aldehydes in Organic Matrices as a Model for Photolytic Processing of Organic Aerosols. SANDRA BLAIR, Dorit Shemesh, Benny Gerber, Adam Bateman, Sergey Nizkorodov, *University of California, Irvine*

Organic aerosols (OA) represent a major component of the atmospheric particulate matter. While the gas-phase photochemical processes leading to the formation of OA have been studied for a number of years, the importance of condensed-phase photochemistry occurring inside atmospheric OA has not been recognized until recently. The mechanisms of even the simplest condensed-phase photochemical processes, the effect of the organic matrix on these processes, and the role of direct vs. indirect photolysis in aging of OA are currently unknown. Our goal is to investigate the condensed-phase chemistry of carbonyl compounds and common constituents of OA embedded into organic matrices that appropriately mimic OA material. Saturated linear aldehydes, such as undecanal, are used as model systems. Our approach is to conduct detailed experiments on gas-phase and condensed phase photochemistry of selected aldehydes and carry out detailed ab initio calculations of their photochemical properties. We will report experiments on photolysis of pure liquid and solid undecanal studied with a combination of GCMS and UVVIS methods. We also present experimental data on gas-phase photolysis of undecanal studied with proton-transfer reaction mass spectrometry for comparison. The experimentally measured photolysis quantum yields and mechanisms will be compared with those predicted by the state-of-the-art on-the-fly photodissociation dynamics ab initio calculations in both gas and condensed phases. The relevance of these results for aging of OA under different atmospheric scenarios will be discussed.

2AC.9

Organosulfate Formation from 2-Methyl-3-Buten-2-ol (MBO) as a Secondary Organic Aerosol (SOA) Tracer in the Atmosphere. HAOFEI ZHANG, David Worton, Michael Lewandowski, John Ortega, Caitlin Rubitschun, Kasper Kristensen, Pedro Campuzano-Jost, Douglas Day, Jose-Luis Jimenez, Mohammed Jaoui, John Offenberg, Tadeusz Kleindienst, Jessica Gilman, Joost de Gouw, Chang Hyoun Park, Gunnar Schade, Amanda Frossard, Lynn Russell, Marianne Glasius, Alex Guenther, Allen H. Goldstein, John Seinfeld, Avram Gold, Richard Kamens, Jason Surratt, *University of North Carolina at Chapel Hill*

2-methyl-3-buten-2-ol (MBO) is an important biogenic volatile organic compound (BVOC) emitted by pine trees and a potential precursor of atmospheric secondary organic aerosol (SOA) in forested regions. In the present study, hydroxyl radical (OH)-initiated oxidation of MBO was examined in smog chambers under varied initial nitric oxide (NO) and aerosol acidity levels. Results indicate measureable SOA from MBO under low-NO conditions. Moreover, increasing aerosol acidity was found to enhance MBO SOA. Chemical characterization of laboratory-generated MBO SOA reveals that an organosulfate species ($C_5H_{12}O6_S$, MW 200) formed and was substantially enhanced with elevated aerosol acidity. Ambient fine aerosol ($PM_{2.5}$) samples collected from the BEARPEX campaign during 2007 and 2009, as well as from the BEACHON-RoMBAS campaign during 2011, were also analyzed. The MBO-derived organosulfate characterized from laboratory-generated aerosol was observed in $PM_{2.5}$ collected from these campaigns, demonstrating that it is a molecular tracer for MBO-initiated SOA in the atmosphere. Furthermore, mass concentrations of the MBO-derived organosulfate are well correlated with MBO mixing ratio, temperature, and acidity in the field campaigns. Importantly, this compound accounted for an average of 0.25% and as high as 1% of the total organic aerosol mass during BEARPEX 2009. An epoxide intermediate generated under low-NO conditions is tentatively proposed to produce MBO SOA.

2AC.10

Characterization of the Heterogeneous Aging of Secondary Organic Aerosols Formed via Isoprene Ozonolysis Using Aerosol Flow Tube - FTIR Spectroscopy. Demetrios Pagonis, Brian Bouchard, Jeff Baker, CINDY DEFOREST HAUSER, *Davidson College*

Isoprene is emitted by plants at a rate of 600 Tg yr-1, and is the second most abundant organic compound in the atmosphere, behind methane. When isoprene reacts with ozone, the oxidation products are less volatile and condense to form secondary organic aerosols (SOA). This is of particular concern in areas such as the southeastern United States, where there has been significant kudzu invasion. Kudzu is a strong emitter of both isoprene and ozone-forming compounds, creating an environment ripe for the production of SOA. These aerosols and their precursors undergo additional reactions after formation called heterogeneous aging. In these studies, we use a relative rates approach to study the heterogeneous aging of SOA generated through isoprene ozonolysis. The formation and aging processes are decoupled in space and time through the combination of a chamber, denuder and aerosol flow tube. The composition, concentration, particle size and number density of the aged aerosol is characterized using Fourier Transform Infrared Spectroscopy (FTIR) and a Scanning Mobility Particle Sizer (SMPS), allowing us to develop a kinetic model for the heterogeneous aging of isoprene SOA.

2AC.11

Computational Study Probing the Potential Energy Surfaces of Acid Catalyzed Particle Phase Reactions. IVAN PILETIC, Edward Edney, Libero Bartolotti, *U.S. Environmental Protection Agency*

The role of acidity in the growth of aerosol particles has been shown to be significant. Frequently, acid catalyzed reactions in aerosols lead to the formation of larger and/or more polar molecules that are less volatile. We have used density functional theory to investigate acid catalyzed condensed phase reactions involving representative low molecular weight epoxides, alcohols, aldehydes and carboxylic acids. The calculations typically involved the incorporation of several explicit solvent molecules (water) for solvation and proton transfer purposes. Long range effects from the surrounding medium in the aerosol phase are simulated using a polarizable continuum model. Reaction barriers and possible intermediates are determined using a nudged elastic band method to locate transition states (saddle points) and stationary points (minima). Refinements of structural optimizations were carried out using the M062x density functional and the 6-311++G** basis set. Transition state theory was applied to estimate reaction rate constants. It is shown that acidic species such as H3O+ may lower reaction barriers by > 10 kcal/mol so that certain reactions such as the hydrolysis of epoxides proceed readily.

2AC.13

The Atmospheric Organic Aerosol Explored Through High Resolution Mass Spectrometry. YIYI WEI, Tingting Cao, Yehia Mechref, Jonathan Thompson, *Texas Tech University*

The complexity of the organic aerosol often frustrates attempts to completely characterize this material on a molecular level. The required chemical analysis necessitates the ability to separate and speciate a broad variety of organics (alcohols, aldehydes, furans, amines etc.) that are often present at < ng m^{-3} levels. Recent advances in molecular mass spectrometry move this suite of techniques towards being an optimal analyzer. For instance, electrospray ionization (ESI) allow ionization of analytes with minimal fragmentation in the source, and high resolution mass analyzers can assign m / z values to within 5 ppm mass accuracy, which can allow unambigious assignment of molecular formula.

In this work, we have explored use of the Orbitrap high resolution mass analyzer to better understand the chemistry occuring during the ozonolysis of squalene within a 3.6 m^3 FEP lined chamber. Secondary aerosol generated in the chamber was collected on a filter from 0 to 1300 squalene ozonolysis lifetimes and analyzed in positive ion mode after extraction with 50:50 water / acetonitrile (ACN) with 0.05% formic acid preent. We observed approx. 1000 peaks in the mass spectrum in the m / z range of 100 - 500 with the most dominant peaks at 163.038, 149.022, and 279.159 m / z units. These peaks correspond to molecular formulas $C_9H_7O_3$, $C_8H_5O_3$, and $C_{16}H_{23}O_4$, respectively. In addition, results from ambient aerosol samples collected in Lubbock, TX will also be presented. The mass spectra of the water / ACN extracts of these samples exhibited over 1000 distinct peaks not present in the blank, illustrating the complexity of the organic aerosol - even in a region not heavily influenced by VOC emissions.

2AC.14

Implications of Aerosol-phase Photocatalytic Epoxidation and Ion-specific Enhancement of Organic Partitioning. GE YU, Frank Keutsch, *University of Wisconsin - Madison*

Organosulfates have been proposed as an important contributor to organic aerosol mass. It has been demonstrated that organosulfates can be formed in aerosol via reaction of epoxides with sulfate, highlighting the importance of understanding mechanisms of epoxide formation. We present a new pathway for epoxide formation via catalytic, photo-sensitized oxidation of alkenes in aerosol by molecular oxygen in the presence of alpha-dicarbonyls. We report the reaction kinetics and reaction products for different alkenes, as well as yields, which can reach 100% in 30 minutes of solar exposure. The high rate constants determined in our experiments as well as high alpha-dicarbonyl concentration in organic aerosol mass estimated by a statistical model suggest that this reaction may limit the lifetime of alkenes in the organic phase. The formation of epoxides has implications for not only organosulfate formation but also the production of other aerosol components, such as polyalcohols and organonitrates, and increases hygroscopicity of pure organic phase particles.

In addition to the formation of organosulfates, inorganic sulfate may influence organic aerosol mass and composition by modifying the partitioning of organic compounds between the gas and aqueous phases. It has recently been demonstrated that the Henry’s law coefficient of glyoxal is dramatically increased by as low as millimolar sulfate concentrations, and underlying physicochemical mechanisms have been proposed to account for this effect. We extend this previous work to other organic species to determine for which types of organics this effect is active and how important this effect may be, e.g., for anthropogenic (sulfate) influence on rural secondary organic aerosol formation.

2AC.15

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

Mineral dust aerosols contain approximately 3% iron by mass and can undergo long range transport resulting in an estimated 14-16 Tg of iron deposited into the oceans annually. Although there is significant iron deposition into the oceans, only a small percentage of it is soluble, and thus bioavailable. In high-nutrient, low chlorophyll ocean regions iron solubility may limit phytoplankton primary productivity. Researchers have examined the atmospheric transport processes iron-bearing particles undergo, but particle size has been overlooked. In this work, the effect of particle size on iron solubility in atmospheric aerosols is examined. Pure iron-containing phases (red hematite, black hematite, magnetite, goethite, illite, kaolinite, and quartz) were separated into five different size fractions (10-2.5, 2.5-1, 1-0.5, 0.5-0.25, and <0.25 micro-meter) and extracted into buffer solutions simulating environments in the transport of aerosol particles. Particle size was confirmed by scanning electron microscopy (SEM). The extracted mineral solutions were analyzed for soluble iron content by inductively coupled plasma-mass spectrometry (ICP-MS). Fe(II) and Fe(III) content was determined by a ferrozine/UV-VIS method. Preliminary results show low iron solubility (~0-0.3%) for iron oxides (hematite, magnetite, and goethite) and higher solubility (1-35%) for clays (kaolinite and illite) when extracted into an acetate and cloudwater buffers (pH 4.25-4.3). The iron solubility of the iron oxides and clays increases to approximately 0.5-3% and 5-70%, respectively, when extracted into a marine aerosol solution (pH 1.7). When extracted into the acetate and cloudwater buffer there is a trend showing higher iron solubility in the largest and smallest size fractions, with lower iron solubility is the mid-range size fraction (1-0.5 micro-meter). When extracted into the marine aerosol solution there is increased iron solubility with decreasing particle size.

2AC.16

A Chamber Study of the Aging of Reaction Products Formed by Photo-Oxidation of Beta-Pinene. MEHRNAZ SARRAFZADEH, Donald Hastie, *York University*

The chemical aging processes can influence both the chemical and physical properties of secondary organic aerosols (SOA) and subsequently their effects on climate change and human health. Further oxidation of primary oxidation products with oxidants such as hydroxyl radicals (OH) and ozone (O3) can result in either less volatile products which contribute to particulate mass or form higher volatility products which do not. However, little is known about the effects of aging on SOA.

In this study, beta-Pinene was oxidized by OH in the presence of NO in an indoor smog chamber until no beta-Pinene was measurable. The reaction products mixture was then subjected to high levels of OH and O3; which corresponded to multiple exposure days in the atmosphere. This was done to investigate the aging effects on organic aerosols. Oxidation products were then analyzed online using an atmospheric pressure chemical ionization tandem mass spectrometer (APCI-MS/MS). Both gas and particle phase products were analyzed to distinguish between the aging effects in the two phases. For investigating particle phase products, an on-line counter flow membrane denuder (CFMD) was successfully integrated with the smog chamber and APCI-MS/MS instrument set-up.

The results of this study highlighted the importance of OH induced aging which led to additional particulate mass formation, whereas aging with O3 did not show any visual impact. Also discussed are the changes in the chemical composition of oxidation products during aging with OH which was due to further oxidation of products in the gas phase and there was no evidence for particle phase reactions.

2AC.17

Detection of a Variety of Amines with Ambient Pressure Proton Transfer Mass Spectrometry. Kimberly Carlson, NATHAN FRESHOUR, Walker Glasoe, Baradan Panta, David Hanson, *Augsburg College*

Ammonia and amines are base molecules in the atmosphere that can have strong interactions with acid species. Among other roles, these nitrogenous base molecules are implicated in new particle formation along with sulfuric acid vapor. Described here are laboratory experiments where these species were monitored with an atmospheric pressure proton transfer mass spectrometer. Detection capabilities and sensitivities were evaluated for a variety of amines: alkyl, aromatic, aminoethanol, etc. Calibration procedures were developed to quantify the permeation rate of home-made permeation tubes. The results of computational fluid dynamics show the typical losses in a cylindrical flow reactor compare well with measurements in the effluent of a flow reactor used for laboratory nucleation studies. Measurements of amines in urban air that show a variety of amino species will be presented.

2AC.18

Selective Depletion of Branched and Higher-Volatility Alkanes in the Heterogeneous OH Oxidation of Motor Oil Particles.

Gabriel Isaacman, ARTHUR CHAN, Theodora Nah, Katheryn Kolesar, Chris Ruehl, David Worton, Drew Gentner, Timothy Dallmann, Thomas Kirchstetter, Christopher Cappa, Robert Harley, Kevin Wilson, Allen H. Goldstein, *University of California, Berkeley*

Motor oil serves as a useful surrogate for anthropogenic particulate emissions due to its compositional similarity to both diesel exhaust and the complex mixture of hydrocarbons observed in typical ambient aerosol samples. However, because of its complexity, detailed analysis of the composition and atmospheric degradation of complex hydrocarbon mixtures is difficult using traditional techniques. In order to improve this understanding, we subjected homogenously nucleated motor oil (15W-40) particles to heterogeneous hydroxyl radical oxidation. Samples were collected and analyzed by gas chromatography using vacuum-ultraviolet ionization and high resolution time-of-flight mass spectrometry (GC/VUV-HRTOFMS). This “soft” ionization technique allows us to classify compounds by carbon number, cyclization, and branching, providing nearly complete resolution of hydrocarbon mixtures. The distribution of branched isomers of alkanes was found to be different between diesel and motor oil, with fresh diesel exhaust shown to have a distribution similar to that of motor oil. In addition, we use high resolution analysis to extract the hydrocarbon fraction of the oxidized motor oil particles and compare relative reaction rates of various compound classes. Branched alkanes are found to have heterogeneous oxidation rates of 1.6 ± 0.3 to 2.1 ± 0.2 times faster than straight-chain alkanes depending on degree of branching, while cyclic compounds oxidize at 0.7 ± 0.2 times the average rate of alkanes. Higher volatility alkanes are observed to oxidize faster, while cyclic compounds do not strongly exhibit volatility dependent oxidation rates. These relative rates are expected to have significant effects on aerosol composition following multi-day atmospheric aging, as cyclization and branching impact ratios of fragmentation and functionalization.

2AC.19

Images Reveal That Atmospheric Particles Can Undergo Liquid-Liquid Phase Separations.

Yuan You, LINDSAY RENBAUM-WOLFF, Marc Carreras-Sospedra, Sarah J. Hanna, Naruki Hiranuma, Saeid Kamal, Mackenzie Smith, Xiaolu Zhang, Rodney Weber, John Shilling, Donald Dabdub, Scot Martin, Allan Bertram, *University of British Columbia*

A large fraction of submicron atmospheric particles contain both organic material and inorganic salts. As the relative humidity cycles in the atmosphere, these mixed particles can undergo a range of phase transitions, possibly including liquid-liquid phase separation. If liquid-liquid phase separation occurs, the gas-particle partitioning of atmospheric semi-volatile organic compounds, the scattering and absorption of solar radiation, and the uptake of reactive gas species on atmospheric particles may be affected. Here, using optical and fluorescence microscopy, we present images that show the coexistence of two non-crystalline phases in particles generated from samples collected on multiple days in Atlanta, Georgia, and in particles generated in the laboratory using simulated atmospheric conditions. These results show that atmospheric particles can undergo liquid-liquid phase separations. Applying these new results in a model analysis representative of the Atlanta region, we find that liquid-liquid phase separation can result in increased concentrations of gas-phase NO_3 and N_2O_5 due to decreased particle uptake of N_2O_5 in this region.

2AC.20

Aqueous Processing of Low Molecular Weight Carbonyls in Ammonium Sulfate Solutions. D M HABIB, Lynn Mazzoleni,*Michigan Technological University*

Glyoxal, methylglyoxal, glyoxylic acid, pyruvic acid, hydroxyacetone, glycoaldehyde, and oxalic acid were introduced individually into an aqueous ammonium sulfate solution. Among them glyoxal, methylglyoxal, glyoxalic acid and glycoaldehyde were observed to form light absorbing compounds with increasing absorption in the UV-Vis region with time. The light absorption and irreversible formation of the higher molecular weight species are related to the interactions of both ammonium and sulfate ions. This was deduced from the considerable differences in UV-Vis absorption between reaction solutions with ammonium sulfate and with ammonium chloride for the reaction mixture of methylglyoxal. The OC/EC measurements of reaction products indicate the formation of low volatility organic compounds and refractory components associated with the pyrolysis of organic compounds and higher temperature refractory compounds. Matrix assisted laser desorption ionization mass spectrometry analysis of the reaction products from methylglyoxal indicates the formation of higher molecular weight compounds up to 800 Da. In general, the mass spectra show a complex array of reaction products in the negative mode. This evidence is further supported by electrospray ionization mass spectrometry (ESI-MS), where we also detected negative ions up to 800 Da. In the experiments with pyruvic acid and glyoxalic acid in aqueous ammonium sulfate, decarboxylation was observed and evidenced by sodium hydroxide trapping of the effervescence. Experiments with oxalic acid showed that it is inactive with respective to the formation of higher molecular weight and light absorbing species. Overall, the pH of the solutions except for those with oxalic acid was found to decrease gradually with time which indicates active participation and consumption of ammonia (in equilibrium with ammonium) and/or production of organic acids in the reactions.

2AC.21

Modeling NOx-dependent Chemistry During Organic Aerosol Aging with the 2D-VBS. WAYNE CHUANG, Neil Donahue,*Carnegie Mellon University*

Organic compounds in the vapor phase undergo extensive chemistry in the atmosphere, resulting in more oxygenated species with higher polarities and lower vapor pressures than the parent species. These products can partition between the vapor and aerosol phases to produce secondary organic aerosols (SOA) and are modeled using the two-dimensional volatility basis set (2D-VBS), which tracks their oxidation states (O:C) along with their volatilities. However, current 2D-VBS implementations do not account for the NOx dependence of organic oxidation chemistry. Polluted air masses from urban areas tend to have higher levels of NOx. Reactions between NO and organo-peroxy radicals (RO2) will change the organic product distribution compared to low-NOx oxdiation. These differences have been treated in the simpler 1D-VBS but not in the 2D-VBS, where composition is tracked in addition to volatility. Organic nitrates, which can be 30-40% of the total high-NOx products, can be accounted for by creating a second layer of the 2D-VBS. High- and low-NOx products can then be treated with separate oxidation “kernels”. A parameter β is introduced to represent the fraction of RO2 that react with NO. Within the model, β is used as a form of mixing of the SOA yields from each condition. This extension of the 2D-VBS produces an atmospherically relevant model of organic aerosols aging and SOA formation, which we will illustrate with box-model simulations of chamber experiments, extrapolated to residence times typical of regional photochemical smog events.

2AC.22

The Role of Multiphase Aging in the Chemistry of Organic Aerosol. KELLY DAUMIT, Jesse Kroll, *MIT*

Atmospheric organic aerosol (OA) is known to undergo rapid oxidation ("aging"), involving changes to particle mass and oxidation state, over the timescale of several hours. However, laboratory studies generally cannot reproduce this rate of aging, requiring longer oxidant exposures to achieve the same degree of oxidation as in the atmosphere. As a result, the phases and mechanisms by which rapid aging of ambient OA occurs are poorly understood. The goal of this work is to determine the relative efficiency of aging OA in various phases through an examination of the partitioning and rates of oxidation. Oxidation of OA components can take place in the gas phase, condensed organic phase, or liquid water phase. The rate of oxidation in each case is a function of the rate coefficient, oxidant concentration, and fraction of the reactant present in that phase. This last quantity is controlled by the organic molecule’s saturation vapor pressure, its Henry's law constant, and the mass concentrations of the solvent (organic aerosol loading or liquid water content). This underscores the necessity for realistic partitioning conditions in experiments designed to represent ambient oxidation. In this work the contributions of these quantities to the oxidation rate of model organics are examined, in an effort to better understand the phase in which OA aging occurs. Aqueous-phase oxidation experiments will be conducted under partitioning conditions representative of the atmosphere, in order to gain insight into the kinetics of aging in the aqueous phase relative to that in the gas phase.

2AC.23

Modeling of Secondary Organic Aerosol from Aromatic Compounds in the Presence of SO2. YUNSEOK IM, Myoseon Jang,*University of Florida*

Atmospheric aerosols play an important role in environmental processes and significant fraction of atmospheric aerosols is a secondary organic aerosol (SOA) which is formed by gas and particle phase photochemical processes in the atmosphere. Even though SOA has been interested and studied by many research groups because of its significant impact on climate change and human health, many parts of chemical and physical processes related with SOA formation are unknown. Even though, some SOA formation models have been developed, their predictions have underestimated the field observations. In this research, a predictive model for the secondary organic aerosol (SOA) formation, including heterogeneous reaction and partitioning [Partitioning Heterogeneous Reaction Consortium Secondary Organic Aerosol Model (PHRCSOA)], has been developed to narrow the gap between the model predicted and field observed SOA mass. The PHRCSOA model was tested for the SOA produced from the photochemical reaction of toluene in presence of different concentrations of NOx and SO2 using the UF Atmospheric Photochemical Outdoor Reactor (UF-APHOR) dual chambers. To study effects of sulfuric acids on toluene SOA formation, SO2 was photochemically oxidized with toluene and applied to the PHRCSOA model of this study. The outdoor chamber study showed that SO2 increases the toluene SOA formation. For example, for the SOA from the toluene experiment (”Tol = 54ppb, NOx =18 ppb, SO2 = 28 ppb), the toluene SOA yield with SO2 increases by 137 % compared to the one without SO2.

2AC.24

Oxidative Aging of Organic Aerosol: Role of Carbon Skeleton and Fragmentation Reactions. JAMES HUNTER, Anthony Carrasquillo, Kelly Daumit, Eben Cross, Douglas Worsnop, Jesse Kroll, *MIT*

The atmospheric aging of organic aerosol involves a complex interplay between oxidation chemistry and gas-particle partitioning. Oxidation may cause molecular fragmentation as well as functionalization, and so the effect of aging may be highly dependent on how fragmentation affects the molecular structure of the precursor. A series of aging experiments has been performed to determine the effect of sustained oxidation on aliphatic hydrocarbon molecules containing 10 to 18 carbon atoms as a function of their structure and vapor pressure. Experiments are performed using a recently-developed chamber aging technique combining long residence times with elevated OH concentrations. Experiments run under high NOx conditions with OH exposures reaching a maximum of approximately 3e11 molecule*seconds/cc, equivalent to several days of exposure to ambient OH concentrations. Linear and cyclic alkane structures of test molecules are specifically chosen and compared to evaluate the effect of fragmentation upon sustained oxidation. Properties such as aerosol mass concentration and oxygen content are reported. Fragmentation reactions of later generation products are hypothesized to limit the aerosol production especially for smaller hydrocarbons. Mass spectrometric measurements of the particle-phase and gas-phase carbon enable a measure of carbon balance, to further constrain the production of gas phase products due to fragmentation processes.

2AC.25

Formation of Secondary Organic Aerosol by the Direct Photolytic Generation of Alkoxy Radicals. ANTHONY CARRASQUILLO, Sean Kessler, Theodora Nah, Kevin Wilson, Douglas Worsnop, Jesse Kroll, *MIT*

Our understanding of the chemistry of secondary organic aerosol (SOA) formation from precursor organic compounds is hindered by the complexities arising from multiple reaction pathways and generations of oxidation. Here, we constrain radical oxidation chemistry to a single reaction pathway (and oxidation generation) by forming SOA from the direct photolytic generation of alkoxy radicals from alkyl nitrite (RONO) species. Direct photolysis of RONO species yields one specific alkoxy radical, which greatly simplifies the subsequent chemistry by allowing for individual reaction steps and pathways to be examined. Environmental chamber experiments with a series of straight chain (C4 – C10) alkyl nitrites were conducted to investigate how the position of the radical species along the carbon backbone influences SOA yields. The distribution of the major product species from each precursor species was determined using an Aerodyne Aerosol Mass Spectrometry (utilizing electron impact ionization and vacuum ultraviolet photoionization techniques) and off-line liquid chromatographic techniques. The time-evolution of individual product species are considered in the context of product yields and gas-particle partitioning, providing new insight into SOA formation from alkanes, and in particular highlighting the important role of minor pathways in SOA formation chemistry.

2AC.26

Characterization of Fine Particles by the ASCM at an Urban Background Area in Kaohsiung, Taiwan. MINNA AURELA, Sanna Saarikoski, Yee-Lin Wu, Risto Hillamo, Min-Shiou Wu, *Finnish Meteorological Institute*

In this study fine particle aerosol chemical composition was measured using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) between November 23 to December 18, 2011 at an urban background area on a roof of at 7-storey building in Kaohsiung, Taiwan (ROC). Kaohsiung is the second largest city in Taiwan, with a population around 2.9 million. Its local emissions are manufacturing, refining, shipbuilding, and other light and heavy industries. A major port is located at the city. The climate is tropical with average temperatures approximately 20 degrees Celsius and approximately three rainy days per month in November and December. In addition to ACSM, which measures non-refractory particulate organics, sulfate, nitrate, ammonium and chloride, other instruments monitored total mass concentration of particles (PM2.5 and PM10), particulate organic and elemental carbon and some gases.

The campaign average of the total mass concentration measured by ACSM was 26 $\mu g\ m^{-3}$. The main analyses component was organics. Its contribution was on average 55% of the all analyzed components by ACSM. The second highest contribution had nitrate (20%) followed by ammonium (12%) and sulfate (10%). According to the rough PMF analyses major part of the organics was oxygenated organic aerosol and only minor part was hydrogenated organic aerosol, which is typically originated from the traffic.

2AC.27

Ship Impacts on Marine Aerosol and Clouds. MATTHEW COGGON, Armin Sorooshian, Andrew Metcalf, Amanda Frossard, Zhen Wang, Taylor Shingler, Jill Craven, Lynn Russell, Haflidi Jonsson, John Seinfeld, *Caltech*

We present properties of background marine aerosol and clouds measured off the coast of central California using state-of-the art instrumentation. These measurements were performed in the shipping lanes between Monterey Bay and San Francisco and represent a unique set of measurements contrasting the properties of clean and emission-impacted marine airspace in below cloud aerosol and cloud drop residuals. Average mass and number concentrations of 2.3 micro-grams m^{-}3 and 600 cm^{-}3 were consistent with previous studies performed off the coast of California. Enhancement of vanadium and cloud droplet number concentration observed concurrently with a decrease in cloud water pH suggested that periods of high aerosol loading were primarily linked to increased ship influence. Mass spectra from a compact time-of-flight aerosol mass spectrometer illustrated an enhancement in the fraction of organic (forg) at m/z 42 and 99 in ship-impacted clouds. These ions were well correlated ($r > 0.8$) and most dominant during periods of enhanced sulfate. These ions were equally correlated outside of cloud and showed similar enhancement with increased sulfate. High-resolution analysis of these masses from ship measurements suggests that the ions responsible for this variation were oxidized, possibly due to cloud processing. We propose that these ions can be used as a metric for determining the extent of ship-impacted marine atmosphere where (forg41 > 0.15; forg99 > 0.04) would imply heavy influence from shipping emissions, (0.05 < forg42 < 0.15 ; 0.01 < forg99 < 0.04) would imply moderate, but persistent influences from shipping emissions and (forg42 < 0.05; forg99 < 0.01) would imply clean, non-ship-influenced air.

2AC.28

Online, Mobile Measurements of the Chemical Composition of Volcanic Smog ("vog").

Eben Cross, ZARA L'HEUREUX, Lisa Wallace, Anna Kelly, Kelly Daumit, Philip Croteau, John Jayne, Douglas Worsnop, Jesse Kroll, *MIT*

Volcanic smog (“vog”) is a major air quality issue in volcanically active areas of the world. Vog is primarily composed of water vapor, sulfur dioxide gas (SO2) and particulate sulfate (SO4). The atmospheric chemistry of vog is characterized in large part by oxidation of SO2 to SO4. Once formed in the atmosphere, the acidic sulfate aerosol is neutralized by ammonia (NH3) resulting in partial-to-fully oxidized sulfate species ranging from sulfuric acid to ammonium sulfate. The phase of the sulfur (gas phase vs. particle phase) and the acidity of the particulate sulfate has a direct influence on the human health and ecosystem impacts of the vog.

Here we describe a recent study aimed at characterizing the evolving composition of vog from Kilauea, an active volcano on the island of Hawai‘i (the Big Island). Measurements were made in January 2012 by a team of fourteen undergraduates, as part of MIT’s Traveling Research Environmental Experiences (TREX) program. A mobile platform instrumented with a suite of real-time aerosol and gas phase monitors was used to intercept and sample vog at multiple locations downwind of the volcano. Instruments included a Teledyne SO2 monitor and an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) for the measurement of particle mass and composition. To our knowledge these measurements represent the first real-time measurement of the composition of volcanic aerosol. This presentation will provide a summary of the results obtained during the 2-week field project, with a focus on sulfate mass loadings, sulfur oxidation rates, and extent of neutralization within the vog. Inter-comparisons between results obtained from the mobile platform and co-located air quality monitoring sites will also be discussed.

2AC.29

Characterization of Submicron Particles at Long Island New York Using a High-Resolution Aerosol Mass Spectrometer.

SHAN ZHOU, Qi Zhang, Jianzhong Xu, Fan Mei, Jian Wang, Stephen Springston, Arthur Sedlacek, Yin-Nan Lee, *University of California, Davis*

The Department of Energy (DOE) sponsored Aerosol Life Cycle Intensive Operational Period (ALC-IOP) field campaign took place at Brookhaven National Laboratory (BNL) on Long Island, New York, from July 1st to August 15th, 2011. An Aerodyne High-Resolution Time-of-flight Aerosol Mass Spectrometer (AMS) was deployed after a temperature-stepping thermodenuder during this study to acquire highly time resolved, quantitative data on the mass-based size distribution, chemical composition, and volatility profile of the non-refractory fraction of submicron particles (NR-PM_1). The average mass concentration of NR-PM_1 was 13.3 (±7.7) $\mu g/m^3$, comprising 24.3% sulfate, 7.3% ammonium, 3.8% nitrate, 0.2% chloride and 64.4% organic species. It was observed that particles were originated from different air masses, including urban plumes from New York City, regional pollution enriched of ammonium sulfate, forest fire plumes transported from Canada, and oceanic emissions showing elevated methanesulfonic acid concentrations. In addition , relatively high concentrations of metal species such as Na, Mg, K, Fe, Mn, Cu, Zn, Sb, Sn and their adduct ions were observed from the night of July 4&^(th) to the early morning of July 5th, indicating the detection of firework smokes from the Independence Day celebration. Due to the influences of different sources, organic aerosol composition and oxidation degree varied substantially during the campaign. In addition, nitrogen-containing organic compounds, likely amines, were found to be an important contributor to secondary organic aerosol (SOA). Positive matrix Factorization of the high-resolution mass spectra of organics will be reported to discuss the sources and processes of OA observed in this study.

2AC.30

Comparison of Spectroscopic Signatures of Smog Chamber and Atmospheric Aerosols. LYNN RUSSELL, Shang Liu, Kabindra Shakya, Ashley Corrigan, Anita Johnson, Paul Ziemann, John Shilling, Lisa Pfaffenberger, Jay Slowik, Andre Prévôt, Josef Dommen, Urs Baltensperger, Hwajin Kim, Suzanne Paulson, Spyros Pandis, Michael Lewandowski, John Offenberg, Tadeusz Kleindienst, Christine Loza, Jill Craven, Lindsay Yee, Katherine Schilling, John Seinfeld, *Scripps Institution of Oceanography, UCSD*

The three largest types of sources that emit vapors that form secondary organic aerosol (SOA) are fossil fuel combustion, biomass and biofuel burning, and biogenic vapor fluxes. Each type of vapor emission has a different characteristic mixture of molecular structures – from the long-chain or aromatic-ringed hydrocarbons of fossil fuels to the branched or non-aromatic rings of biogenic vapors, with biomass and biofuel burning vapors having branched, aromatic, and other ringed compounds with some oxidized groups. As these compounds are oxidized by combustion or photochemistry, they add oxygenated groups but retain some of the carbon backbone that characterized the original molecule. Spectroscopic analysis can be used to track the initial hydrocarbon backbones to distinguish different types of oxygenated SOA. In this study, we compare both NEXAFS and FTIR spectra from smog chamber studies with those collected from spectra isolated from atmospheric particles dominated by one of these three SOA source types. Atmospheric SOA associated with combustion sources is consistent with both alkane and aromatic precursors. The remote forest observations have ratios of carboxylic acid, organic hydroxyl, and non-acid carbonyl groups similar to those observed for isoprene and monoterpene chamber studies. Forest fires include biogenic emissions that produce SOA with organic components similar to isoprene and monoterpene chamber studies, also resulting in non-acid carbonyl groups in SOA.

2AC.31

Long-Term Measurements of Organic Aerosol and its Components at the DOE Atmospheric Radiation Measurement Sites.QI ZHANG, Jerome Fast, Caroline Parworth, Timothy Shippert, Chitra Sivaraman, Fan Mei, Alison Tilp, *University of California, Davis*

Secondary organic aerosols (SOA) comprise a large fraction of the aerosol mass in the atmosphere at many locations; however, the formation of SOA is poorly understood and represented by atmospheric models. This deficiency represents a large source of uncertainty in quantification of aerosol effects on radiation and clouds, and consequently the prediction of future climate. Evaluation and development of aerosol process modules require data products generated from field observations. Aerosol Mass Spectrometers (AMS) have been frequently used in field campaigns for characterizing aerosol composition and elucidating aerosol sources and processes. Three Aerosol Chemical Speciation Monitors (ACSM) were recently added to two long-term measurement sites (Tropical Western Pacific and Southern Great Plains) and a mobile facility supported by the Department of Energy Atmospheric Radiation Measurement (ARM) program. The ACSM is a “mini” version of the AMS developed for continuous, low maintenance operation. The typical time resolution of AMS measurements is 2 – 5 min at fixed-sites and 30 s or less on mobile-platforms (e.g., aircraft), while the time resolution of ACSM is generally 30 min. We are currently developing code that takes measurements of total organic matter and mass spectral information from the ACSM and derives the primary and secondary fractions of organic matter. The code will be run operationally within the Data Management Facility of ARM, and the new data product will soon be available on the ARM archive. This presentation will describe how the organic aerosol components are derived, the quality assurance (QA) procedures, and comparisons of side-by-side measurements from AMS and ACSM instruments. Data from over a year-long period from the ARM Southern Great Plains will be presented, along with an analysis that explains the seasonal and multi-day variations in inorganic and organic aerosol components.

2AC.32

Chemically-Constrained CMAQ Evaluation of Organic Compounds with CALNEX Field Measurements.

ANNMARIE CARLTON, Kirk Baker, Tadeusz Kleindienst, John Offenberg, Mohammed Jaoui, *Rutgers University*

CMAQ predictions of gas- and aerosol-phase organic compounds are evaluated with measurements at two locations, Pasadena and Bakersfield California, USA during the CalNex campaign. Analysis of secondary organic aerosol (SOA) tracers indicates that species in CA are chemically different from previous measurements in the Eastern U.S. Specifically, methyltetrols while routinely the predominant SOA species measured in the Eastern U.S. are do not exhibit similar dominance during CalNex. Individual SOA species mass concentrations derived from xylenes, toluene, isoprene and monoterpenes are underpredicted relative to measurements, even though there is no bias or an overprediction for the VOC precursors. Sesquiterpene SOA tracer concentrations are below method detection limits (MDLs) throughout CalNex at both locations, while the model predicts that the SOA species is present. CMAQ's chemically specific organic carbon predictions are presented in the context of 1- and 2-dimensional volatility distributions. There are gaps and inconsistencies in the model's saturation vapor pressures (C*) and oxygen-to-carbon ratios (O:C) for organic aerosol when compared to theory and observations. The findings suggest that model development focused on improving representation of organic aerosol with saturation vapor pressures $-3 <= \log10C* <= -1$ and O:C > 0.2 would likely be most efficient for reconciling model predictions with atmospheric measurements.

2AC.33

Feasibility of the Detection of Trace Elements in Particulate Matter Using Online High Resolution Aerosol Mass Spectrometry.

DARA SALCEDO, Alexander Laskin, Vaithiyalingam Shutthanandan, Jose-Luis Jimenez, *Universidad Nacional Autónoma de México*

The feasibility of using an online thermal-desorption electron-ionization high-resolution aerosol mass spectrometer (HR-AMS) for the detection of particulate trace elements was investigated analyzing data from Mexico City obtained during the MILAGRO 2006 field campaign. Having the ability to detect and quantify airborne trace elements with much higher time resolution than is currently achievable with more conventional techniques (such as PIXE, XRF and ICP) is important to studies related to aerosol sources and health effects. The widespread availability and use of the HR-AMS, along with its high sensitivity and time resolution, makes this potential application of interest. High resolution mass spectral analysis, isotopic ratios, and ratios of different ions containing the same elements were used to constrain the chemical identity of the measured ions. The detection of Cu, Zn, As, Se, Sn, and Sb is reported. Concentration time series obtained from the AMS data were compared to concentration records determined from offline analysis of particle samples from the same times and locations by ICP (PM2.5) and PIXE (PM1.1 and PM0.3). The AMS shows promise for real-time detection of some trace elements, although additional work including laboratory calibrations with different chemical forms of these elements are needed to further develop this technique and to understand the differences with the ambient data from the other techniques.

2AC.34

Particulate Matter Chemistry in the San Joaquin Valley. SURESH RAJA, Srikar M. Reddy, Neelesh Sule, Whitney Rowe, Christopher Marlais, Scott Nester, Philip K. Hopke, Lin Lin, Xia Xiaoyan, Sriraam Ramanathan Chandrasekaran, Jon Klassen, James W. Sweet, *Providence Engineering and Environmental Group*

Particle pollution, especially fine particles with diameter less than 2.5 microns (PM2.5), is known to cause serious health problems as well as degrade visibility. In order to understand the changes in PM2.5 composition over time with an emphasis during the winter, a PM2.5 speciation sampling campaign was conducted at the San Joaquin Valley Air Pollution Control District's Tranquillity monitoring site from November 7, 2011 to March 1, 2012. The PM2.5 speciation sampling campaign included 24-hour samples collected every third-day using three instruments: (1) a RAAS 2.5-400 speciation sampler and (2) a Tisch model, TE-1000, high volume sampler. In addition to this, a Magee Scientific Instruments, model AE-42, Aethalometer was continuously operated during this interval. Dominant ionic species in the Tranquillity samples were nitrate (NO3-) and ammonium (NH4+). Correlation plots of ammonium and nitrate suggested that a large excess of nitrate ions was present beyond that required to form ammonium nitrate. Analysis of excess sulfate concentrations revealed that when no excess sulfate was available, the PM2.5 mass concentrations were higher. This result was statistically significant at the 95% confidence level. The PM2.5 mass concentrations were higher when no excess sulfate was available because sufficient ammonia was available to react with nitric acid to form more ammonium nitrate particles. This, as a result, increased the PM2.5 mass concentration. In addition to this, speciation data collected from 2007 to 2011 by California Air Resources Board (CARB) in Fresno County was further analyzed to study the variations in PM2.5 chemistry. Analysis of data collected from this study, and from the CARB speciation network suggests that reductions in SO2 emissions may not be as effective as expected in mitigating high PM2.5 concentrations, and are unlikely to be effective without NOx control at the same time in this region.

2AC.35

The Linked Aqueous-Phase Oxidation of Glyoxal and SO2: Light-Absorbing Products. DAVID DE HAAN, W. Ryan Sueme, Eric Czer, Ashley Torkelson, Alec Rynaski, *University of San Diego*

Sulfur dioxide (SO2) and glyoxal (CHOCHO) both participate in aqueous-phase oxidation reactions in the atmosphere, forming sulfate, oxalic acid, and under certain conditions, oligomers. These two oxidation processes are often considered independently, yet they are linked by the rapid, reversible formation of an adduct molecule, as shown by Olson and Hoffmann in 1988. At basic pH in oxygenated solutions, the oxidation of the adduct molecule is known to produce a series of colorful, aromatic, redox-active C5 and C6 oligomers that no longer contain sulfur. We show that these reactions occur all the way down to pH 4, and may therefore be relevant to atmospheric cloud droplets. Three known light-absorbing products are identified in slightly acidic glyoxal + bisulfite reaction mixtures by LCMS, of which croconic acid (a yellow compound) is the most stable against oxidation. The complex mass spectra observed, especially at later reaction times, indicate that many other products are formed that have not been previously identified. Multi-day comparisons of these mixtures using LCMS and UV-Vis absorbance measurements indicate that even after the three known light-absorbing compounds have oxidized, the reaction samples remain yellow for many days. This suggests that there are one or more additional light-absorbing compounds produced by the reaction between glyoxal and bisulfite under slightly acidic conditions.

2AC.36

Laboratory Studies of α-Pinene Nitate Production and Aerosol Partitioning. JOEL RINDELAUB, Kevin McAvey, Paul Shepson,*Purdue University*

The oxidation pathways of biogenic volatile organic compounds (BVOCs) and their respective products are still highly uncertain. One pathway of significance is the formation of organic nitrates, which can lead to secondary organic aerosol (SOA) formation and may serve as a temporary or a permanent reservoir for NOx. However, connection between organic nitrate production and aerosol phase partitioning and observed aerosol phase concentrations has remained elusive. Through laboratory-based α-pinene oxidation experiments in a photochemical reaction chamber, the total yield of α-pinene-derived nitrates for both the gas and particle phases was determined as a function of seed aerosol acidity and water content. We observe a very strong dependence of the aerosol phase RONO2 yields on humidity, and a highly variable partitioning between the two phases. These experiments will further our understanding of BVOC oxidation pathways, the partitioning of low vapor pressure products into the aerosol phase, and organic nitrate particle phase processing.

2AC.37

One-Pot Derivatization Methods for Obtaining Functional Group Distributions of Aerosol Constituents. ALICIA KALAFUT-PETTIBONE, W. Sean McGivern, *National Institute of Standards and Technology*

Secondary organic aerosols (SOAs) are formed through gas-phase oxidation and condensation of volatile organic compounds, followed by additional reactions in the condensed phase. The chemical analysis of the complex reaction mixtures commonly found in SOAs has proven difficult and time-consuming. LC-MS/MS is commonly used for screening of unknown compounds in water or sediment matrices, although it is rarely applied to the analysis of atmospheric aerosol constituents due to the fact that ionization is problematic for many volatile organic compounds. Here we present a methodology for the rapid determination of approximate functional group distributions using LC-UV and LC-MS/MS techniques. We have developed simple and effective one-pot derivatization methods adapted from biochemical and gas-phase applications which increase sensitivity to the analytes of interest. These methods are designed to probe carboxylic acid, hydroxyl, and carbonyl groups, and are conducive for analysis of aerosol filter extracts.

2AC.38

Aromatic Secondary Organic Aerosol Formation in the Presence of Sea Salt Aerosols. ROSS BEARDSLEY, Myoseon Jang, Yunseok Im, Ori Barber, Carrie Delcomyn, Ned Witherspoon, *University of Florida*

Dual, large outdoor chambers were used to investigate the effect of heterogeneous aqueous phase chemistry on the secondary organic aerosol yields of the photooxidation products of aromatic hydrocarbons in the coastal environment. Toluene and 1,3,5-trimethylbenzene were photochemically oxidized in the presence and absence of inorganic seeds (sea salt aerosols or NaCl) at low NO_x conditions. Overall, the presence of sea salt aerosols (SSA), which were shown to contain water even at very low relative humidities, led to higher SOA yields than the presence of NaCl seeds and the seedless condition in all cases. In order to evaluate the impact of the aqueous phase reaction of aerosols on SOA yield, the aerosol organic mass (OM) was decoupled into the organic mass from partitioning (OM_P) and the organic mass from heterogeneous aqueous phase reactions (OM_{aq}). The results provided suggest that SOA yields in the coastal environment will be much higher than those produced in terrestrial environment. To study the effect of SOA formation on the chemical composition of SSA, inorganic species were measured using a Particle-Into-Liquid-Sampler coupled to ion chromatograph and aerosol functional groups were analyzed using a Fourier Transform Infrared (FTIR) spectrometer. The FTIR data studies also suggested that hygroscopic properties of SSA were influenced by SOA. The aged SSA gradually grows with increasing RH while the fresh SSA shows a clear phase transition. The depletion of Cl^- ion due to the accommodation of nitric acid and carboxylic acids on the surface of SSA corresponds with changes in aerosol hygroscopic properties.

2AC.39

Hygroscopic Growth of Mixed Aerosol Particles Composed of Inorganic and Organic Compounds of Atmospheric Relevance. IDANIA ZAMORA, Mark Jacobson, *Stanford University*

The hygroscopic growth of atmospheric particles has far-reaching effects on atmospheric chemistry and Earth's climate. Water-soluble organic carbon (WSOC) constitutes a significant fraction of the dry submicron mass of atmospheric aerosols, thus affecting their water uptake properties. Although the WSOC fraction is comprised of a large amount of compounds, a set of model substances can be used to describe its behavior. For this study, mixtures of Nordic Reference fulvic acid (NRFA), with various combinations of inorganic salts (sodium chloride and ammonium sulfate) and other representative organic compounds (levoglucosan and succinic acid), were studied. We measured the equilibrium water vapor pressure over bulk solutions of these mixtures as a function of temperature and concentration. Hygroscopic growth as a function of water activity at $25^{o}C$ was calculated from these data for particles of equivalent composition. The water vapor pressure as a function of temperature curve for a NRFA/inorganic salt solution was governed by the inorganic compound even for a solution saturated in both NRFA and salt. This effect was observed for the curves of NRFA mixtures with each salt, which mimicked the curves for the saturated pure salt solutions. While no hygroscopic growth was observed for a 2:1 NRFA/levoglucosan mass ratio mixture, a solution with a 1:3 NRFA/levoglucosan mass ratio presented a hygroscopic growth factor (G_f) of 1.51 and 2.39 at a relative humidity (RH) of 95% and 98%, respectively. Two of the mixtures were based on chemical composition data for different aerosol types. While the solution representing organic aerosols (40% NRFA / 40% succinic acid / 20% levoglucosan) did not exhibit water uptake up to 99% RH, the solution representing biomass burning aerosols (25% NRFA / 27% succinic acid / 18% levoglucosan / 30% ammonium sulfate) had a G_f of 1.83 and 3.33 at RH = 95% and 98%, respectively.

2AC.40

Model Analysis of Aerosol Reaction Chamber Studies of Aqueous Aerosol SOA (aaSOA) Formation. ANDREW SUMNER, Joseph Woo, V. Faye McNeill, *Columbia University*

The reactive uptake of glyoxal by wet aerosols is believed to be a significant source of secondary organic aerosol (SOA). Several recent laboratory studies have been performed with the goal of characterizing this process, but there has not been consensus on the effects of photochemistry on SOA growth and the identities of the product species formed.

We recently developed GAMMA (Gas Aerosol Model for Mechanism Analysis), a photochemical box model with coupled gas-phase and detailed aqueous aerosol-phase chemistry. We applied GAMMA to simulate recent aerosol chamber studies of SOA formation by the uptake of glyoxal by wet aerosol under dark and irradiated conditions (Galloway et al. 2009, 2011; Volkamer et al. 2009). We achieved closure to within 10% between simulated SOA growth and the results of most of the experiments with the same model of gas-aerosol equilibrium and aqueous chemistry.

Based on our analysis, SOA growth is dominated by reversible uptake of glyoxal as described by Henry's Law, independent of photochemistry. Our results show that while some organic acids, organosulfates, and other oxidation products are formed under irradiated conditions, these product species contribute negligible aerosol mass. Under irradiated conditions, the photochemical destruction of gas-phase glyoxal may perturb the gas-aerosol equilibrium, leading to decreased SOA production during batch mode aerosol chamber experiments.

2AC.41

Secondary Organic Aerosol Formation from Acid-Catalyzed Uptake of α-Pinene Oxide to Aqueous Sulfate Particles.JOSEPH WOO, Greg Drozd, Allison Schwier, V. Faye McNeill, *Columbia University*

Significant uptake of alpha-pinene oxide (aPO) onto ammonium sulfate and sulfuric acid aerosol has been observed and characterized. Size-selected, monodisperse aerosol samples were exposed to gas-phase aPO at concentrations ranging from 0.2-5ppm in a continuous flow 3.5m^3 PTFE chamber, at relative humidities 30-60±5%. Uptake of aPO onto sampled aerosols under these conditions was measured via scanning mobility particle sizer (SMPS), indicating volume increases of up to 270% of their original values.

Aerosol growth was shown to be a strong function of initial particle pH, which is consistent with acid-catalyzed formation of alpha pinene oxide-derived diol (aPO-diol) and organosulfate (aPO-OS) species. Observed total mass uptake was also enhanced by increased gas-phase aPO concentrations and initial aerosol size.

Based on the expected O:C ratio of the particles, liquid-liquid phase separation is expected. Continued particle growth is observed even at high growth factors, suggesting that, even when organic content is high, acidic water continues to be accessible for uptake of aPO. However, the partitioning coefficient for aPO decreases with increasing growth factor, suggesting that uptake becomes less efficient.

2AC.42

Investigation of a Particle into Liquid Sampler to Study the Formation and Ageing of Secondary Organic Aerosol.JACQUELINE HAMILTON, Kelly L. Pereira, Andrew R. Rickard, William J. Bloss, M. Salim Alam, Marie Camredon, Amalia Munoz, Monica Vasquez, Esther Garcia, Mila Rodenas, Teresa Espallardo, *University of York*

The atmospheric oxidation of Volatile Organic Compounds (VOCs) in the presence of NOx results in the formation of tropospheric ozone and Secondary Organic Aerosol (SOA). Whilst SOA is known to affect both climate and human health, the VOC oxidation pathways leading to SOA formation are poorly understood. This is in part due to the vast number and the low concentration of SOA species present in the ambient atmosphere. Atmospheric simulation chambers such as the EUropean PHOtoREactor (EUPHORE) in Valencia, Spain, are often used to study SOA formation from a single VOC precursor under controlled conditions. SOA composition and formation can be studied using online techniques such as AMS, which provide high time resolution but limited structural information or offline filters samples can provide low time resolution but high chemical complexity.

In this work we report time resolved SOA composition analysis using a Particle into Liquid Sampler (PILS) followed by Liquid Chromatography Ion-Trap Mass Spectrometry and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Experiments were performed at EUPHORE investigating the formation and composition of Methyl Chavicol SOA. Methyl Chavicol was identified as the highest floral emission from an oil palm plantation in Borneo and has also been observed in US pine forests. Methyl Chavicol oxidation was investigated using a series of photosmog and ozonolysis experiments with varying ratios of NOx:VOC. An extensive range of instruments were used to monitor radical and product formation. Samples were collected using the PILS at 30 minute intervals with filters taken at the end of each experiment for comparison. A number of key oxidation products have been identified and can be compared to model simulations. Time profiles can be used to determine the importance of first, second & higher oxidation products and may indicate which species are undergoing oxidation or heterogeneous reactions during aerosol ageing.

2AC.43

Particle Formation, Growth and Composition from Exposed Ocean Vegetation. ANDREW HORAN, Daniel MacDonald, George Luther, Murray Johnston, *University of Delaware*

The research question to be addressed in this work is: Do gaseous emissions from marine biota cause new particle formation in ambient air? Answering this question is important because new particle formation contributes substantially to the ambient particle number concentration, which can influence visibility, human and ecosystem health, and global climate. In these experiments air is drawn over a sample of macro- or micro- algae. Gaseous emissions from biota in the sample are mixed with OH radicals generated in a photolysis chamber to nucleate and grow particles. Particle size and composition are monitored with a scanning mobility particle sizer (SMPS) and the nano aerosol mass spectrometer (NAMS). Initial experiments were performed with emiliania huxleyi, thalassiosira pseudonana, laminaria, ulva and fucus samples. Gaseous emissions from all of these species were found to produce particles when exposed to OH. Macroalgae gave higher yields of particulate matter than microalgae. Particle sizes were generally in the 10 to 80 nm size range. Elemental analysis with NAMS showed that they were composed mostly of carbon, plus some nitrogen, oxygen and sulfur. Ongoing work is directed toward identifying key gas and particle phase molecular species, with the goal of characterizing particle formation and growth mechanisms.

2AC.44

Organic Matrix Effects on Aqueous Processing in Atmospheric Aerosols. GREG DROZD, V. Faye McNeill, *Columbia University*

The aqueous processing of organic compounds in atmospheric particles affects important particle properties, such as hygroscopicity and absorption of light. The chemical environment in particles that have deliquesced but have not yet effloresced is quite unique, with necessarily supersaturated salt concentrations. Recent studies on phase separations in atmospheric particles indicate that water soluble organic material (WSOC) that is highly oxidized (O:C > 0.7) remains in a single phase with ammonium sulfate and water.(1) This organic matrix has the potential to make the particle system differ greatly from a bulk solution in several ways (e.g. viscosity, dielectric constant,etc.). In this work we probe the effect of organic matrices on the reaction of glyoxal and methylglyoxal with ammonium sulfate, using highly soluble organics to serve as surrogates for WSOC. We find that at an organic to sulfate mass ratio of 2 to 1, glucose reduces the rate of product formation by 30%. Methanol and ethanol have pH dependent effects on reaction rates. Reduced conductivity in solutions with an organic matrix suggests lower charge carrier density due to increased ion pairing in the highly concentrated solution. The reduced ammonium activity due to ion pairing contributes to the observed reduction in reaction rate. Organic matrices may affect the rate of aqueous processing and hence the formation of light absorbing or hygroscopicity altering compounds, particularly in conditions that are common inside or near clouds, which will result in changes in cloud properties, such as brightness and lifetime.

1. Bertram et al., Atm. Chem Phys., 11, 10995, 2011.

2AC.45

Sulfuric Acid Hydration and Its Atmospheric Implications. BERHANE TEMELSO, George Shields, *Bucknell University*

The binary H_2SO_4-H_2O nucleation is considered to be an important pathway for the formation of secondary aerosols in the atmosphere. We investigated the thermodynamics of sulfuric acid hydration using ab initio quantum mechanical methods. For $H_2SO_4(H_2O)_n$, $(H_2SO_4)_2(H_2O)_n$, $HSO_4^-(H_2O)_n$ and $SO_4^{2-}(H_2O)_n$ where n = 1−6, we used a scheme combining molecular dynamics configurational sampling with high-level ab initio calculations to locate the global and many low lying local minima for each cluster size. From the Boltzmann averaged Gibbs free energies, we derived important conclusions about acid dissociation in small clusters, the stability of neutral and ionic species and the abundance of small sulfuric acid hydrates under atmospheric conditions. The extent of sulfuric acid hydration determined from our calculations is substantially different from predictions of simpler models and experiments. The implications of these findings on the discrepancy between experimental and theoretical nucleation rates as well as the different aerosol nucleation mechanisms is explored.

2AC.46

Secondary Organic Particle Growth Under Different Conditions in a Flow Tube Reactor. YUE ZHANG, Scot Martin, Franz Geiger, *Harvard University*

A flow tube reactor was developed and used to simulate secondary organic particle formation from alpha-pinene ozonolysis under different reactants concentration conditions. The flow tube was designed to induce turbulence and mixing of the reactants. The alpha-pinene and ozone were injected into the flow tube reactor in different concentrations ranging from 0.125 ppm (3.08×10^12 molec cm^-3) to 10 ppm (2.5×10^14 molec cm^-3) for alpha-pinene and 0.10 ppm (2.5×10^12 molec cm^-3) to 500 ppm (1.2×10^16 molec cm^-3) for ozone.

The size distributions of the secondary organic particles were studied using a Scanning Mobility Particle Sizer (SMPS). The number concentration of the particles increased from a 0 to (1.26±0.02)×10^7 cm^-3, and the mass concentration increased from 0 to (4.0±0.1)×10^5 ug m^-3. Changes in the particle number concentrations and size distributions suggested that the growth mechanisms of the particles may be different at different precursor concentrations. As an example, for an alpha-pinene concentration of 3.08×10^12 molec cm^-3 reacted with excess ozone, the measured particle mode diameter was 25 nm and both coagulation and condensational growth were significant. When the alpha-pinene concentration was increased to 2.5×10^14 molec cm^-3, the particle mode size increased to 240 nm and coagulation between particles became the dominant growth mechanism. This result shows that the dominant particle growth mechanism can be shifted between condensation and coagulation, which may be useful for studying the particle growing process and whether particles produced from the same precursors have different properties when they grow from different mechanisms.

2AE.2

Time-Resolved Chemical Characterization of Ambient PM2.5 in Stockton, California. ARANTZAZU EIGUREN-FERNANDEZ, Gregory Lewis, Steven Spielman, Susanne Hering, *Aerosol Dynamics Inc.*

Our newly developed Growth Tube-based three-stage collectors were deployed at the Air Resources Board monitoring station located in Stockton (CA) to evaluate their performance under real field conditions. Three parallel systems were deployed and dry-depositions of ambient PM2.5 were collected between November 2011 and February 2012. Two systems collected 12-hour samples at 1.5 lpm for the identification and characterization of particle-bound polycyclic aromatic hydrocarbon (PAHs) by HPLC-FLD, and sulfate and nitrate by IC-ECD. For the chemical characterization the plates containing the dry-PM2.5 samples were directly placed in the autosamplers and both analyses were conducted without previous extraction, filtration and volume evaporation steps. A 1 lpm sampler was used to collect 6-hour samples for the characterization of the elemental composition using a Laser Induced Breakdown System (LIBS). Parallel filters were collected for 48-hours and analyzed for PAHs. Average concentrations found on the time-resolved samples will be compared with concentrations found on the filters as a method to assess sample collection efficiency and possible sampling artifacts of the three-stage sampler.

2AE.3

Virus, Bacteria, Gas and Odour Reductions by an Innovative Air Cleaning System Developed for Animal Housing. VALÉRIE LÉTOURNEAU, Caroline Duchaine, Martin Belzile, Matthieu Girard, Stéphane P. Lemay, *IRDA, Canada*

Canada produces more than 30 million pigs per year and is now the third largest exporter of pigs. While economically beneficial for rural communities, animal housings can emit substantial amounts of airborne bacteria and viruses, some of those of concern for public and animal health. A device such as an air treatment unit (ATU) combined with the building ventilation system might be a way to reduce airborne virus dispersion such as influenza virus or porcine circovirus from buildings. The effectiveness of ATUs to reduce airborne virus and bacteria has been evaluated by installing the device to treat the air exhausted from pig experimental chambers and by injecting non-pathogenic virus surrogates (P008 and PhiX174 phages) with a 24-jet nebuliser upwind of ATUs. Bacteria and artificially-introduced phages have been sampled up- and downwind of ATUs with wet cyclones Coriolis. ATUs were operating at different conditions (three empty bed retention times with the same superficial air velocity, two types of synthetic media and two recirculation times for a nutritive solution). Preliminary results show that 0.8 micrometers aerosolized particles containing P008 and PhiX174 phages are not captured by the studied ATUs. However, we did observe reduced bacteria concentrations as well as lower odour and ammonia levels downwind each evaluated ATUs. Bacteria population diversity will be studied up- and downwind each ATUs by Denaturing Gradient Gel Electrophoresis (DGGE) and pyrosequencing. Furthermore, fluorescent microspheres of different diameters will be injected into ATUs to determine their physical trapping by the studied system. According to our results, ATUs developed by IRDA are effective to reduce airborne bacteria, odour and ammonia emitted from pig housing.

2AE.4

Development of an Air-Liquid Direct Exposure System for In Vitro Cell Exposure to Airborne Sub-Micron and Nano-Particles. TA-CHIH HSIAO, Chun-Wan Chen, Yun-Ching Cheng, Ya-Chien Changchien, *National Central University, Jhongli City, Taiwan*

To study adverse cellular effects induced by inhalable substances, three methodologies have generally been employed: (1) animal experiments, (2) ex vivo studies of cells of bronchial lavage or biopsies and (3) in vitro systems of exposure of lung cells to pollutants under controlled conditions [Devlin, Frampton and Ghio, 2005]. Although in vitro models lack the ability to account for all intercellular interactions in the cells' natural environment, studies using in vitro exposure models enable investigators to examine the effects of inhaled toxins on specific cell types, and are important to determine potential cellular mechanisms mediating these responses [Volcken at al., 2009]. In addition, in vitro studies are relatively inexpensive, compared with ex vivo studies and animal experiments. However, the traditional in vitro testing method represents an unrealistic way of inhalation exposure, since the in vivo exposure occurs at the air-liquid interface and not under fully immersed (submerged) conditions [Lenz et al., 2009]. The physico-chemical properties of particles, such as the size, surface area, morphology, and chemical composition would be altered significantly if the particles are suspended and/or dissolved in medium solution. [Tippe, Heinzmann and Roth, 2002].

In recent years, the air-liquid direct/air-liquid interface (ALI) exposure method is considered as a more realistic experimental scheme for in vitro cell exposure to airborne particles. In this study, a newly-designed ESP-type ALI exposure chamber was constructed, and its performance was evaluated under different operating conditions. The effects of different geometric dimensions were investigated. The preliminary results demonstrated the ALI chamber /system designed in this study is a promising and feasible method for in vitro cell exposure to airborne Sub-micron and Nano- particles.

2AE.5

Fine Particle Exposures During Vehicle Fire Suppression: Mobile Direct Reading Sampling. DOUGLAS EVANS, Kenneth Fent, James Couch, *NIOSH DART*

Objective: According to both the US Fire Administration and the National Fire Protection Association, fire departments responded to in excess of 300,000 vehicle fires per year on average, more frequent than residential fires and making up approximately one quarter of all responses. Despite the common nature of vehicle fires, relatively few studies characterizing the emissions or potential for firefighter exposures have been conducted.

Methods: Six vehicle fires were initiated (three engine and three cabin), with subsequent fire suppression conducted by a local fire crew during fire training exercises. Through flexible metallic duct, air samples were drawn from the location of fire crew (nozzle operator) to a mobile aerosol instrument sampling platform, for simultaneous measurements of particle number, respirable particle mass, active surface area, photoelectric response, particle size distribution and air quality parameters. Chemical vapors were also monitored, but these results have been presented elsewhere.

Results: Fire crews were potentially exposed to combustion products as the smoke plume backed and veered. These instances occurred during both knockdown and overhaul phases of the response. Fifteen minute average particle concentrations of 324,000 particles/cm3 and 5.9 mg/m3 respirable mass were attained, although transient peak concentrations were substantially greater.

Conclusions: Potential for firefighter exposure to particles was primarily determined by the direction of the wind during fire suppression and included both the knockdown and overhaul phases of the fire response. To reduce the risk from exposure to airborne contaminants, firefighters should don self contained breathing apparatus (SCBA) on arrival at the fire scene and doff SCBA only after overhaul is complete.

2AE.6

A Case Study in Fusion of Surface PM2.5 Observations and 3D Air Quality Model Output. SINAN SOUSAN, Tiangfeng Chai, Jaemeen Baek, Scott Spak, Naresh Kumar, Jacob Oleson, Sarika Kulkarni, Gregory Carmichael, Charles Stanier, *University of Iowa*

PM2.5 exposure estimates for United States at high spatial and temporal resolution are highly desirable for climate, visibility and health applications. In particular, accurate, high resolution, and spatially and temporally continuous datasets may enable advanced epidemiological studies focused on identifying more and less harmful types of particulate matter. Data assimilation via optimal interpolation (OI) was used to assimilate satellite AOD and surface PM2.5 measurements into Models-3 Community Multiscale Air Quality Model (CMAQ) model output. Data assimilation using MODIS satellite-based aerosol optical depth was conducted over the United States for 2002. Evaluation was conducted separately for six geographic regions of the U.S. The best combinations of error settings and averaging schemes led to a domain average improvement in fractional error from 1.2 to 0.97 at IMPROVE monitoring sites, and from 0.99 to 0.89 at STN monitoring sites. Somewhat larger improvements to fractional bias were observed. However, for 38% of the month-region combinations, MODIS OI degraded the forward model skill. Root causes of the limitations of the technique will be presented.

An alternate approach is to utilize surface measurements over the United States. The use of surface PM2.5 data will eliminates uncertainty associated from both satellite retrievals and calculations that enable the model and satellite data to be intercompared. But the point-nature of the surface observation versus the grid cell averaging of the 3D model (i.e. representation error) must be dealt with. Results from the Hollingworth-Lonnberg observational method (for determing model error covariance), and approaches for handling representation error will be presented together with results from OI of over 1500 monitoring locations. Data withholding schemes for evaluation of the OI output will also be presented.

2AE.7

Determining the Recovery Efficiencies of Two Aerosol Samplers for Bacteria, Yeast, and Fungi. JOHN TROMBLEY, Jordan Bohannon, Jonathan Spurgin, Larry Bowen, *Southern Research*

Two common methods of collecting bioaerosols for analysis are filtration and liquid impingement. During filtration, bacterial, viral and fungal particles are deposited onto the filter through impaction and interception. Liquid impingers utilize inertial impaction to deposit particles onto the body of the impinger and particle collection is enhanced through diffusion into the liquid. In this poster, we compared the recovery efficiencies of a custom designed, low-flow rate stainless steel liquid impinger and 47 mm gelatin filters for a variety of microorganisms consisting of a spore-forming bacteria (Bacillus anthracis Sterne), a non spore-forming bacteria (Acinetobacter baumannii), a yeast (Candida albicans) and a fungus (Aspergillus fumigates). Suspensions of each organism were aerosolized using a Collison 3-Jet Nebulizer and directed into a radial plenum. The plenum was ventilated at a constant 12 L/min bias flow rate which provided homogenous atmospheres for sampling. Liquid impingers were prepared with 50 mL phosphate buffered saline and gelatin filters were loaded into sterile filter holders prior to each test. Single liquid impinger and gelatin filer samples were collected simultaneously for 15 minutes from iso-axial sample ports on the radial plenum. Three suspension concentrations of each organism were tested. Following collection, each sample was analyzed in duplicate using standard microbiological methods. For B. anthracis Sterne and A. fumigates, greater recovery efficiencies were observed with the gelatin filters. For C. albicans, recovery efficiency was greater with gelatin filters but was nearly equivalent in two out of three tests. The recovery efficiency for A. baumannii was greatest when the liquid impinge was used with the exception of one test. Overall, the results demonstrate that the type of aerosol sampler used can significantly affect the recovery efficiencies of culturable microorganisms, potentially affecting aerosol concentration and dosimetry calculations.

2AE.8

Measurement of Silica on Filter Samples of Coal Dust Using a Field-Portable FTIR Method. NATE MURPHY, Zachary Briggs, Andrew Kilpatrick, Courtney Quinn, Mackenzie Wadas, Emanuele Cauda, Art Miller, *NIOSH*

The inhalation of toxic substances is a serious danger faced by miners. Inhalation of silica is of particular concern due to the recent rise in cases of coal workers pneumoconiosis and silicosis. There is currently no field-portable instrument to measure airborne silica to give miners timely feedback on their exposure. NIOSH is therefore investigating and developing technologies for end-of-shift or real time measurement of silica in coal mine dusts. In a recent study, Fourier Transform Infra-Red spectrometry (FTIR), conducted in transmission mode, was used to estimate the mass of silica in coal dust samples deposited onto a PVC filter. However, transmission-based FTIR is not applicable for analyzing filters used in the Personal Dust Monitor (PDM) that will be increasingly employed in US coal mines. This study therefore focused on the use of FTIR conducted in Diffuse Reflectance (DR) mode as a method for measuring silica on PDM filters. The DR method was used to analyze lab-generated filter samples of pure silica (Minusil) and coal dust, prepared at five different mass loadings in the ranges 100-800 µg and 500-4000 µg respectively. Results suggest that DR can accurately quantify silica in coal dust deposited on PVC filters, and to a lesser degree on the newly developed “ashable PDM filters”. The DR measurements correlated well with the mass of silica on PVC and ashable filter samples (linear regressions yielded R^2 values of approximately 0.95 and 0.90 respectively). However, when applied to PDM filters in their current form, DR-quantification of silica is not possible. It was determined that the problem stems from the current use of quartz fiber filters in the PDM. It was concluded that the PDM filters could be analyzed for silica more accurately if redesigned with silica quantification in mind, and if the new ashable filters are used, the accuracy will be limited to approximately +/- 15% RSD.

2AE.9

Evaluation of a 7-Year Air Quality Simulation Study for Eastern United States.

HONGLIANG ZHANG, Gang Chen, Qi Ying, Jianlin Hu, Michael Kleeman, *Texas A&M University*

Ozone and fine particulate matter have been shown to have adverse effects on human health. 3D air quality models can provide detailed ozone and PM concentrations and chemical components information for epidemiology analysis. In this study, a 7-year (2000-2006) air quality simulation is conducted over East US and the outputs will be used to connect PM exposure with human health outcomes after being validated. High resolution (4x4 km) domains are used to provide detailed air quality predictions of ozone, SO2, NOx, CO, PM2.5 mass and PM2.5 EC, POA and SOA at 7 cities: Chicago (IL), NYC (NY), Detroit (MI), Pittsburgh (PA), St. Paul (MN), Baltimore (MD), and Winston-Salem (NC). In this study, the performance of the meteorology model (WRF v3.2.1) and the air quality model (CMAQ v4.7.1) in predicting the observed meteorology and air quality are evaluated with all available surface observation data. Population averaged exposures to various air pollutants will be calculated. The ability of the model simulations to reproduce the observation are evaluated using different averaging times (hourly, daily, weekly and monthly) and different spatial averaging scales (from fixed stations to county-level) and all modeled species. This information provides useful guidance for epidemiologists to properly averaging the model predicted data before applying them to further statistical analysis.

2AE.10

Mineral and Heavy Metal Concentration in Air and Health Effects of North Kosovo.

AFRIM SYLA, Fatbardh Syla, *University of Prishtina, Kosovo*

In different region of Kosovo has been increasing concern about the entry of potentially harmful substances into the air and food destination for human consumption;-because heavy metals can be responsible for a variety of acute and chronic toxic effects of the population. The monitoring of such substances in air, water, soil or in plants consumed by ruminants used for meat production is time consuming and expensive.

Mineral concentrations of air samples ranged from 21.2 to 59.1 microgram per gram. The results of this study quantified the concentrations of three toxic metals (Pb, Cr, Ni). Studies regarding accumulation of values for health effects of the population is attempted.

2AE.11

Estimation of Residential Exposure to Coal Powered Power Plant Emissions: From Regional to Biological Specimens.

QUENTIN MALLOY, Cortina Johnson, James Raymer, Jonathan Thornburg, Elizabeth Frey, Sangeeta Gupta, *RTI International*

The southern Delaware area surrounding the town of Millsboro has been previously designated as a cancer cluster because of the elevated lung and bladder cancer rates. In order to study the potential linkage between the local coal-fired power plant and the increased cancer rates, a two part study was developed to examine regional, residential, and personal $PM_2.5$ samples along with biological samples. Thirty-two participants were recruited to be sampled over the course of a 4 week campaign while the power plant was shut down for upgrades. Samples were obtained at one semi-rural background site and four sampling sites located approximately 2.5 miles from the power plant. Participants had PM samplers placed outside and inside their homes along with being outfitted with a personal PM sampler. Outdoor residential $PM_2.5$ averaged over the course of the campaign was 16.4 micrograms/m^3, while indoor samples averaged 43.3 micrograms/m^3. Personal samples averaged 24.3 micrograms/m^3. Elemental analysis by XRF indicated PM enriched with typical crustal materials such as Ca and Si along with other common elements of sulfur and zinc. Background samples indicated good spatial uniformity in composition and mass with the exception of the Northeast site which was enriched with Si compared to the other three samplers. Blood and urine samples indicated elevated levels of arsenic or selenium in 12 of the 32 participants.

2AE.12

Measurements of PM2.5 Concentration and Composition in the Vicinity of Barnett Shale Natural Gas Production Facilities for Population Exposure Assessment.

BARBARA ZIELINSKA, Eric Fujita, David Campbell, *Desert Research Institute*

The Barnett Shale study was conducted in April-May 2010 to provide a better understanding of population exposure to air toxics associated with gas production operations in the Barnett Shale region of North Texas. As part of this study, PM2.5 samples were collected downwind of gas production areas, using MiniVol portable air samplers for 7 continuous days over one month period. One location was at a single private residence near a well with emissions from condensate tanks. The second facility was a gas compressor station located near a small community. The spatial variations in PM2.5 concentrations were determined at various distances and directions from this source. Particles were collected on Teflon and pre-fired quartz filters that were analyzed for mass and elements (Teflon filters) and for organic and elemental carbon (OC and EC) by thermal/optical reflectance (TOR) method (quartz filters). In addition, quartz filter samples were analyzed for polycyclic aromatic hydrocarbons (PAH), using gas chromatography/mass spectrometry (GC/MS) technique. The results indicate contribution of local sources and transport from the Dallas/Fort Worth metropolitan area.

2AE.13

Advances in Particulate Matter Exposure Assessment Instrumentation. Charles Rodes, JONATHAN THORNBURG, *RTI International*

Recent advances in exposure assessment technologies, especially for difficult cohorts like children or senior citizens, enable stronger correlation between the environmental stressor and adverse health outcome. The MicroPEM technology provides exposure data that can significantly enhance health and safety in both residential and occupational settings in an unobtrusive package. The ability to reduce exposure misclassification bias is the key to strengthening the exposure-health link. The MicroPEM is deployed in three current particulate matter exposure studies. One study is examining environmental causes of acute respiratory disease in children. Senior citizen’s exposure to carcinogens in particulate matter from nearby point sources is another. Lastly, exposures to biomass cookstove smoke are being measured in developing countries. Successes and improvements will be discussed using data quality indicators and practical considerations for deploying the MicroPEM in each study. The focus will be the ability to link exposure data to the specific health outcome of interest for each study. Additional facets to be discussed include prediction of inhaled dose from the accelerometer and nephelometer data, compliance with study protocols as measured by an accelerometer, integrated filter gravimetric and speciation detection limits, automatic nephelometer calibration and relative humidity correction, comparison of data from the MicroPEM and other exposure monitor technologies used in previous studies, MicroPEM performance in high concentration environments, system cycle options to obtain 7-day samples, and feasibility of conducting large scale mail-out studies.

2AE.14

Polycyclic Aromatic Hydrocarbons (PAHs) Concentration and Related Carcinogenic Potencies in PM10 at a Semi Arid Region of India. AMIT MASIH, Ajay Taneja, *St. Andrew's College, Gorakhpur, India*

Atmospheric particulate matter from four different areas within Agra city (a semi-arid region) were collected using respirable dust samplers during the 2008 summer season and were then extracted with dichloromethane using an automated Soxhlet Extraction System (Soxtherm®). The extracts were analyzed for 17 target Polycyclic Aromatic Hydrocarbons (PAHs). The total PAH (TPAH) concentrations were 76.6 ± 3.6, 27.9 ± 2.9, 23.7 ± 2.3 and 6.5 ± 1.7 nanograms per cubic meter (ng m-3), respectively, at the industrial, residential, roadside and agricultural sites. The combined mean concentration of TPAH was 33.9 ± 2.6 ng m-3 for all sites. The industrial site had the highest TPAH concentration followed in order by the residential, roadside and agricultural sites. Indeno(1,2,3-cd)pyrene, benzo(g,h,i)perylene and benzo(b)fluoranthene were the predominant compounds found in the samples collected from all of the sites. The carcinogenic potencies related to PAHs have been calculated by using Toxic Equivalent Factors (TEFs) compiled from the literature.

2AN.1

Vapor Nucleation Rate Surfaces for Some Systems with Polymorphous Phase Transitions. Michael Anisimov, Elena Fominykh, PHILIP K. HOPKE, *Tech. Design Inst. of Scientific Instrument Engr SB RAS*

The formation of new phase embryos is described by nucleation theory. However, nucleation is not yet fully understood. The goal of the present research is to design nucleation rate surface topologies for systems with Polymorphous Phase Transitions. Substantial inconsistencies have been reported among experimental data that may originate from the use of different experimental approaches. These inconsistencies lead to the hypothesis that typical vapor/liquid nucleation rate measurements include an uncontrolled parameter [M. P. Anisimov, E. G. Fominykh, P. K. Hopke. Vapor-Gas/Liquid Nucleation Experiments: A Review of the Challenges. J. Aerosol Sci. 40, 733-746, 2009]. It looks attractive to develop new ideas to get vision of the nucleation rate surface topology. Our idea for the nucleation rate surface semiempirical design over the phase equilibria diagrams was used [M. P. Anisimov, P. K. Hopke at al. Relation of phase state diagrams and surfaces of new phase nucleation rates. (1998) J. Phys. Chem. V. 109(4) P.1435-1444]. Several nucleation rate topologies for systems with the monotropic and enantiotropic polymorphic phase transitions have been designed. It was found that multichannel vapor nucleation appeared in the all of these cases. Each nucleation channel is associated the individual nucleation rate surface. The traditional use of nucleation rate theory in a one channel approximation for these systems was completely invalid .

2AN.2

Modeling the Evolution of Exhaust Plume During the Dilution Process: In-lab and On-road. Yan Wang, Bo Yang, ZHEMING TONG, Eric Lipsky, Allen Robinson, Topi Ronkko, Jorma Keskinen, Max Zhang, *Cornell University*

The development of emission inventories relies on the laboratory emission testing. Numerous experimental results have indicated that particle emission measurements are sensitive to how dilution is conducted. The objective of our study is to investigate the characteristics of dilution processes in different environments (i.e., in fabricated dilution systems, as free jet and in the wake of moving vehicles) and their effects on particle emission measurement. An environmental turbulent reacting flow model, the Comprehensive Turbulent Aerosol Dynamics and Gas Chemistry (CTAG), developed by Energy and Environment Research Laboratory in Cornell University, is employed to simulate the turbulent flow field and aerosol dynamics.

We first investigate the aerosol dynamics during the dilution process inside different types of dilution tunnels, including 1) the T-mixing Caltech lab diluter 2) a portable coaxial-mixing CMU field diluter 3) the ejector diluter and 4) the porous diluter. Then the evolution of diesel exhaust is captured as free jet and under on-road conditions. Simulation result of particle size distribution indicates that the dilution process of exhaust plays an important role for the measurement of particle number emissions, especially the formation of new ultrafine particles. It is also shown that nucleation has a strong relationship with the dilution rate, which is one major difference between the three types of environments. Higher dilution rate tends to favor the formation of the ultrafine particles due to the faster mixing rate (e.g., the T-mixing lab tunnel v.s. the coaxial-mixing field tunnel). The evolution of exhaust during the dilution is also affected by the property of dilution gas (e.g., temperature, humidity) and exhaust (e.g., sulfuric acid concentration), of which the sensitivity analysis have been conducted.

The numerical study can help understanding the dilution process and its effect on aerosol dynamics, and can provide useful information for the development of a harmonized sampling methodology.

2AN.3

New Particle Formation and Growth Observed at Fukue Island, Japan in March 2012. SEYOUNG KIM, Takafumi Seto, Yoshio Otani, Akinori Takami, Naoki Kaneyasu, Toshiyuki Fujimoto, Kikuo Okuyama, *Kanazawa university*

We investigated the particle size distribution, total number concentration of particles and chemical composition of atmospheric aerosol at Fukue Island (128.7°E, 32.8°N) in Japan from March 9 to 17, 2012. Aerosol particles size distribution from 14 nm to 670 nm and total number concentration of particles were monitored by Scanning Mobility Particle Sizer (SMPS) (model 3081, TSI) every 240 sec resolution and Particle Condensation Counter (CPC) (model 3776, TSI) every 1 min resolution. A particle transfer event on March 11 and two new particle formation and growth events on March 12 and 15 were observed. The transfer event on March 11 was associated with an increase in particle concentration with the mobility diameter from 100 to 200 nm and it was considered to be the transport of contaminated air mass from the continent. In case of other two events, the onset of particle formation was identified late afternoon (15:00 and 18:00). The particle growth rate during these two events ranged from 1.88 to 2.92 nm h-1.

2AN.4

Neutral Sulfuric Acid Clusters during Strong Nucleation Events in a Sulfate-Rich Urban Atmosphere. JUN ZHAO, Fred Eisele, Peter McMurry, James N. Smith, *University of Minnesota*

New particle formation (NPF) in the polluted boundary layer arises from the clustering of electrically neutral compounds. Newly formed particles may affect concentrations of cloud condensation nuclei (CCN), thereby affecting cloud formation and global climate, so it is important to understand NPF when modeling climate. During the summer of 2009, we carried out measurements in Atlanta, GA, at a site that was frequently impacted by plumes from nearby coal-fired power plants. Measurements included concentrations of nucleating vapors, clusters formed by nucleation obtained with a specially-designed chemical ionization mass spectrometer and particle number distributions down to 1 nm (Jiang et al., 2011). This work will describe measurements of neutral molecular clusters obtained with the Cluster Chemical Ionization Mass Spectrometer (the Cluster CIMS). The concentrations of neutral sulfuric acid-containing clusters are obtained by accounting for the ion-induced clustering process in the sampling inlet, after subtracting background signals. We found that background signals for clusters correlate with temporal variations of malonic acid (mw=104), and we therefore used malonic acid as a tracer for background signals at cluster m/z values.

J. Jiang, J. Zhao, M. Chen, J. Scheckman, B. J. Williams, F. L. Eisele, and P. H. McMurry. First measurements of atmospheric cluster and 1-2 nm particle number distribution functions during nucleation events. Aerosol Science & Technology, 45(4), II-V (2011)

2AN.5

Resolving Size-dependent Particle Growth Rates below 2 nm from the Particle Size Magnifier. Katrianne Lehtipalo, Siegfried Schobesberger, Alessandro Franchin, Tuomo Nieminen, Juha Kangasluoma, Jenni Kontkanen, JYRI MIKKILÄ, Tuukka Petäjä, Markku Kulmala, *University of Helsinki*

The molecular level processes leading to new particle formation are not yet completely understood, mainly due to difficulties in detecting the smallest neutral clusters and particles. New kinds of condensation particle counters allow deriving the formation and growth rates directly from measurements also in the size range below 2 nm, which is the size critical for nucleation.

The Airmodus A09 Particle Size Magnifier (PSM) was used to resolve the size distribution of particles below 2 nm. The growth rates (GR) were calculated from the difference between the appearance times of the newly formed particle population with different cut-off sizes of the scanning PSM. The method was used to for example to nucleation experiments in the CLOUD-chamber and for field measurements at the Hyytiälä SMEAR II measurement station . The growth rates were also compared to the growth of charged sulphuric acid clusters measured with the APi-TOF mass spectrometer, and to the growth rates of 1.6-3 nm ions derived from ion spectrometers. However, the PSM gives additional information on the behaviour of the smallest neutral particles at the beginning of the new particle formation process. This is crucial since nucleation in the boundary layer is most probably dominated by neutral mechanisms. The initial growth rates determine what fraction of the newly formed particles eventually reach sizes, where they can act as CCN and influence the climate.

2AN.6

A novel kinetics mechanism for particle formation from methanesulfonic acid, amines and water. MATT DAWSON, Mychel E. Varner, Veronique Perraud, Micheal, J. Ezell, Benny Gerber, Barbara J. Finlayson-Pitts, *University of California, Irvine*

Aerosol formation in the atmosphere has been shown to be strongly dependent on sulfuric acid (H2SO4, SA), with recent indications that ammonia and amines play an important role. Typically, nucleation rates from this system are calculated according to a single-step kinetics equation whose exponential dependence on gas-phase SA concentration can be used with nucleation theory to determine the number of molecules of SA in the critical cluster. However, models still tend to underpredict nucleation rates in the atmosphere, indicating that there may be other sources of atmospheric aerosols or that the equations used to describe nucleation may need to be revisited, particularly for multicomponent nucleation. Here we present a novel multi-step kinetics mechanism appropriate for multicomponent nucleation based on results from laboratory studies of particle formation from methanesulfonic acid (CH3SO3H, MSA), amines and water. MSA is formed alongside SA in the oxidation of organosulfur compounds in the atmosphere and amines have a variety of both biogenic and anthropogenic sources. Experiments were performed in a unique, slow flow, large volume flow-tube reactor at 295 K and 1 atm under conditions of varying relative humidity. Particle size distributions are measured using a scanning mobility particle sizer (SMPS) and gas-phase MSA concentrations are determined by filter collection and subsequent analysis by LC-MS. Also presented are results from ab initio calculations of the smallest clusters of MSA, amines and water. Indications from the experimental and model results that nucleation proceeds via a complex kinetics mechanism along with atmospheric implications are discussed.

2CC.1

Global Perspectives on Aerosol Hygroscopicity and Cloud Forming Ability: A Synthesis of 8 Airborne and Field Campaigns. TERRY LATHEM, Athanasios Nenes, *Georgia Institute of Technology*

The feedbacks among aerosols, clouds, and radiation are important components for understanding Earth's climate system and quantifying human-induced climate change, yet the magnitude of these feedbacks remain highly uncertain. Characterizing the ability of aerosols to uptake water vapor and form cloud condensation nuclei (CCN) are key to understanding the microphysics behind cloud formation, as well as assess the impact aerosols have on the Earth system. We present a synthesis of CCN and aerosol measurements from 8 different field campaigns and for volcanic ash samples collected around the world. We investigate the CCN activity, hygroscopicity, and impact of these aerosols, which include samples of: boreal forest fires, the high arctic, the marine boundary layer, atmospheric dust, urban pollution, ship plumes, volcanic eruptions, and hurricanes. The hygroscopicity of the different aerosol is quantified by their ability to nucleate cloud drops under controlled levels of water vapor supersaturation and we further explore the origin of the particle hygroscopicity (being from the presence of deliquescent soluble material or adsorption onto insoluble surfaces). Finally, we utilize the data to make predictions of CCN formation and to test the current microphysical theories for the impact of particle chemistry on droplet formation. We find that organics dominant the particle hygroscopicity for many regions and aerosol source types. The comprehensive nature of the CCN measurements makes this a valuable data set for constraining current uncertainties associated with predicting CCN and cloud droplet number concentrations around the world.

2CC.2

Cloud Condensation Nuclei Activity and Hygroscopicity of In-situ Biomass Burning Aerosol. TERRY LATHEM, Bruce Anderson, Andreas Beyersdorf, Lee Thornhill, Edward Winstead, Joe Shaw, Michael Thomas, Glenn Shaw, Athanasios Nenes,*Georgia Institute of Technology*

Biomass burning (BB) is a major source of aerosol with both natural and anthropogenic origins. Emissions are expected to increase in a warming climate and the ability of smoke to be transported across the globe increases the impacts on the earth system, especially the Arctic. The overall hygroscopicity and aging characteristics of BB aerosol is not well quantified, although many studies suggest BB aerosol is efficient cloud condensation nuclei (CCN). Recent laboratory studies of controlled single-fuel burns reveal that the hygroscopic properties of primary smoke particles can be highly variable, depending on both the fuel source and age, with decreasing variability as samples age and become more oxidized. However, BB aerosol in the atmosphere can be a complex mixture of multiple fuel types, undergoing potential rapid aging and mixing with background aerosol, so it is also important to quantify properties of BB particles in the ambient environment.

In this study, we investigate the hygroscopic properties of in-situ BB aerosol generated from active boreal forest fires in the regions of Montana and Canada. Extensive airborne data of boreal forest fire smoke was collected during the 2008 NASA ARCTAS campaign, and we present a detailed characterization of the physical, chemical, and hygroscopic properties of the aerosol collected over Canada. Additional in-situ smoke data was collected at a ground site at Montana State University during the summer of 2009. We find that BB aerosol is efficient CCN, despite high organic content, because a significant fraction of the organic material is water soluble and hygroscopic. CCN predictions, including AMS chemistry and measured water soluble organic carbon, are in excellent agreement with observations, matching within +/- 25%. We also explore how aging influences particle hygroscopicity and investigate observations of new particle formation within BB plumes.

2CC.3

Hygroscopic Growth Measurements of Ambient Aerosol at a Suburban Site in Hong Kong: Seasonal Trends and Water-Uptake Behavior as a Function of Relative Humidity. Ming Chee Yeung, CHAK K. CHAN, *Hong Kong University of Science and Technology*

Rapid economic growth and industrialization in the Pearl River Delta (PRD) region of South-Eastern China in the past decades have led to poor air quality in this region. Most of the previous aerosol studies in this region focused on the characterization of chemical composition. However, measurements of hygroscopic properties, which are crucial to a proper description of aerosol climate effect, are scarce.

In the work, we conducted real-time hygroscopic growth measurements using a BMI Humidified-Tandem Differential Mobility Analyzer at a suburban site in Hong Kong of the PRD region starting May 2011. The particle diameter growth factors (GF) at 90% relative humidity (RH) were measured for dry particle diameters between 35 and 250 nm, covering a month in each of the four seasons for investigating the seasonal variations.

The GFs were generally similar with occasional variations over the study periods. Lower GFs (1.4 to 1.6) of the Aitken mode (dry diameter = 35 to 75 nm) than those of the accumulation mode (dry diameter = 100 to 250 nm, GF = 1.5 to 1.7) were observed. Uni-modal distributions were often observed for the accumulation mode. In the case of Aitken, the occurrence of bi-modal distributions was relatively more frequent with two groups of particles: either non- or less-hygroscopic (GF = 1.0 to 1.2) and more-hygroscopic (GF = ~1.5). Closure between the measured GFs and predictions based on chemical composition measured by Aerosol Mass Spectrometer will also be discussed.

We also performed RH scanning to measure the GFs as a function of RH (both deliquescence and efflorescence branches) with the purpose of understanding the hygroscopic behaviors of aerosols at lower RHs. Although many of the previous studies reported continuous water-uptake behaviors without obvious deliquescence, we observed hygroscopic hysteresis in most cases. GF parameterizations will be applied for various meteorological periods and groups of chemical composition, which are useful to modeling the hygroscopic GFs for various ambient conditions and chemical composition.

This work was supported by the University Grants Committee (SEG-HKUST07) and the Environmental Conservation Funds (ECF) of Hong Kong (ECWW09EG04)

2CC.4

Investigating Potential Biases in Aerosol Light Absorption Measurements. CHRISTINE WALSH, Elisabeth Andrews, John Ogren, Patrick Sheridan, Anna Gannet Hallar, Paola Massoli, Andy Freeman, Daniel Lack, Justin Langridge, *NOAA; Lund University*

Currently, there is no single instrument for quantifying the aerosol light absorption coefficient (sigma ap) that offers accurate measurements, simplicity in use, and reasonable cost. Filter-based techniques, which combine simplicity and low cost, can result in measurement biases under some conditions. Possible discrepancies in the filter-based measurement of σap were investigated utilizing a subset of measurements from two field campaigns: aircraft data from 8 flights over California during the CalNex field campaign of April- May 2010, and data obtained at Storm Peak Laboratory in Steamboat Springs, Colorado between January - June 2011 during the STORMVEX campaign. Each study differed in aim and instrumentation, but both provided opportunities for addressing uncertainties in determining σap. Here, the potential for biases in the filter-based measurement of σap are considered.

Filter-based measurements of sigma ap are obtained in both of these campaigns with the Particle Soot Absorption Photometer (PSAP). This method has potential measurement biases including interference from scattering particles, which can be corrected for after the measurements are obtained, and from liquid organic aerosols (OA) which is not yet well understood or quantified. Reference measurements of sigma ap were provided directly with a Photo-Acoustic Spectrometer during the CalNex campaign and as the difference between aerosol extinction and scattering coefficients, sigma ap = sigma ext - sigma sp, in the STORMVEX campaign; a Cavity Attenuated Phase Shift extinction monitor measured σext and an integrating nephelometer measured sigma sp.

Data are then analyzed for consistencies (e.g., closure), potential biases, and relationships to other aerosol properties. The PSAP measurements from CalNex and STORMVEX do not appear to be subject to a bias caused by organic carbon that has been suggested by other experiments. This could be due to differences in the aerosol composition and/or loading and should be the focus of further research efforts. Both campaigns provide further insight on the potential for variations and uncertainties that occur during measurements of aerosol sigma ap.

2CC.5

Coatings on Light Absorbing Aerosols: Optical Effects, Morphology, and Composition. LULU MA, Hao Tang, Jonathan Thompson, *Texas Tech University*

Atmospheric aerosols are often internally mixed when dispersed in earth's atmosphere. Internally mixed particles can exhibit very different physical properties when directly compared with their more chemically pure counterparts. For instance, mixing hydrocarbon – like material with sulfates can vastly alter hygroscopicity, and several investigators have suggested light absorption can increase when light absorbing cores are embedded within non-absorbing coatings. This presentation will outline what we have learned about the fundamental physical processes that occur when a coated, light-absorbing particle interacts with an intense beam of electromagnetic radiation. We will present results of a TEM and SMPS study that addresses beam-induced morphology changes for select particle types. In addition, cavity ring down spectrometry (CRDS) combined with nephelometry has been used to probe extinction and scattering coefficients of aerosols at 532 nm with and without the intense laser illumination. This allows an assessment of changes in optical properties induced by the intense beam. In addition, a discussion of laser irradiance required to observe such changes will be undertaken.

2CC.6

A Model Study on the CCN Activation of Multicomponent Organic Aerosols. ILONA RIIPINEN, Narges Rastak, Spyros Pandis,*Carnegie Mellon University*

Organic compounds consitute a major fraction of atmospheric aerosol particles in both rural and urban environments. Knowledge on the cloud activation properties of these organic particles is thus needed for accurate predictions of cloud condensation nuclei (CCN) concentrations and furthermore the aerosol-cloud interactions. These predictions are, however, complicated by the multitude of organic compounds present in the atmosphere, many of which are still unknown. Theoretical approaches simplifying the behavior of these complex mixtures are thus needed for feasible, yet accurate enough, model calculations on the behaviour or organic CCN. We studied the CCN activation behaviour or multicomponent organic mixtures by applying the Köhler theory for complex organic aerosol particles with variable dry sizes and thermodynamic properties, such as solubility distributions of the constituents. We probed the conditions at which the complex organic particles were predicted to completely dissolve to water at the point of activation, as opposed to forming separate aqueous and insoluble phases in the activated cloud droplet. Our results can be used to simplify the behaviour complex organic mixtures, yielding accurate predictions of the CCN-activation of a given aerosol population with minimal computational effort.

2CC.7

Power-Law Patterns in Electromagnetic Scattering for Nonspherical Particles. MATTHEW BERG, *Mississippi State Univeristy*

The angular scattered-light intensity, or scattering curve, for a spherical particle is known to display approximate power-law structures when formulated in terms of the scattering wave vector and plotted in log-log scale. Empirically based studies reveal that the structures have common behavior across a wide variety of particle size and refractive index. These patterns, as they are called, are useful as they can relate the scattering curve to particle properties in some cases. This presentation will demonstrate the occurrence of the patterns for spheroidal particles and explain why they occur.

2CC.8

Droplet Number Prediction Uncertainties from CCN: An Integrated Assessment Using Observations and a Global Model Adjoint. RICHARD MOORE, Vlassis Karydis, Shannon Capps, Athanasios Nenes, *Georgia Institute of Technology*

Aerosols, acting as cloud condensation nuclei (CCN) to form clouds, are known to be a significant but highly uncertain contributor to the Earth's climate. Current large-scale models almost exclusively use Kohler theory to predict CCN concentrations from aerosol size, chemical composition, and ambient water vapor supersaturation; however, given limited computational resources, models must make simplifying assumptions that introduce error into their application of Kohler theory. Consequently, a number of past field studies have attempted to quantify this error by comparing measured CCN concentrations to those predicted from simplified theory. Yet, this uncertainty represents only one link in our understanding of the aerosol-cloud climate impacts. The second link is the combination of CCN concentrations with cloud dynamics to determine the overall cloud droplet number concentration (CDNC). Limited attention to date has focused on extrapolating these CCN uncertainty studies to evaluate their impact on the overall CDNC uncertainty, and hence, climate.

We present results from a combined experimental and modeling study incorporating field data of aerosol size, composition, and CCN activity measured in diverse environments throughout North America, including the Alaskan Arctic, agricultural areas, and urban centers. First, the adjoint of a CDNC parameterization, driven by aerosol populations and updraft velocities obtained from a year-long execution of the NASA GMI chemical transport model, is used to determine the regional sensitivity of CDNC to CCN concentration. Then, these sensitivities are used to extrapolate the field-measurement-derived CCN uncertainties to the overall CDNC uncertainty associated with simplified Kohler theory predictions. It is found that this uncertainty is much lower over polluted continental regions than in more pristine environments. Given the past measurement focus on continental environments, this finding motivates future work in pristine regions in order to quantify the impact of and uncertainty associated with transient processes in effecting changes in cloud properties.

2CC.9

Comparison of Surface and Aircraft Cloud Condensation Nuclei Measurements in North Dakota. NICOLE BART, David Delene, *University of North Dakota*

Particular matter suspend in the atmosphere that provides a surface for water vapor to condense onto is termed Cloud Condensation Nuclei (CCN). CCN activation produces cloud droplets that can eventually develop in to rain. Atmospheric CCN number concentration is determined using a counter that pulls an air sample into a supersatured environment and counts the number of droplets that form. CCN counters can be operated at the surface or deployed on aircraft to obtain measurements below cloud base. When conducting scientific analysis, cloud base is typically the most desirable location; however, the expense and difficulty of aircraft CCN measurements limits their availability. The research objective is to determine under what meteorological conditions surface based CCN measurements would be used to infer cloud base CCN concentrations. Knowing how accurately cloud base CCN concentrations can be inferred from surface measurements could allow long term, continuous surface-based measurements to be use in many aerosol-cloud interaction studies.

During the summer of 2010, seven aircraft flights were conducted in North Dakota that measured cloud based CCN concentrations. Concurrent with the aircraft measurement, surface CCN measurements were conducted in Grand Fork, North Dakota. Analysis of the cloud base and surface CCN concentrations shows a good correlation (R2=0.42); however, the surface CCN concentration was more than 50% lower than the cloud base CCN concentration. Both aircraft and surface CCN counters were calibrated using the same Scanning Mobility Particle Sizer (SMPS) system and show good agreement when running the CCN counts side by side. During the summer of 2012, additional aircraft and surface CCN measurements are planned.

2CC.10

Future Air Quality in a Changing Climate in the Eastern United States. MELISSA DAY, Benjamin Murphy, Spyros Pandis,*Carnegie Mellon University*

Future changes in climate (including changes in temperature, mixing heights, rainfall, etc.) will affect urban and regional air quality. To examine the effect of climate change on ozone and fine (under 2.5 micrometers) particulate matter (PM), we use the Global-REgional Climate-Air Pollution modeling System (GRE-CAPS). GRE-CAPS couples the Goddard Institute for Space Studies (GISS) II prime general circulation / chemical transport model (GCM/CTM), the MM5 regional meteorological model, and PMCAMx-2008, a regional chemical transport model. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) was added to provide meteorologically-reactive biogenic emissions. Meteorology from ten representative years in the 1990s (present-day) and ten from the 2050s (future) is used. Future meteorology is based on the Intergovernmental Panel on Climate Change (IPCC) A2 scenario, detailing a heterogeneous world without a focus on sustainability. The future model predictions of ozone levels and fine PM constituents for the Eastern US are compared to present-day distributions, averages and extremes. Previous work by Dawson et al. (2009) covered similar ground, but lacked dynamic biogenic emissions, treated the primary organic aerosol as non-volatile and non-reactive, and simulated only the first generation of secondary organic aerosol production. In PMCAMx-2008, organic aerosol (OA) is simulated using the volatility basis set approach, in which primary emissions are semi-volatile and gas phase organic compounds are oxidized and result in products with lower volatility. For this reason, special focus is given to OA changes, particularly because the OA response to climate change is more uncertain than that of other fine PM components.

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2CC.11

Analyses and Forecasts of Long Range Transport of Particulates to North America. DOUGLAS WESTPHAL, Rudolf Husar, Shawn McClure, James Campbell, Edward Hyer, Walter Sessions, Wynn Eberhard, Jianglong Zhang, *US Naval Research Laboratory*

The Naval Research Laboratory has developed the Navy Aerosol Analysis and Prediction System (NAAPS) which, since 1999, has produced global analyses and 6-day forecasts of sulfate, smoke, dust and sea salt aerosols and visibility. The analysis used for initialization is produced by the NRL Atmospheric Variational Data Assimilation System for aerosol optical depth (NAVDAS-AOD), the only operational aerosol data assimilation system. Together, NAAPS and NAVDAS-AOD provide an efficient method for assimilating satellite data (MODIS, MISR, and CALIPSO) to produce consistent 3-D analyses with significant value to scientists and Air Quality (AQ) decision-makers. The global coverage directly provides quantitative information on the impact of international aerosol particles on the Americas. NASA has funded a new capability for providing NAAPS analyses to the community via the Federated Data System (DataFed) and the Visibility Information Exchange Web System (VIEWS). Example applications include the interpretation of observations of Saharan dust over N. America and the impact of dust on SST retrievals.

2CC.12

Ice Nuclei Produced from Prescribed Fires in Southeastern United States. CHRISTINA S. MCCLUSKEY, Paul DeMott, Anthony J. Prenni, Amy P. Sullivan, Gavin McMeeking, Yury Desyaterik, Gary D. Franc, Thomas C. Hill, Sonia Kreidenweis, *Colorado State University*

The role of various aerosol particle types acting as ice nuclei (IN) in affecting cold cloud microphysics, and how the concentrations of IN active under certain cloud conditions depend on major aerosol sources and chemical characteristics remain poorly understood. Such understanding is needed to explain the impact of IN on cloud phase and precipitation processes, as well as their indirect influence on climate. Previous chemical analyses of captured IN have shown that carbonaceous aerosols can serve as IN, and laboratory studies confirm that biomass combustion of some fuel types may represent a large source of IN to the atmosphere.

In this study, we aim to provide a better understanding of the contribution of biomass burning as an IN source. IN number concentration at various temperatures was measured with a continuous flow diffusion chamber operated in the condensation/immersion freezing nucleation mode during one background day and four large prescribed burns in southwest Georgia. Measurements were located within close range of fires using a mobile laboratory. IN were captured as activated ice crystals for offline measurement of residual aerosol elemental composition (via TEM). Also measured for relation to IN measurements were bulk aerosol composition, mass concentrations and size distribution. The fires were fueled by four different materials typically burned in the southeast United States during springtime; wiregrass, pine needles, small shrubs, and longleaf pine trees. Fire flame phase, fuel mass consumed, meteorological conditions, and soil types were also categorized.

Temporal dependence of IN concentrations at various activation temperatures, how these varied with smoke concentrations, the relation of IN activity and variability to bulk aerosol characteristics, and the varied compositions of IN found will be presented. Results demonstrate the clear potential contribution of burning as a source of IN of different types while the regional impact on clouds remains to be explored.

2CC.13

Heterogeneous Ice Nucleation and Water Uptake by Field-Collected Atmospheric Particles Below 273 K. BINGBING WANG, Alexander Laskin, Tobias Roedel, Mary Gilles, Ryan Moffet, Alexei Tivanski, Daniel Knopf, *Pacific Northwest National Laboratory*

Ice nucleation initiated by aerosol particles through heterogeneous nucleation is not well understood. Onset conditions of water uptake and heterogeneous ice nucleation by particles collected in Los Angeles and Mexico City were determined as a function of temperature (200-273 K) and relative humidity with respect to ice (RH_{ice}). Single particle characterization was provided by micro-spectroscopic analyses using computer controlled scanning electron microscopy with energy dispersive analysis of X-rays (CCSEM/EDX) and scanning transmission X-ray microscopy with near edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS). Four dominant particle types were identified including soot associated with organics, soot with organic and inorganics, inorganic particles of marine origin coated with organic material, and Pb/Zn-containing particles apportioned to emissions relevant to waste incineration. Above 230 K, significant differences in onsets of water uptake and immersion freezing of different particle types were observed. Below 230 K, particles exhibited high deposition ice nucleation efficiencies and nucleated ice at RH_{ice} well below homogeneous ice nucleation limits. The data suggest that water uptake and immersion freezing are more sensitive to changes in particle chemical composition compared to deposition ice nucleation. The investigated anthropogenic and marine influenced particles, exhibiting various chemical and physical properties, showed distinctly different ice nucleation efficiencies and can serve as efficient IN at atmospheric conditions typical for cirrus and mixed-phase clouds.

2CC.14

Wintertime Measurements of Scavenging Ratios of Sea-Salt Components for Snow and Rain in Niigata Prefecture, Japan.SHIN OHARA, Shin-ichi Fujita, Soichiro Sugimoto, Akira Takahashi, *Central Research Institute of Electric Power Industry*

Scavenging ratios of Na^+ for rain and snow were evaluated in order to examine the differences in scavenging process of sea-salt aerosol between snow and rain in Niigata Prefecture, Japan. Concentrations of chemical constituents in precipitation and aerosol were measured at a site in Niigata Plane, located along the Sea of Japan, during winter season of 2008 - 2010. The geometric mean of the scavenging ratio of Na^+ for snow was greater than that for rain. As well as Na^+, the geometric mean of the scavenging ratio of Cl^- and Mg^{2+} for snow was greater than that for rain, whereas the geometric mean of the scavenging ratio of non-sea-salt components including NH_4^+, nss-SO_4^{2-}, NO_3^- for snow were almost equal to that for rain. The scavenging ratio of Na^+ for snow remained constant with surface air temperature, while that for rain decreased with surface air temperature, falling to approximately one order smaller than that for snow. These results indicate that snow can be a more efficient scavenger of sea-salt aerosol than rain. Furthermore, the results suggest that the difference in scavenging ratio of sea-salt components between snow and rain would be attributed to relatively larger contribution of below-cloud scavenging to precipitation scavenging of sea-salt aerosol compared to non-sea-salt components, and the greater efficiency of below-cloud scavenging of sea-salt aerosol for snow than that for rain.

2CC.15

Assessing the Importance of Contact Ice Nucleation.

DANIEL CZICZO, Yi-wen Huang, *MIT*

The indirect effect of aerosols on global radiative forcing via its impact on cloud formation is one of the key unknown in aerosol science. Though our understanding of warm cloud formation is fair, our inability to fully describe cold cloud formation limits us in determining and predicting future climate change. It is believed that deposition freezing and immersion freezing are important ice nucleation mechanisms. Less known is the mode called “contact freezing”, which involves particles coming into contact with a water droplet to form an ice nuclei (IN). Some experimental studies have shown that ice formation due to contact freezing is initiated at higher temperatures than immersion freezing. However, few experiments have been performed using atmospherically relevant conditions.

We have constructed a laboratory experiment to assess the importance of ice nucleation via contact freezing. The system consists of an injector which is designed to bring a water droplet into contact with aerosol particles at controlled temperatures. The collision between the water droplet and the aerosol particle(s) may induce ice nucleation. A FTIR spectrometer is used to monitor ice presence and water vapor partitioning in the flow tube at multiple positions and help determine the onset temperature of contact freezing. At the end of the flow tube, a counterflow virtual impactor (CVI) is affixed to reject aerosol particles and let through only the large particles. The flow containing the IN is directed to the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument which performs in situ chemical analysis of a single particle.

2CC.16

Efficiency of Biological Aerosol for Contact Mode Freezing.

JOSEPH NIEHAUS, Xin Xin Woodward, Will Cantrell, *Michigan Technological University*

Biological particles such as pollen and bacteria have been implicated in cloud formation processes (Mohler et al. 2007). They are of particular interest due to their ability to nucleate ice at temperatures warmer than -20 C. Although mineral dust is the most abundant ice nucleus present in the atmosphere, it has not been found to be relevant for temperatures warmer than -25 C (see e.g. Neidermeier 2010). Contact nucleation, where particles catalyze the phase transition at the air/water interface, is one suspect for high temperature ice nucleation. In some laboratory tests, side by side comparisons of contact vs. immersion mode nucleation saw a difference in freezing temperatures of 5 C.

We have studied ice nucleation by Snomax, a commercially available form of the bacteria Pseudomonas syringae, in both the contact and immersion mode. The freezing efficiency, defined as the ratio of freezing events to the number of bacterial cells deposited to a supercooled water droplet, was greater in the contact mode for all temperatures in the range -3 to -8 C. In the contact mode at -3 C, there is one freezing event for every 80,000 cells that impact the surface of the supercooled water droplet. By -7 C, the efficiency has risen to one freezing event for every 100 cells. In contrast, in the immersion mode, the efficiency was one freezing event for every 10 million cells at -3 C and one in 3000 cells at -7 C. The difference between contact and immersion modes diminishes as temperatures decrease.

2CC.17

Cloud Condensation Nuclei Measurements at a High Elevation Site: Composition and Hygroscopicity. BETH FRIEDMAN, Alla Zelenyuk, Josef Beranek, Gourihar Kulkarni, Mikhail Pekour, Anna Gannet Hallar, Ian McCubbin, Joel A. Thornton, Daniel Cziczo,*University of Washington*

Field measurements of cloud condensation nuclei (CCN) were conducted in March 2011 at Storm Peak Laboratory (elevation 3220 m a.s.l.) in Steamboat Springs, CO. Measurements of CCN number concentrations and droplet size distributions at supersaturations of 0.08%, 0.1%, 0.2%, 0.4%, and 0.7% were conducted in parallel with Scanning Mobility Particle Sizer (SMPS) measurements of size distributions and number concentrations of ambient particles. SMPS number concentrations of the overall ambient aerosol population were used to calculate the fraction of particles activating as droplets at the supersaturations studied. Single Particle Laser Ablation Time-of-Flight mass spectrometer (SPLAT II) was used to characterize number concentration, size, internal composition, and densities of individual particles present in the ambient air. κ-Köhler theory, particle size measurements, number concentrations of CCN and CN, and single particle composition measurements were utilized to predict CCN concentrations and assess particle hygroscopicity and the importance of particle mixing state in CCN activation and prediction. Case studies with detailed compositional information, as well as free tropospheric CCN concentrations, will also be presented.

2CC.18

Formation of Semi-solid, Oligomerized Aqueous SOA: Cloud and Aerosol Lab Simulations. LELIA HAWKINS, Amanda Lemire, Katherine Muller, David De Haan, Molly J. Baril, Alec Rynaski, Nahzaneen Sedehi, *Harvey Mudd College*

Glyoxal and methylglyoxal form high molecular weight (HMW), N-containing compounds during simulated cloud processing with small amines, amino acids, and ammonium sulfate (AS); the measured residual particles are semi-solid and may require equilibration with humid air beyond the traditional 1-2 s residence time in hygroscopicity tandem differential mobility analysis (HTDMA). Using a novel HTDMA system that allows varied residence time in the humidification chamber, the hygroscopic growth (HG) of each of the resulting products of simulated cloud processing was measured. Gradual deliquescence was observed beginning at 40% RH. Using longer humidification times (20 min vs 3.4 s) produced an increase in growth factors for the glyoxal-methylamine (19% by vol) and methylglyoxal-methylamine (8% by vol) systems, indicating that the 3.4 s residence time was insufficient to achieve equilibrium. Semi-solid products showed a measurable impact on the deliquescence relative humidity (DRH) and growth of AS aerosol, with up to 7% reduction in DRH and up to 10% reduction in growth factor at 80% relative humidity. Droplet evaporation experiments showed that the mixed glyoxal-AS particles, but not methylglyoxal-AS, require at least 30 min of drying to achieve equilibrium, due to the reduced diffusivity of water in the semi-solid particles. To compliment the HTDMA measurements, atomic force microscopy was used to probe the viscosity (liquid-like, glassy, rubbery, crystalline) of the simulated particles. Results show that for some SOA mimics, particles are more like rubber than organic liquid or crystalline solids.

2CC.19

Effect of Secondary Organic Aerosol Amount and Condensational Behavior on Global Aerosol Size Distributions. STEPHEN D'ANDREA, Dominick Spracklen, Ilona Riipinen, Jeffrey Pierce, *Dalhousie University*

Recent research has shown that secondary organic aerosols (SOA) are major contributors to ultrafine particle growth to climatically relevant sizes, increasing global cloud condensation nuclei concentrations within the continental boundary layer (BL). While many global models contain only biogenic sources of SOA (emissions generally 10-30 Tg yr^{-1}), recent studies have shown an additional source of SOA around 100 Tg yr^{-1} is required to match measurements. Additionally, many models treat SOA solely as semivolatile which leads to condensation of SOA onto the aerosol mass distribution; recent closure studies with field measurements show that a significant fraction of SOA condenses to the aerosol surface area suggesting a very low volatility. We explore the significance of these two findings using GEOS-Chem-TOMAS global aerosol microphysics model. The additional SOA was added to the model globally by distributing the 100 Tg yr^{-1} correlated with the global fraction of carbon monoxide within each grid box. The condensation of SOA was varied to condense via the aerosol mass distribution and the aerosol surface area. The percent change in particles of size $D_p > 80$ nm (CN80) within the BL between the base simulation (10-30 Tg yr^{-1}) and the additional SOA (100 Tg yr^{-1}) both using the surface area condensation scheme yielded a global change of 28%, in regions with large CO emissions the increase in CN80 exceeds 100%. The percent change in CN80 within the BL between the surface area and mass distribution condensation schemes both without the additional SOA yielded a global change of 3% but exceeds 25% in biogenically active regions. Thus, the additional SOA as well as treating SOA as very low volatile cause a significant global increase in the number of climatically relevant sized particles and we must continue to refine our SOA treatments in aerosol microphysics models.

2CC.20

Optical Properties of Hematite and Fine Desert Dust Aerosols. HANS MOOSMULLER, Allison Aiken, Mavendra Dubey, Garrett Frey, Bruce Garro, Johann Engelbrecht, *Desert Research Institute*

Globally, aerosol mass emissions and optical depths are dominated by entrained mineral dust. While most minerals occurring in dust aerosols do not absorb solar radiation, some minerals cause significant absorption, thereby lowering the single scatter albedo (SSA) significantly below one, potentially contributing to a warmer and drier atmosphere. Therefore, the optical properties of globally relevant dust aerosols need to be characterized to reduce uncertainties in their radiative forcings. A well-known absorbing component found in dust aerosols is hematite, Fe2O3, which absorbs strongly in the blue-green spectral region, giving some soils, rocks, and dust aerosols their characteristic red color.

We discuss measurements of the optical properties of ~30 dust aerosols, including a pure hematite standard, hematite-containing mineral dust standards ranging from 9-34% hematite by mass, and various dust samples collected from around the world. Samples are suspended from aqueous solution and/or from dry atomization with a cyclone re-suspension chamber yielding the fine fraction relevant for long-range transport. Size distributions were characterized with an optical aerosol spectrometer; absorption and scattering coefficients were measured with a three-wavelength photoacoustic soot spectrometer (PASS-3) at 405, 532, and 781 nm and with an ultraviolet photoacoustic soot spectrometer (PASS-UV) at 375 nm yielding wavelength-dependent mass absorption coefficients (MAC's), SSA's, and wavelength dependent Angstrom exponents. Hematite MAC's are an order of magnitude smaller than those of black carbon (BC) at 405 nm and 532 nm and are largely non-absorbing at 781 nm with SSA's of 0.49 0.68 and 0.98, respectively.

2CC.21

Measurement of Halyomorpha Halys (Brown Marmorated Stink Bug) Biogenic Volatile Organic Compounds and Their Role in Secondary Aerosol Formation.

Danielle Solomon, DABRINA DUTCHER, Timothy Raymond, *Bucknell University*

The oxidation of biogenic volatile organic compounds (BVOCs) is a significant source of atmospheric aerosols, yet there is still much to be learned about their sources, and interactions and reactivity. The brown marmorated stink bug is a newly established invasive species of stink bug spreading throughout the United States. Due to the lack of natural predators and lack of approved agricultural pesticides this species has achieved a significant number density in many regions and is even causing significant crop losses. The aims of this project were to identify and quantify the BVOCs found in the defense pheromones of the brown marmorated stink bug and to determine whether these BVOCs would oxidize in the presence of ozone to nucleate and form aerosol particles. Several compounds were identified in the BVOC emissions of brown marmorated stink bug by gas chromatography – mass spectrometry. These identified compounds include Tridecane, 5-Ethyl-2(5H)-furanone, and E-2-Decenal. In the presence of ~100 ppb ozone the emissions of brown marmorated stink bug oxidized to form aerosol particles. This reaction resulted in 0.2 micrograms/cubic meter/bug of particle mass concentration. It was also found that these secondary organic aerosol particles could act as cloud condensation nuclei.

2CC.22

Modeling the Surface Tension of Complex Organic-Inorganic Solutions.

Allison Schwier, Giuliana Viglione, V. FAYE MCNEILL,*Columbia University*

Organic material is ubiquitously found in atmospheric aerosols, and a large fraction of it can be surface-active species, residing primarily at the gas-aerosol interface. These organics can form an interfacial film as well as depress surface tension, affecting trace gas uptake and cloud condensation nuclei ability, respectively. It is important to be able to predict the surface tension of atmospherically relevant complex mixtures to better understand the effects on atmospheric aerosols and their properties.

Currently, existing surface tension models have described complex systems in very dilute salt solutions or purely in water; however, these models should take into account aerosol environments (high ionic content) as well as be able to describe reactive systems. In this work, we present varying complex organic-inorganic solutions of amino acids, carboxylic acids and alpha-dicarbonyls in ammonium sulfate. We show that using an additive Szyszkowski-Langmuir equation and incorporating salt parameters reproduces most experimental data well, including reactive systems. We also discuss methods of incorporating salt effects, such as salt-organic interactions and "salting out".

2CC.23

Organic Composition of Submicron Aerosols in Cloud and Below Cloud in La Jolla, California: the Role of Organic Aerosols in Cloud Formation. ASHLEY CORRIGAN, Rob Modini, Anita Johnson, Janin Guzman Morales, Lynn Russell, Desiree Toom-Sauntry, Annie-Marie Macdonald, John Liggio, Richard Leaitch, Jason Schroder, Allan Bertram, Alex K. Y. Lee, Ran Zhao, Jonathan Abbatt, *Scripps Institution of Oceanography, UCSD*

Submicron particles were collected from May 8- July 4, 2012 at two platforms in La Jolla, CA: Mount Soledad (251 masl) and Scripps Institution of Oceanography pier (14 masl) to investigate the role of organic and black carbon aerosol in and below cloud base. A counterflow virtual impactor (CVI) was used to sample cloud residuals during cloud events on Mount Soledad. During cloud events, chemical composition of cloud residuals was analyzed by aerosol mass spectrometry (AMS), single particle soot photometer (SP2), photo acoustic soot photometer (PASS), and chemical ionization mass spectrometry (CIMS). Organic composition of atmospheric aerosol at both platforms was measured using Fourier transform infrared (FTIR) spectroscopy, aerosol mass spectrometry (AMS at Mount Soledad), and aerosol chemical speciation monitor (ACSM at SIO Pier), to determine differences in organic aerosol in and below cloud base. Campaign average organic functional groups from Fourier transform infrared (FTIR) analysis of PM1 aerosol included alkane, carboxylic acid, organic hydroxyl, organonitrate, non-carboxylic acid carbonyl, and primary amine. Measurements of particle-phase organic functional groups and inorganic ions collected during the Mount Soledad campaign are compared with gas-phase and inorganic aerosol precursors to elucidate controlling factors on secondary organic aerosol formation. Preliminary results indicate the important role organic aerosols play in marine stratocumulus cloud formation.

2CH.1

Nanometer-rated Liquid Filter Evaluation using the TSI Nanoparticle Nebulizer. TSZ YAN LING, Axel Zerrath, David Pui,*University of Minnesota*

State-of-the-art liquid particle counters have a detection limit of about 50 nm. This causes challenges in experimental evaluation of nanometer-rated liquid filters, which are used in industries requiring high-purity water and chemicals. It is commonly agreed that air-borne nanoparticle generation, classification and detection methods are more sensitive compared to the liquid-borne nanoparticle counterparts. Therefore, by properly dispersing the liquid-borne nanoparticles into air-borne form and having them measured by appropriate aerosol instruments, namely the Scanning Mobility Particle Sizer (SMPS), the sensitivity of the current liquid-borne nanoparticle characterization methods can be greatly enhanced. A major concern of using a conventional atomizer as a nanoparticle dispersion tool is the interference of residue particles, which are particles that are dried from droplets containing no solid particles. It is necessary that residue particles are controlled to be as small as possible to avoid them from overlapping with the solid particles as shown in a size distribution measurement.

TSI Inc. has newly developed the Nanoparticle Nebulizer, which can nebulize much smaller droplets compared to conventional atomizers, and therefore the residue problem encountered can be avoided. In this study, we applied the Nanoparticle Nebulizer to study the performance of nanometer-rated liquid filters using the aerosolization technique. Gold and PSL particles of sizes 80, 50 and 30 nm were used to challenge the filters. Hydrosols upstream and downstream of the filters were collected and the nanoparticle concentrations were measured using the Nanoparticle Nebulizer/SMPS system. Efficiency of the liquid filters as a function of particle size was obtained and compared with measurements made with another hydrosol analyzer, the Nanoparticle Tracking Analyzer. Both methods show results comparable with each other.

2CH.2

Combined Influences of Electrophoresis and Thermophoresis on Particle Deposition on a Flat Plate Exposed to a Parallel Airflow. HANDOL LEE, Se-Jin Yook, *Hanyang University*

Particle deposition velocity onto a flat surface has been intensively studied through experimental and numerical methods. Effects of electrophoresis and/or thermophoresis on particle deposition velocity have also been examined by assuming a free-standing wafer placed in a vertical airflow. However, few studies have been performed to investigate the combined effects of electrophoresis and thermophoresis on particle deposition velocity onto wafers or photomasks exposed to a parallel airflow. In this study, Statistical Lagrangian Particle Tracking (SLPT) model was employed with the use of FLUENT and DPM. The particle deposition velocities obtained by the SLPT model were in good agreement with the theoretical results predicted by Liu and Ahn (Particle deposition on semiconductor wafers, Aerosol Sci. Technol. 6, 215-224, 1987), when both electrophoresis and thermophoresis were excluded from consideration. In addition, the SLPT model was found to correctly estimate the particle deposition velocity under the combined influences of electrophoresis and thermophoresis, when the particle deposition velocities onto a free-standing wafer in a vertical airflow were compared between the SLPT model prediction and the experimental data of Opiolka et al. (Combined effects of electrophoresis and thermophoresis on particle deposition onto flat surfaces, J. Aerosol Sci. 25, 665-671, 1994). Finally, the particle deposition velocity onto a flat plate in a parallel airflow was investigated by applying electrophoresis and thermophoresis simultaneously.

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2CH.3

A Cylindrical Water-Film Electrostatic Precipitator to Remove Fine Particles or SO2/NO Gases. Bangwoo Han, Hak-Joon Kim, Dong-Keun Song, YONG-JIN KIM, *Korea Institute of Machinery and Materials*

A cylindrical water film electrostatic precipitator (ESP) has been investigated for the treatment of fine particles or SO2 and NO gases. For removal of fine particles, D.C. high voltage of about 10-20 kV was applied to the wire-cylinder ESP and for SO2 and NO gases, pulse high voltage of 30-40 kV with a rising time of 100 ns was applied to the same ESP. Inner wall of the ESP was uniformly coated with TiO2 nanoparticles with an average size of 15 nm. Ammonia and propylene gases were added into the ESP as additives for the treatment of SO2 and NO gases. Uniform water film with a water supply of about 3.0 l/min/m2 was successfully achieved at the inner wall of the ESP. Corona discharging characteristics such as voltage-current curves between the ESPs with and without water film were almost the same. This indicated that water film did not influence on the corona discharge phenomenon in the ESP due to uniformly formed thin water layer on the wall of the ESP. Particle collection efficiencies at different applied voltages to the ESP were also almost the same between ESPs with and without water film. Gas decomposition efficiencies for SO2 and NO between the ESPs with and without water film were also almost the same for both SO2 and NO. During dust loading, particle collection efficiency gradually decreased with time owing to a lower electric field between polluted electrodes of the ESP. This was completely avoided by forming a thin water film on the collection electrode in the ESP. It is expected that our water-film ESP will be a highly durable system for the treatment of fine particles and/or SO2 and NO emission gases.

2CH.4

The Electrical and Particle Removal Performance of Dry and Wet Electrostatic Precipitators at a 0.7 MW-Oxygen Pulverized Coal Combustion Pilot Plant. Hak-Joon Kim, Bangwoo Han, YONG-JIN KIM, Sang-In Keel, Jin-Han Yun, Tae-Hyung Kim, Jung-Hee Hong, *Korea Institute of Machinery and Materials*

The electrical and particle removal performance of dry and wet electrostatic precipitators were evaluated at a 0.7 MW-oxygen pulverized coal combustion (Oxy-PC) pilot plant in Daejeon, Republic of Korea. For the gas cleaning of the pilot plant, in-furnace deSOx method was used, spraying limestones directly into the furnace with a normalized stoichiometric ratio (NSR) of 2.0. The particle removal system for the pilot plant was composed of a dry ESP which cleaned whole volume of total flue gas and a wet ESP which cleaned 40% of the total gas, while 60% of the gas recycled into the boiler. The dry ESP with rigid-edge type electrodes and rectangular type collection plates developed by the KC Cottrell and the wet ESP with rigid-edge electrodes and water-film collection plates developed by the KIMM were used. The experiments showed that corona current under a given applied voltage at the oxy-PC combustion with the in-furnace deSOx was lower than that at air-PC combustion without the in-furnace deSOx. Mass concentration during Oxy-PC combustion with the deSOx method of the NSR of 2.0 was 2.5 times larger than that during air-PC combustion, and particle size distribution based on mass during air-firing mode was bi-modal (0.8 and 2.7 micro-meter), while that during oxy-PC mode was tri-modal (0.8, 1.94, and 13.35 micro-meter). The total collection efficiency with the dry and wet ESPs was 99.9%, while the efficiency only with dry ESP was 98.95%. It can be concluded that the usage of both dry and wet ESPs with water film collection plates could guarantee almost zero-emission less 1 milligram per cubic meter of particles for the CCS (Carbon Capture and Storage) facilities of the Oxy-PC combustion.

2CH.5

Experimental Investigation of Haze and Particle Formation by Airborne Molecular Contamination under Irradiation.CHANG HYUK KIM, Zhili Zuo, David Pui, *University of Minnesota*

During the last couple of decades, most problems related to airborne particles in semiconductor industry have been solved by using HEPA and ULPA filtration systems. However, as lasers with shorter wavelength and photo masks with smaller feature size are used during the manufacturing process, the control of non-filterable airborne molecular contamination (AMC) has become a new problem. Though at very low concentration levels (several ppb to ppt), AMC can be converted to nanoparticles once irradiated by high energy beams, causing haze formation on photo masks and consequently significant yield reduction and increased fabrication cost. Therefore, it is important to understand the mechanisms for AMC- and radiation-induced particle formation.

The objective of this study was to determine the critical conditions for particle nucleation and haze formation. Ammonia and sulfuric dioxide, two major components of AMC, were diluted with nitrogen or air down to ppb level, mixed with each other, and delivered to the irradiation chamber. The chamber was made of stainless steel and prebaked at 200 degrees Celsius to minimize interference from impurities such as chamber outgassing. The nucleation of the gas mixture in the chamber was assisted by the irradiation of soft X-ray, which simulates an extreme condition of the radiation-induced nucleation. A photo mask was also placed in the irradiation chamber for monitoring haze formation. An ultrafine condensation particle counter was used to measure the number concentration of generated particles and the degree of haze formation on the surface of the photo mask was quantified by a wafer surface scanner. Correlations between the AMC concentrations and the level of haze/particle formation are presented. The effect of humidity, temperature and residence time will be also investigated.

2CH.6

Optimization of the Novel Collector for Diesel Emissions Control. TAEWON HAN, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

We recently developed a novel diesel exhaust control device, the Electrostatic Screen Battery for Emissions Control (ESBEC). The prototype ESBEC consists of multiple sets of two screens, where one screen of each set is supplied with high voltage and the other is grounded, producing electrostatic field across the screens. The screens are covered by a hydrophobic coating to wash off the collected particles for continuous use of the Battery. The device features high particle collection efficiency without adding to the exhaust backpressure and there is no need for thermal regeneration of collected particles. In preliminary tests, 95% of diesel exhaust particle mass entering the battery was collected. However, the preliminary data also indicated that commercial ionizers used to charge the incoming particles were unsuitable for a field-applicable instrument due to particle losses and ozone production. Furthermore, the particle deposition across the device was not uniform impeding its long-term applications.

Thus, as part of the further development of this diesel control device into a field deployable unit, we designed and tested a carbon fiber based ionizer. The preliminary tests showed that ESBEC with a carbon fiber ionizer can remove more than 99% of 1.0 micro-meter fluorescent polystyrene latex particles entering the device. To ensure a more uniform diesel exhaust deposition across the battery thus prolonging the time before service, we tested ESBEC with screens of varying porosities and with different distances between the screens. The data indicate that positioning coarser screens closer to the inlet improves uniformity of particle deposition across the device. Once the combination of charger and collector is optimized, the ESBEC will be retooled from a heat tolerant material, such as machinable ceramics (e.g., glass-ceramic and Macor). The performance of ESBEC will then be tested with actual diesel exhaust of different concentrations and for different operation times.

2CH.7

Effect of Particle and Filter Charges on Particle Loading Characteristics of Air Filter Media. Hyun-Seol Park, WEONGYU SHIN, *Korea Institute of Energy Research*

Applications of electrostatic force into aerosol filtration have been utilized for enhancing the collection efficiency of air filter without increasing the pressure drop across the filter. Electrostatic forces acting between particles and filter media make an effect on transient filtration properties with particle loading as well as initial filtration efficiency. In this study, we have examined the effect of partcle and filter charges on particle loading characteristics of air filter media. Particle deposition pattern on filter fibers is changed by types of electrostatic forces and the intensity of each electrostatic force. The changed pattern affects the filtration performance, especially on the pressue drop. In this work, two filter charge states and three particle charge states were used as test conditions. One filter is a commercial electret filter medium which is corona-charged. The other is the same filter except that the filter charge is removed by dipping the commercial charged filter into IPA for a few minutes and drying. Electrically neutral particles(uncharged particles), particles having Boltzmann equilibrium charge distribution, and highly charged particles by a corona charger were loaded on each of test filter media, respectively. There was big difference of areal mass loading to reach 500Pa of pressure drop between highly charged particle case and the others regardless of filter charge. It was also found that the corona charged particles formed much porous structure of deposit while the neutralized and uncharged particles were deposited in a pattern of evenly packed structure on the face of filter media. The porous pattern of corona charged particles made much lower pressure drop across filter media for the same areal mass loading compared to other cases. The filter charge made only slight difference in the pressure drop, thus it was negligible compared to the effect of corona charged particles.

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2CH.8

Comparison of Charging States between Electrospun and Electret Meltblown Filter Media through Filtration Test for Submicrometer Aerosol. Hyun-Seol Park, WEONGYU SHIN, *Korea Institute of Energy Research*

Electrically charged air filters have a great advantage because electrostatic forces acting between filter fibers and oncoming particles enhance the filtration efficiency without increasing air resistance through the filter. In this study, we have compared the electric charging state of electrospun filter media and corona charged meltblown filter media. Electrospun filter media were prepared by a lab scale electrospinning machine, and the meltblown filter was commercial one, which was electrically charged by a corona filter charging methods. To verify the effect of filter charge, the collection efficiency was measured for test filters before and after discharging. To remove the filter charge, filter samples were discharged via isopropanol dipping method. In detail, all tested filter media were completely immersed in isopropanol bath for 10 min, and dried for 60 min at 70C. The collection efficiencies for monodisperse particles ranging 30 ~ 250 nm were compared. When a filter media get charged, collection efficiency of the filter should be distinguished from that of uncharged one. In this study, the meltblown filter media showed a big difference incollection efficiency between charged and discharged filters. In some cases, the collection efficiency decreased from 99% to 40%. On the other hand, electrospun filters showed only little difference. As a result of direct measurement of surface potential of test filters, the electric charge of electrospun filter was drastically decayed and finally reached to zero in a few seconds, for some cases in hours, while the corona charged meltblown filter media showed very slight loss of charge for over 20 hours. Generally it was known that the electrospun fiber has some charges during spinning process. Even though limited to this study, however, it can be concluded that the electrospun filters have no effective electrical charges.

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2CH.9

Effects of Spray Surfactant and Particle Charge on Respirable Dust Control. MEI WANG, Peter Raynor, *University of Minnesota*

Objective
This research measured the effects of spray surfactant and particle charge on the capture of respirable particles by water spray droplets.

Methods
Polystyrene latex particles with diameters of 0.6, 1.0, or 2.1 micro-meter were generated in a variable speed wind tunnel. Particles were given either a neutralized, unneutralized, net positive, or net negative charge condition using a neutralizer and a diffusion charger. Some of the particles were removed as they passed through sprays with 0, 1×10^{-6} 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. Size and concentration were then measured using an aerodynamic particle sizer. Measurements with the spray on and off allowed calculation of efficiency. Overall collection efficiencies, as well as efficiencies of particles with specific charge levels, were measured.

Results
The overall collection efficiency significantly increased with increasing particle diameter ($p<0.001$): collection efficiencies of 19.0±8.7%, 57.6±16.1%, and 95.9±60.9% (Mean±SD) were observed for particles 0.6, 1.0, and 2.1 micro-meter in diameter, respectively. Particle charge condition, surfactant type, and surfactant concentration do not significantly affect the overall collection efficiency. Strongly-charged particles tend to be collected more efficiently than weakly-charged particles. Negative particles are collected most efficiently by cationic surfactant sprays and least efficiently by anionic surfactant sprays, whereas positive particles are collected most efficiently by low concentration anionic surfactant sprays and least efficiently by cationic surfactant sprays. Collection efficiency is associated more strongly with surfactant spray droplet charge level rather than with surfactant classification.

Conclusions
Particle diameter is the most important determinant of the collection efficiency. The charge level of the surfactant spray droplets may also critically impact the particle collection efficiency, especially for charged particles.

2CH.10

Biosafety Level 3 Bio-Aerosol Generation System. JOSEPH LACIRIGNOLA, Jonathan Richardson, Robert Martinez, Edward Froehlich, Andreas Gennis, Richard Vanderbeek, Mary Wade, Todd Sickler, Amber Prugh, Kevin Hung, *MIT*

A novel system has been developed for producing bio-aerosol samples under a wide range of conditions with Biosafety Level 3 (BSL-3) samples. This system can produce controlled aerosols from either wet or dry materials and can mimic a wide range of environmental conditions. The system is controlled remotely and can be decontaminated in-place using vaporous hydrogen peroxide (VHP). The system has been demonstrated to operate for hours at a time producing highly stable aerosol samples for the Multi-wavelength Aerosol Signature Testbed (MAST) phase 1 project. Prior to being fabricated, the system was modeled using computation fluid dynamics (CFD) software to predict the particles size output. Subsequent system measurements verified that the CFD models were correct. This poster will present the design and performance of the system.

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2CH.11

Room Scale Deposition of Chem/Bio Decontaminants Dispersed through Commercially Available Induction Spray Charging Nozzles. Joshua Hubbard, Rita Betty, Daniel Lucero, Danielle Rivera, ANDRES SANCHEZ, Brandon Servantes, *Sandia National Laboratories*

Inertial, electrostatic, and gravitational droplet deposition velocities were measured in a 2.5 x 2.5 x 2.5 meter spray chamber. Commercially available chem/bio decontaminant (DF-200) was dispersed through two electrostatic induction nozzles: a two fluid nozzle from Electrostatic Spray Systems (ESS) used for agricultural purposes, and a rotary atomizer from Illinois Tool Works (ITW) designed for automotive paint applications. Spray droplet size distributions were measured with a Malvern Spraytec light scattering instrument. DF-200 was then tagged with sodium fluorescein and sprayed with and without droplet charging to assess the effects of electrostatics on chamber deposition. Stainless steel coupons were placed in multiple locations in different orientations to differentiate between the following deposition mechanisms: inertial, gravitational, and electrostatic. Chamber aerosol concentrations were measured with fiberglass filters and SKC biosamplers. Coupons were recovered from the chamber and serial dilutions were performed to quantify the aerosol mass deposited. The average deposition flux (g/m^2s) was normalized by the average air concentration (g/m^3) to obtain the average deposition velocity (m/s) for each surface. Floor deposition was in good agreement with gravitational settling velocities. Vertical surfaces outside the spray plume showed significantly enhanced deposition (one to two orders of magnitude higher) when droplets were charged.

2CH.12

High-Speed High-Resolution Tracking of Micrometer Particle Detachment and Resuspension on Different Surfaces. ASMAA KASSAB, Victor Ugaz, Maria D. King, Yassin Hassan, *Texas A&M University*

In an effort to understand the phenomena behind particle resuspension, the condition under which a transient fluid flow causes single spherical glass beads particles to detach from glass, ceramic and hardwood substrates was investigated experimentally. Initially, individual particles were deposited on the different substrates located at the lower surface of a rectangular 3x4 inch duct by gravitational settling, after which adjustable speed blowers were used to impose air flows from an open entrance at average velocities up to 16 m/s. The trajectory of the individual particle motion immediately before liftoff was precisely captured by continuously monitoring the particles with a high speed camera. The camera image acquisition is synchronized with the blowers to automatically trigger the camera while starting the air flow with a specially designed electric circuit with 2.5 x 10^{-}4 s maximum error in time recording.

Particle tracking obtained from high-speed imaging of individual particle trajectories, revealing a complex motion characterized by an initial bouncing or/and rolling motion along the surface prior to liftoff. In general, bigger particles tend to bounce higher and lift off to lower heights compared to smaller sizes especially in the ceramic substrates. The time it will take for the particle to start its initial movement after imposing air flow at 16 m/s is in the range of 0.33 to 2.6 s with no clear dependence on particle size (10-50 micro-meter) or surface roughness (in our experimental range), however that time is expected to increase with decreasing the air velocity. Particles travel 8 times more in the horizontal direction than the vertical direction in a viewing window of (920 x 420) micro-meters. The higher the vertical position the greater the particle velocity and the faster the particle will resuspend and completely leave the contact with the surface.

2CH.13

Evaluation of Outdoor Surface Adhesion and Reaerosolization of Anthrax: Reaerosolization from a Sod Matrix. JACKY ANN ROSATI ROWE, Laurie Brixey, Zora Drake-Richmon, Jonathan Thornburg, Alfred Eisner, *US EPA*

A large outdoor release of Bacillus anthracis could result in spores being dispersed and deposited on a wide range of outdoor surfaces. In the 2001 Bacillus anthracis letter incidents, the spores that deposited on various indoor surfaces were reaerosolized (i.e., reaerosolized) by human activity, which not only spread contamination but exposed persons in contaminated areas to inhalation hazards (Weis et al., 2002). In addition, spores adhered to shoes and clothing and were tracked to other buildings and locations by evacuees and first responders. Based on prior research, it is known that temperature, humidity, air movement, and physical disruption affect the amount of reaerosolization and tracking (Rosati et al., 2008). This research sought to determine the reaerosolization fraction from a soil/sod matrix if such an incident were to occur.

Turf type tall fescue sod (soil-grass matrix) was chosen to represent the type of grass used on the National Mall in Washington, D.C. This sod was placed in shallow trays and was sprayed with a solution containing Bacillus thuringiensis var. kurstaki (BtK) in sterile distilled water. A controlled large scale wind tunnel was used for testing. Environmental conditions included an ambient temperature of 23°C, a wind speed of 2.2 m/s, and an RH of 30% and 70%. Filter-based sampling was used to evaluate the amount of spores reaerosolized.

Reaerosolization was determined to be consistent after the initial (0 h) sample even though the grass-soil matrix became dessicated as the experiment progressed. The fraction reaerosolized at low RH (1.33 x 10-4) was an order of magnitude higher than the fraction reaerosolized during high RH tests at the same wind speed (1.95 x 10-5). This is likely because a significantly greater force was required to detach the spores under high RH conditions.

2CH.14

Collection Efficiency of a New Portable Electrostatic Precipitator (BIODOSI) Designed for the Collection of Airborne Pathogens. ROLAND SARDA-ESTEVE, Jean-Maxime Roux, Jean Sciare, Guillaume Delapierre, Marie-Helene Nadal, *LSCE (CEA-CNRS-UVSQ)*

A portable (<500g), silent, and autonomous (several hours) bioaerosol collector (BIODOSI) is currently being developed at CEA with the final objective to collect very efficiently airborne pathogens such as supermicron bacteria and spores but also submicron viruses which potential is often lacking for existing portable biocollectors. Particles are collected on a dry surface and concentrated afterwards in a small liquid medium to be analyzed by culture, PCR, immunoassays, mass spectrometry, Raman spectroscopy, to name a few. To be representative of individual exposure, the nominal flowrate of the BIODOSI collector is chosen to be closed to human breathing (10 LPM). This low flowrate also meets the compactness required for a portable and silent instrument which gets rid of heavy and noisy pumping systems. A brief description of the first BIODOSI prototype is provided here. The aerosol collection efficiency of this first prototype is also presented. It was performed by using non biological particles (NaCl, KCl) for a wide range of aerosol sizes. Based on SMPS measurements, very high collection efficiencies (>98%) were observed for 22 size bins ranging from 10nm to 800nm demonstrating the potential of the BIODOSI to collect submicron bioaerosols. Qualifications in ambient conditions have been also performed leading to similar high collection efficiencies for submicron and supermicron particles. Further qualifications in ambient conditions are currently performed in which specific polysaccharides (mannitol, arabitol) are used to trace ambient fungal spores (Bauer et al., 2008) and chemically determine the collection efficiency of the BIODOSI for this class of bioaerosols.

Reference: Bauer, H. et al., Arabitol and mannitol as tracers for the quantification of airborne fungal spores, Atmospheric Environment, 42, 588–593, 2008.

2CH.15

Development of Calibration Standards for BW Aerosol Sensors. JESSE LINNELL, Trina Vian, Jay Eversole, Vasanthi Sivaprakasam, John Tucker, Joseph Morency, Adam Dai, *MIT*

In response to recent increases in potential biological warfare (BW) threats from either state-sponsored or terrorist actors, there has been a period of rapid development and deployment of BW aerosol detection systems. Now that the first generation of these systems has become operational, attention has turned to related sustainment issues and maintenance requirements such as routine calibration of these sensors.

The Joint Project Manager for Biological Defense, the Naval Research Laboratory (NRL) and MIT Lincoln Laboratory (MIT LL) are currently collaborating on a program to address challenges associated with determination of degradation of operational BW sensors known as point detectors. The two main thrusts of this program are the development of a suitable aerosol particle reference standard, and a portable aerosol generation system ruggedized for field use. Since the system must be capable of field site use, the calibration aerosol material must be non-hazardous and potentially commercially available with highly reliable and repeatable properties. NRL has taken on the first task by examining commercially available polymer beads in terms of their spectral optical properties to determine suitable candidates for biological particle surrogates.

In parallel, MIT Lincoln Laboratory has focused on the second challenge of developing a mobile aerosol generation and conditioning system that will deliver reliable and repeatable low aerosol concentrations for sensor tests. A test methodology has been designed that minimizes test duration while identifying sensors that require maintenance at a 99.95% confidence level. This aerosol generation system, referred to as the Interim Point Detector Analyzer, is currently being automated and repackaged for smaller size and portability, and will soon undergo extensive field tests under a variety of environmental conditions.

This poster will summarize the NRL and MIT LL work to date on the IPDA development effort.

2CO.1

Spatial Variation of Particle Number Emissions of a Hybrid 2010 Toyota Camry Hybrid and Comparable Conventional Vehicle. MATT CONGER, *UVM*

The deleterious effects of ultrafine particles upon human health and the environment have resulted in an interest in quantifying the temporal and spatial patterns of vehicle particle emissions. Particle Number (PN) emission rates (#/s) for conventional vehicles (CV) have been extensively studied and positively correlate with higher engine loads and aggressive driving. Hybrid Electric Vehicles (HEV), powered by both an internal combustion engine (ICE) and an on-board electrical propulsion system, show frequent on-off cycling of the ICE and associated intermittent emissions. In urban areas, lower speed stop-and-go driving conditions result in a higher frequency ICE cycling compared with higher speed highway driving. These differences in ICE operation result in greatly differing patterns of PN emission rates between the two vehicle types. A significant increase in hybrid vehicle models available coupled with an increasing penetration of HEVs in to the U.S. passenger vehicle market gives rise to the importance of investigating these differences in PN emissions.

This study compares the real-world spatial variation of PN emission rates (based on TSI 3090 Engine Exhaust Particle Sizer measurements) between one conventional and one hybrid 2010 Toyota Camry over a variety of road classes in Chittenden County, Vermont. Using the University of Vermont TOTEMS on-board data package, PN emission rates (#/s) were compared across 82 roadway links across 8 road classes, a single driver and an identical 50 km route for 8 CV and 6 HEV sampling runs. Conventional vehicle PN emission rates overall were slightly higher than hybrid (2.61 and 2.24 x 1010 #/s, respectively), but urban driving found CV PN emission rates (1.55 1010 #/s) only half of the hybrid (3.12 x 1010 #/s). These finding suggest significant differences in spatial distribution of PN emission rates resulting from differing infrastructure attributes and may be instrumental in the modeling of hybrid emissions.

2CO.2

Morphology of Aerosol Particles at Freeway On-Ramps. SWARUP CHINA, Neila Salvadori, Claudio Mazzoleni, *Michigan Technological University*

Atmospheric aerosols impact the environment and climate by affecting Earth's radiation balance, cloud formation and atmospheric chemistry. Vehicles are the dominant source of pollution in urban environments. Diesel and gasoline particulate matter emissions are primarily composed of agglomerated soot particles and volatile organic and sulfur compounds. The morphology of atmospheric particles influences their optical properties and therefore their radiative forcing; the morphology also affects the particles' transport and lifecycle. In this study we investigated morphological and structural properties of road-side aerosol particles at six different cloverleaf freeway on-ramps in the Detroit–Ann Arbor geographical area in Southern Michigan. The aerosol samples were collected on nuclepore polycarbonate filters and characterized by scanning electron microscope. Qualitative elemental compositions were determined using energy dispersive X–ray spectroscopy.

Particles were found in various shapes such as spherical, fractal-like aggregates or soot, irregularly shaped, and particles with multiple inclusions. Particles were divided into few groups based on their morphology. The fraction of fractal-like particles with respect to the total number of particles counted was then associated with the traffic density (number of passing vehicles per minute) and the vehicle type (e.g.; passenger vehicle vs. truck) to study the contribution of traffic to the ambient soot concentration near freeways. Three dimensional fractal properties of soot aggregates were studied using 2d projected images for different driving conditions. Morphological parameters (i.e. aspect ratio, circularity and roundness) showed a good correlation with particle size. We will present the variability in soot particle morphology at different times of the day and the morphology dependence with several influencing factors such as the vehicle specific power (that represents the driving conditions), the vehicle model year and fuel type, and the local meteorological conditions.

2CO.3

Controlled Studies on Aerosol Formation During Biomass Combustion in a Flat Flame Reactor.

JIAXI FANG, Anna Leavey, Pratim Biswas, *Washington University in St Louis*

Billions of people worldwide rely on biomass to cook their food each day. Biomass is also receiving renewed interest as a potential carbon-neutral energy alternative. The use of biomass as a fuel has the advantages of being renewable and sustainable; however burning it typically results in higher PM emissions often due to use of poorly designed combustion systems. In rural areas, the resulting poor air quality has been shown to significantly contribute to the global burden of respiratory and other diseases. Despite this enormous reliance on biomass, and its severe health consequences, there is a surprising paucity of fundamental studies examining particle formation during the initial stages of biomass combustion. This is an important omission given that particles are primarily formed at this stage of the combustion process.

A flat flame reactor was designed to study the early stages of combustion. Studying the well controlled rapid pyrolysis of biomass, factors contributing to particulate emissions were examined. Four different types of biomass, including juliflora ,cotton stalk, poplar, and applewood were pyrolysed in a methane-air flat flame. Particulate matter formed was characterized through measuring the CO emissions and surface, mass, and particle number size distributions. The moisture content of biomass feed stock was varied from 0%- 25% moisture content while the particle feed sizes were maintained below 100um to maintain a thermally thin regime. Thermo-gravimetric Analysis (TGA) was also conducted on the biomass to obtain mass fraction data(% volatiles, moisture content) along with kinetic data. Experiments have shown that factors contributing to reduced the efficiency of devolitilization promote higher emissions as such factors will be discussed in this presentation. Results from this study can be used to optimize biomass combustion for use as fuel in household settings to minimize negative impacts due to poor air quality. Implications on atmospheric aerosols will also be elucidated.

2CO.4

Impact of Natural Gas Fuel Composition on PM Mass, Number, and Size Distribution from Heavy-duty Vehicles.

MARYAM HAJBABAEI, Zhongqing Zheng, Thomas D. Durbin, Kent C. Johnson, J. Wayne Miller, David R. Cocker III, Georgios Karavalakis,*University of California, Riverside*

Natural gas (NG) use as an alternative transportation fuel is expanding in recent years. Natural Gas Vehicles (NGVs) are generally believed to produce low emissions of non-methane hydrocarbons (NMHC), carbon monoxide (CO), oxides of nitrogen (NOx), and particulate matter (PM). In California, the use of natural gas is increasing predominantly due to expanded power and home heating needs. With increasing demand for natural gas and liquefied natural gas (LNG), a wider range of sources is needed from new producing fields under development in the western US and new local sources of natural gas.

In this study, the impacts of natural gas composition on criteria and toxic emissions are evaluated for NGVs. Three heavy-duty vehicles were tested on a heavy-duty chassis dynamometer. Two transit buses, with 2009 Cummins ISL-G 8.9 L and 2003 John Deere 8.1L 6081H engines, respectively, were tested on the Central Business District (CBD) test cycle. A waste hauler truck with a Cummins 8.3L C Gas Plus engine was tested on the William H. Martin (WHM) refuse truck cycle. A total of six or seven blends including two gases representative of Texas and Rocky Mountain Pipeline Gases, a Peruvian LNG, a Middle East LNG-Untreated with high Wobbe number (above 1400), two gases representative of those located within the state that have low methane number as well as varying hydrocarbon compositions, and a CNG blend produced from an LNG fuel tank with similar properties to the first two gases were used. The results of PM mass, number, and size distribution for these tests will be presented here. In general, PM mass was very low for all the three vehicles. Some fuel composition effect was observed on particle number and size distribution, which was mainly due to hydrocarbon content of the blends.

2CO.5

An Empirical Model for Predicting the Amount of Gaseous Emissions Based on Instantaneous Modified Combustion Efficiency (MCE). SEYEDEHSAN HOSSEINI, Li Qi, Heejung S. Jung, J. Wayne Miller, David Weise, David R. Cocker III, *University of California, Riverside*

Due to the complex nature of combustion pathways in biomass burning, there has been little to no success in characterizing and modeling the transient emissions. In this study, an empirical model capable of estimating the transient gaseous emissions from combustion of biomass fuels based on instantaneous Modified Combustion Efficiency (iMCE) is presented. The emissions from a total of 64 burns were investigated. The vegetation types included fuels from Southwestern and Southeastern U.S, and the experiments were conducted at the facility of U.S. Forest Science Laboratory in Missoula, MT in 2009. Transient concentration of various organic compounds including formaldehyde, acetaldehyde, benzene, naphthalene, toluene, C8-C11 aromatics were measured using a proton transfer reaction mass spectrometry (PTR-MS) and a negative ion proton transfer chemical ionization mass spectrometry (NI-PT-CIMS). Concentrations of CO and CO2 were measured by an open-path Fourier transform infrared spectroscopy (OP-FTIR). The results showed that a certain portion of the following transient-response plots are linear for a compound of interest 'X': 1) instantaneous emission ratios of compound X (ERx) vs. iMCE for flaming phase and 2) Conc. of compound X vs. conc. of CO2 for smoldering phase. Combining the two linear parts, a function for calculating instantaneous conc. of the compound for the whole duration of the burn based on CO and CO2 can be obtained (parameterized based on k1 and k2). Furthermore, k1 does not vary that much from different burns or fuel types (Formaldehyde: k1=-0.11±0.002, Toluene: k1=-0.370±0.039, Naphthalene: k1=-0.221±0.059). However, k2 correlates linearly with the ratio of CO to CO2 (slope of α) during smoldering phase (R2=0.92 and R2=0.89). These parameters allows the user to simulate the emissions accurately based on easily collectable data (CO,CO2). A unique response function was found for each compound without consideration of fuel type, fuel moisture but solely based on instantaneous fire CO, CO2, k1, k2(α), and combustion phase.

2CO.6

Emission Characterization from Residential Scale Boilers Using Grass as Fuel. SRIRAAM RAMANATHAN CHANDRASEKARAN, Philip K. Hopke, Michael Newtown, Arthur Hurlbut, *Clarkson University*

Biomass combustion is gaining interest as a replacement for fossil fuels because woody fuels are a renewable resource and can be cost-effective as the price of fossil fuel rises. Although, biomass combustion reduces the dependency on fossil fuel and is cost effective, the potential adverse health effects associated with this source of both gaseous and particulate emissions. Although most research concentrates on wood as a fuel, there is an interest in alternative, fast growing plants like grasses. Grasses have several advantages over other feedstocks. The energy content from grass pellets is similar to wood pellets and is a rapidly renewable resource with multiple harvests per year. Grasses can be grown on marginal farmlands that would otherwise not be used. The composition of grasses is generally not very suitable for combustion because its ash content, nitrogen, potassium and chlorine concentrations are higher than wood. Because of the mineral composition of these grass ash, it tends to melt in the boiler leading to damage to the appliance and potential problems with burning the fuel. These problems could potentially be addressed using soil management techniques or by using an advanced staged combustion units. The objective of the study was to characterize the emissions from six different residential scale appliances using grass and wood pellets as fuel at low and high load conditions. The emissions in the stack were drawn through an in-stack PM_10 and PM_2.5 cyclone into a dilution sampling system conforming to EPA's conditional test method CTM-039. Criteria pollutants including PM_2.5, NO_x, SO_2 and CO were continuously monitored. Particles size distributions in the range from 5.6 to 560 nm were obtained using a Fast Mobility Particle Sizer (FMPS). Quartz, PUF, and Teflon filters were collected to analyze the organic carbon, semi volatiles and elemental composition of PM_2.5.

2CO.7

Light-Duty Diesel Engine Exhaust Particle Number Distribution Differences between Petro-Diesel and Different Blends of Soy Biodiesel Fuels. TYLER FERALIO, Britt Holmén, Jim Dunshee, *University of Vermont*

Recent energy and climate policies, such as EISA, encourage the production and use of biofuels. As a result, there has been an increase in the use of biodiesel in the transportation sector despite limited understanding of its health and environmental effects. In urban areas, transportation sources are one of the main contributors to particulate air pollution. This shift in fuel use, therefore, affects the particle number size distribution and particle composition found in the air we breathe. The aim of this study is to quantify the differences in emissions from these fuels in order to increase understanding of the potential health effects. To that end, preliminary 'engine-out' emissions data were collected from a Volkswagen 1.9 Liter SDi naturally aspirated light-duty diesel engine running on different blends of soy-based biodiesel. The data were collected while the dynamometer was loading the engine to maintain 2000 RPM at 45 percent throttle (approximately 40 percent load at this RPM). Soy biodiesel fuel blends were B0, B20, B50, and B100. Tailpipe exhaust was diluted using a mini-diluter system with a dilution ratio of approximately 56 and 1Hz particle distributions (32 channels, 5.6 - 560nm) were measured with a TSI 3090 EEPS.

Results are similar to trends found in the literature. The particle number distribution of petro-diesel was unimodal (modal diameter 52.3nm) with an average peak concentration of 2.7416e7 particles/cc. As the concentration of biodiesel was increased, the PN distribution developed additional particle diameter modes. The B100 distribution showed three distinct modes centered at 10.8, 17.8, and 31.7nm with peak concentrations averaging 1.3829e8, 1.2726e8, and 1.3381e8 particles/cc, respectively.

These preliminary data will be used to build an artificial neural network model to predict PN emissions as a function of engine operating parameters and fuel type using standard OBD-II data and measured fuel properties.

2CO.8

Chemical Characterization of Primary and Secondary Biodiesel Exhaust Particulate Matter. JOHN KASUMBA, Britt Holmén,*University of Vermont*

Recent research has shown that emissions of some criteria pollutants e.g., particulate matter (PM), CO, and SO_2 from biodiesel are less than those from petrodiesel. However, studies have also indicated that unregulated toxic emissions like carbonyls from biodiesel are higher compared to those from petrodiesel. Also, there is little information concerning the interaction of biodiesel exhaust PM with atmospheric oxidants such as ozone. The oxidation products of ozone/biodiesel PM reaction could have more severe health and environmental impacts than the primary emissions.

An Armfield CM-12 Automotive Diesel Engine operated in an aggressive cycle driving mode was used to generate PM from various biodiesel feedstocks (soybean, canola, and animal fat). The PM emissions were sampled by a variety of instruments: engine exhaust particle sizer, EEPS (TSI Model 3090) for measuring particle size distributions between 5.6 and 560 nm in real-time; electrical low pressure impactor, ELPI (Dekati LTD) for particle mass distributions, size-resolved chemistry and number concentrations between 7 nm and 10 micrometers; Teflon filters for gravimetric mass, and quartz fiber filters (QFF) for chemical analysis of the exhaust PM using gas chromatography mass spectrometry (GCMS). The polar fraction of primary biodiesel exhaust PM (soybean B20) was found to be 60.8% of the non-polar fraction in the elutable organic mass, while the polar fraction of primary diesel exhaust (B00) was 6.8% of the non-polar fraction in the elutable organic mass. These results show that exposure to primary biodiesel exhaust PM may lead to a higher oxidative stress than exposure to primary diesel exhaust PM.

Biodiesel PM was further exposed to different ozone concentrations over a 24-hour period at room temperature to determine and quantify the products of the reactions between ozone and the biodiesel exhaust PM. Carbonyls, carboxylic acids, PAHs, and quinones are the compounds quantified in these experiments.

2CO.9

Mapping the Operation of the Miniature Combustion Aerosol Standard (mini-CAST) Soot Generator. RICHARD MOORE, Andreas Beyersdorf, Suzanne Crumeyrolle, Lee Thornhill, Edward Winstead, Luke Ziemba, Bruce Anderson, *NASA Langley Research Center*

Soot aerosol derived from combustion processes have been shown to affect the Earth's radiation budget via direct absorption and scattering of solar radiation and by acting as cloud condensation nuclei (CCN) or ice nuclei (IN) to form clouds. In addition, ultrafine soot particles and associated polycyclic aromatic hydrocarbon (PAH) compounds likely pose significant health risks to the public. Consequently, much work in recent decades has focused on quantifying the properties of both ambient soot and that directly emitted from combustion sources. Relevant properties include soot concentration, size and morphology and the presence of inorganic and organic coatings on the soot surface. Investigating the role of each of these properties in determining climate and health impacts directly from ambient measurements is challenging because of low ambient mass loadings and because soot often coexists with atmospheric aerosol with a high degree of chemical complexity. Consequently, laboratory studies are needed to deconvolve these dependencies. A crucial component in these studies is having a reliable and reproducible combustion aerosol generator. A promising commercially-available generator is the Jing Ltd. Combustion Aerosol Standard (mini-CAST), which generates soot using a nitrogen-quenched, non-premixed, propane diffusion flame.

We present a comprehensive characterization of soot produced by the mini-CAST over the range of operating conditions, including variation of fuel, oxidation air, and mixing nitrogen flow rates. Measurements of particle size were found to be fairly constant and reproducible over a period of weeks to months, while number concentration varied due, in part, to soot accumulation in the flow system. In addition, OC-EC analysis from bulk filter measurements and SP2-derived coating thicknesses show a significant variation in residual organics including PAHs coating the soot surface over the range of measured sizes, which influences the effective density. The effectiveness of removing these coatings with a heated catalytic stripper will be discussed.

2CO.10

Comparison of Measurement Methods for Black Carbon in Diesel Engine Exhaust. SANNA SAARIKOSKI, Samara Carbone, Matti Happonen, Antti Rostedt, Topi Ronkko, Jyrki Ristimäki, Jorma Keskinen, Risto Hillamo, *Finnish Meteorological Institute*

Black carbon (BC) is a by-product of both anthropogenic (e.g. fossil fuel) and natural incomplete burning (wild fires). Being a strong absorber of solar radiation it is a key component in global warming, and due to its health effects, an important factor of air pollution. Diesel engines are one anthropogenic source of BC. However, there is a gap of knowledge between the parameters required by the models and the current measurement results of diesel derived BC. The aim of this study was to compare three methods for measuring BC from diesel exhaust.

The measurements were performed in the emission laboratory of Wärtsilä Finland Oy in 2011. Medium speed diesel engine was tested with ultra-low sulphur diesel fuel. Eight engine load points were measured. Black carbon was measured with filter smoke number (FSN), multi-angle absorption photometer (MAAP) and soot particle aerosol mass spectrometer (SP-AMS). In addition to BC, particle size distributions were measured with two scanning mobility particle sizers and particle mass concentration with tapered element oscillating microbalance.

Black carbon concentrations in the diesel engine exhaust varied from 0.2 to 4.9 mg m-3 measured by the FSN. FSN measured BC from the undiluted exhaust whereas the MAAP and SP-AMS measured diluted emissions with the BC concentration ranging from 0.3 to 56 µg m-3. The BC concentrations from MAAP and SP-AMS correlated strongly with that from the FSN. However, BC concentrations from the SP-AMS were much lower than those from the FSN and MAAP. The dispersion of small and nonspherical particles in the aerodynamic lens inlet of the SP-AMS may cause particles to miss the laser vaporizer, and therefore they were not detected by the SP-AMS.

This work was supported by the the Cluster for Energy and Environment (CLEEN Ltd) Measurement, Monitoring and Environmental Assessment (MMEA) Work package 4.5.2.

2CO.11

Investigations of Particle Number and Gas-Phase Tailpipe Pollutants from Comparable Hybrid and Conventional Vehicles.

KAREN SENTOFF, Britt Holmén, Matt Conger, *University of Vermont*

A significant proportion of anthropogenic air pollution can be attributed to the light-duty vehicle fleet. As new vehicle technologies are introduced to address fuel consumption and pollution concerns, methods for estimating emissions from alternative vehicles will become more pertinent. Primary mechanisms of ultrafine particle generation from light-duty vehicles are nucleation or condensation of gas-phase pollutants following gasoline combustion and exhaust after treatment. Previous studies have linked gas-phase pollutants to ultrafine particle number or mass emissions, but little work has been done to date to predict particle number emissions with vehicle operation parameters and gas-phase co-pollutants. Tailpipe emissions data from hybrid and conventional 2010 Toyota Camry vehicles were collected during real world driving over a period of 18 months. Samples from the tailpipe were transferred into the vehicles and analyzed in real-time by a TSI Engine Exhaust Particle Sizer and a MKS MultiGas 2030 Analyzer. The relationship of vehicle operating modes, gas-phase pollutants, and particle size distributions were investigated. Emissions data were binned by vehicle specific power (VSP) and three speed regimes (<25, 25-50, and >50 miles per hour) in accordance with current modeling methods. Initial results revealed the need for unique modeling approaches depending on vehicle type. Increasing VSP and speed operating modes generally corresponded to higher mean emission rates for the conventional vehicle. A shift of high emission events for the hybrid vehicle to the high VSP, mid-range speed regime was observed for gas-phase pollutants (i.e. carbon monoxide and ammonia) and particle number emissions. Additionally, particle emission rates were significantly higher for high VSP, low speed hybrid operation as compared to the conventional vehicle. The shift of high emission events to lower speed regimes were likely attributable to the transition between all-electric and engine-on hybrid operation as well as target engine loading during highway speed operation.

2CO.13

Characterize Emissions from Diesel Vehicles Equipped with Urea-Selective Catalytic Reduction (SCR) Systems.

MAHMOUD YASSINE, Ewa Dabek-Zlotorzynska, Debbie Rosenblatt, Greg Rideout, *Environment Canada*

It is important to understand the effects of engine and after-treatment technologies such as urea-selective catalytic control (SCR) systems that may have on the reduction or formation of the full spectrum of chemical species that are not currently identified. The quantification of these compounds is therefore essential for identifying potential adverse environmental and health effects, and ensuring that the emission inventories used in atmospheric modeling activities and in health risk assessments are accurate.

This work presents data on the first assessment of thermal decomposition by-products, namely cyanuric acid, biuret, dicyandiamide, ammeline, ammelide, melamine and isocyanic acid, in emissions from diesel engine employing urea-SCR technology. This was achieved by developing and applying new methods, namely liquid chromatography-mass spectrometry and ion chromatography. Analysis of filter samples collected during transient chassis dynamometer tests show that the presence of target analytes with cyanuric acid and ammelide are the most abundant compounds in the exhaust. The presence of trace levels of volatile isocyanic acid in diesel emission was also detected. Preliminary data showed that the emitted N-containing species were clearly influenced by the driving cycle and showed a strong correlation with the average speed and load of the driving cycle.

2CO.14

Visualization of Filter Pore Bridging with Diesel Particles from Two Different Size Distributions. SIMON PAYNE, Nick Collings, *University of Cambridge*

Particulate bridging over filter pores is responsible for the steep initial increase in engine exhaust back pressure as a clean Diesel Particle Filter (DPF) is loaded. It is of significant advantage to engine operation to mitigate this pressure drop penalty by minimising deposition of particles deep within the pores and forming a cake as rapidly as possible. Understanding of the pore bridging process is immensely aided by visualization with scanning electron microscopy (SEM). The same pores of a silicon carbide (SiC) filter wall were loaded successively with diesel particles from two different size distributions. The first aerosol was sampled from the exhaust of the Cambustion Diesel Particulate Generator (DPG) and the second from a medium-duty diesel engine via a catalytic stripper; the modal electrical mobility diameters were 120 and 60 nanometers respectively.

While initial filtration efficiency in the SiC wall was higher with the smaller engine aerosol, the transition from deep-bed to cake filtration occurred at a higher pressure drop and SEM images show a greater amount of particulate matter from the smaller aerosol was deposited deep within the walls. Smaller particles appear to deposit uniformly along the necks of pores giving the appearance of gradually shrinking pores. It was found that aggregates several hundred nanometers in diameter contribute to the growth of dendrites that extend over pores up to 20 microns across, which is particularly evident with the DPG aerosol. If particles several microns in size are present, these can cause sudden plugging of smaller pores which substantially reduces the pre-cake pressure drop penalty. The nature of pore-filling is best characterised by a locally defined interception parameter; a threshold value of 0.05 for the ratio of particle to pore size was estimated for the transition between shrinking pore behaviour and the dominant action of dendrites.

2CO.15

Aerosol Microphysical Properties from Canadian Boreal Forest Fires Measured during BORTAS. KIMIKO SAKAMOTO, James Allan, Hugh Coe, Jonathan Taylor, Thomas Duck, Jeffrey Pierce, *Dalhousie University*

Biomass burning emissions contribute significantly to aerosol concentrations in many regions of the atmosphere. Plume-aerosol characteristics vary according to age, fuel type, and region. These differences are poorly represented in regional and global aerosol models, and they contribute to large uncertainties in predicted size distributions in biomass-burning-dominated regions. The BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS) measurement campaign was designed to invesigate boreal biomass burning emissions over Atlantic Canada during July-August of 2011. Aged (2-3 days) biomass burning aerosols originating from western Ontario were measured by an SMPS and AMS on board the British Atmospheric Research Aircraft. The presence of plumes were identified through CO concentrations and acetonitrile enhancement ratios. In-plume aerosol size distributions were collected for six aged plume profiles. The size distributions show a single-mode median diameter of ~ 200 nm, and the dependince of aerosol size on various factors will be discussed.

2CO.16

Morphology of Particles Produced by Aviation Gas Turbines. Hugo Tjong, STEVEN ROGAK, Jason Olfert, Tyler Johnson, Jonathan Symonds, Kevin Thomson, Gregory Smallwood, *University of British Columbia*

Forty seven TEM grids containing particulate emission from aviation jet engines were produced as part of an effort to verify the practicability and robustness of the working draft nvPM ARP methodology defined by the SAE E-31 Committee. Grids were collected coincident with other particulate instrument measurement over a range of engine loads.

Images from the grids show that particulate emission from a jet engine has different characteristics compared to the emission from internal combustion engines. Whereas the PM emission produced by ICE dominated by open aggregate structure with minimum VOC concentration, most of the grids collected from a jet engine display substantial traces of VOC which exist in forms of droplets, mixed with EC (identified by typical fractal soot morphology) and an oily film on the surface of the TEM grid. There were minor quantities of unidentified particles including some with needle-like shapes.

The morphology of the EC shows a large variation in terms of primary particle diameter (dp), aggregate size and radius of gyration. The dp variation was found consistently across all grids while the aggregate size and radius of gyration were found to vary grid by grid.

A CPMA-DMS system was also used to measure the effective density of aircraft particulate. The density ranged from 600 to 1100 kg/m3 and was particle size and engine loading dependent. These results also supported the presence of volatile material with the denuded density being lower than the undenuded. By fitting the density distribution with a power law, the mass mobility exponent was determined to be 2.7 to 2.9 or near spherical morphology.

Laser Induced Incandescence measurements were taken simultaneously; trends with loads will be compared with those in the TEM and CPMA measurements.

2CO.17

In-use Emission Factors from Traditional and Upgraded Cookstoves in Rural Karnataka, India. ANDREW GRIESHOP, Grishma Jain, Karthik Sethuraman, Ther Aung, T Pradeep, Narayanswami S, Julian Marshall, *North Carolina State University*

Primitive use of biomass for cooking in developing countries has outsized impacts on human mortality and on emissions of short and long-lived climate forcing agents. Addressing these impacts requires substantial improvements in efficiency and emission performance of cooking appliances. This poster presents data collected during a randomized control trial of a carbon-credit funded stove replacement program conducted by SAMUHA, an Indian NGO. The program replaced traditional stoves with ‘rocket’ type stoves (Chulika, ISquareD, Bangalore, India) in 72 of 187 study households in the village of Hire Waddarkal in Karnataka, India. Emission measurements were conducted during family stove use in homes before and after cookstove replacement with an autonomous instrument package. The Stove Emission Measurement System (STEMS) was deployed for 50 baseline and 54 post-intervention cooking periods. STEMS uses an in-plume probe to collect filter samples for offline determination of PM2.5 and particulate organic and elemental carbon (OC/EC) mass along with real time (1-2 s) CO2, CO, PM light scattering and absorption (at 3 wavelengths) data. Data were used to calculate fuel-based CO, PM2.5, OC and EC emission factors and to examine emission characteristics of traditional and intervention stoves under varying usage. PM emission factors from the improved stoves were not substantially reduced relative to baseline measurements, though emission factors range widely across tests. Fuel-use data indicate that stove thermal efficiency was improved in the Chulika, resulting in a modest reduction in overall PM emissions. In general, Chulika EC emission factors were higher than those for baseline stoves. Results of this study highlight the large levels of variability in emissions associated with in-home use of both baseline and post-intervention stoves. They also reinforce others’ findings that some stoves marketed and perceived as ‘clean’ do not provide sufficient emission reductions.

2CO.18

Characterization of Soot Particle Deposition Rates and Optical Effects. DE-LING LIU, Stephen Didziulis, Jesse Fowler, *The Aerospace Corporation*

Concerns were raised for potential spacecraft contamination inside a launch vehicle payload faring (PLF) from soot particles created in the rocket ignition plume. Soot particles could be ingested through the leak paths in PLF envelope, which in turn poses contamination risk to spacecraft optics, solar cells, and thermal control surfaces. To gain a good understanding regarding the potential risk due to soot particle ingestion, analyses and laboratory experiments were performed to determine soot deposition rates onto surfaces and the light absorbing characteristics of the deposited species.

A test setup consisting of a cylindrical chamber as a PLF simulator was constructed to examine the behavior of soot particle deposition. Soot particles were generated and introduced into the chamber. After the soot generation source ceased, the particle size distribution as a function of time was determined using an aerodynamic particle sizer (APS) and a scanning mobility particle sizer (SMPS). Light weight fused silica substrates were placed inside the chamber for soot particle deposition, and their light transmission spectra from 200 nm to 2000 nm were characterized ex situ as a function of deposited soot mass. The measured particle deposition rates spanned from 0.03 h-1 to 0.2 h-1 for particles of 0.04 to 2.5 micron, in agreement with the literature data. Soot particles were found to cause significant light absorption in the wavelength region of 200 to 300 nm, likely attributed to semi-volatile organic compounds adsorption/condensation on the surfaces of soot particles. The experimentally determined deposition rates in comparison of the time scale of launch ascent, and optical effects of soot particles provide some insights into the potential impact of soot particle contamination as a result of launch plume ingestion.

2FM.1

Numerical Modeling of a Low-Pressure Radio Frequency Argon-Silane Plasma in Which Silicon Particles Nucleate and Grow. PULKIT AGARWAL, Steven Girshick, *University of Minnesota*

Numerical simulations were conducted to predict the spatiotemporal evolution of a low-pressure radio frequency capacitively-coupled parallel-plate argon-silane plasma in which silicon nanoparticles nucleate and grow. The 1-D numerical model self-consistently couples the behavior of the plasma and of the aerosol. The plasma model includes population balance equations for electrons and ions, the electron energy equation under the assumption of a Maxwellian electron velocity distribution, Poisson's equation for the electric field, and the chemical kinetics of small silicon hydrides created by plasma dissociation of silane. The aerosol general dynamic equation is solved using a sectional model for the distributions of particle size and charge. Particle charging by electron and ion attachment is modeled using orbital motion limited theory. Particle size- and charge-dependent coagulation is calculated, accounting for image potentials induced in interactions between charged and neutral particles. Particle transport effects considered include neutral gas drag, ion drag, the electrostatic force, Brownian diffusion and gravity. The silane chemistry model predicts the spatiotemporal profiles of the production rates of species believed to be most involved in particle nucleation and growth. These production rates, multiplied by suitable scaling factors, are used to predict nucleation and surface growth rates. Simulation results are presented for a case that corresponds to experiments in the literature, with RF frequency 13.56 MHz, applied voltage amplitude 55 V, pressure 17 Pa, electrode gap 4 cm, and gas velocity through the upper (showerhead) electrode of 26.3 cm/s.

2FM.2

Method for Enhanced C60 Yield in Plasma-Aerosol Reactor with Liquid Nitrogen Trap. MIKHAIL JOURAVLEV, *POSTECH*

The effect of the remarkably enhanced yield of C60 fullerenes in the aerosol discharge chamber due to the additional presence of a strong spatial temperature gradient is demonstrated [1].

The aim of this experiment was to determine the influence of temperature gradients on the yield of C60 synthesized in an arc discharge aerosol chamber. It was shown that the presence of a strong temperature gradient produced by attaching a liquid nitrogen trap to a chamber orifice resulted in an increase of the C60 fullerene relative yield by a factor of 2.7. We believe this increased relative yield is a result of the induced flow of impurities out of the chamber and into the flask where they are absorbed on the flask walls.

To introduce a strong spatial temperature gradient, the orifice of a liquid nitrogen trap at 78 K was connected to the top orifice of the aerosol-plasma chamber. The presence of the nitrogen trap reduces the partial pressure of volatile impurities in the main chamber – these impurities are condensed in the Dewar flask and cease to influence the fullerene synthesis. The role of the temperature gradients in the increased yield of C60 and fullerene-like (graphene) structures is discussed. The reaction is not fully reversible and carbon soot substance is formed as a secondary product in the form of carbon aerosol particles. The increasing concentration of C60 was easily recognized from the characteristic UV-spectra of aerosol particles toluene solvents. The result of this paper will be useful for improvement of fullerene synthesis technology and for application to constructing new types of aerosol-plasma reactors as well as for synthesis of graphene. A possible extension of this method is to change the simple orifice and connection tubes of the aerosol chamber by the Laval’s nozzle for the creation of both temperatures gradients and gradients of the pressure.

1. M.Jouravlev, arXiv:1105.3576

2FM.3

Silicon Nanocrystal Solvation: From Plasma to Stable Colloidal Dispersion. LANCE M. WHEELER, Uwe R. Kortshagen,*University of Minnesota*

Colloidal synthesis of prevailing semiconductor nanocrystals (NCs) leads to long-chain ligand termination of the surface. Though the ligands provide colloidal stability in nonpolar solvents, these ligands hinder charge transport when cast into thin films for optoelectronic device integration. Silicon offers a more abundant, non-toxic alternative to the heavily-research metal chalcogenide NC, but unreliable synthesis and inability to process from liquids has lead to stifled progress toward optoelectronic devices. Here we present a single-step nonthermal plasma synthesis method of Si NCs that allows tailoring of the NC surface to be controllably terminated with chlorine and hydrogen. We demonstrate this surface chemistry to be imperative for achieving stable dispersions of Si NCs without ligands. Choice of solvent plays an equally critical role, and we outline solvent criteria needed to achieve stable, highly concentrated dispersions of Si NCs. We employ dynamic light scattering (DLS) and UV-Vis spectroscopy to determine dispersion concentration and explore the physical and chemical characteristics of colloidal interactions using dialkyl ketones as the model system. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy reveals acid-base interactions at the NC surface as well as intermolecular solvent interactions that lead to dense packing and ordering of solvent molecules around the Si NCs. We attribute these phenomena to a novel stabilization mechanism for nanoscale, highly concentrated dispersions—solvation. Demonstration of thin films that are continuous and crack-free validate our efforts for colloidal stability and represent a significant step toward cost-effective, roll-to-roll integration of Si NCs into optoelectronics.

2FM.4

Production and Characterization of Boron Nanoparticles Synthesized With a Thermal Plasma System. WEONGYU SHIN, Steven Calder, Ozan Ugurlu, Steven Girshick, *Chungnam National University*

A new method for the production of boron nanoparticles is described. Boron trichloride is dissociated through injection into thermal plasma followed by a nucleation process producing boron nanoparticles. The ambient oxidation of the as-produced nanoparticles is also investigated. The nanoparticles were characterized with scanning transmission electron microscopy, electron energy loss spectroscopy, X-ray photoelectron spectroscopy, and Fourier transform infrared spectroscopy to investigate their purity and stability under ambient conditions.

2FM.5

Production and Characterization of SiO2 Nanoparticles Synthesized with an Electron Beam Irradiation System. JIN HYOUNG KIM, Youngku Sohn, WeonGyu Shin, *Chungnam National University*

We have first demonstrated that SiO2 nanoparticles can be synthesized using an electron beam irradiation system in an ambient condition. The vibrational modes shown in FT-IR spectra, and the binding energy of Si 2p in X-ray photoelectron spectrum confirm that SiO2 nanoparticles were formed during the process. In this study, the average particle size of nanoparticles was reduced from 210 nm to 73 nm by reducing the residence time of the precursor vapor inside the reaction chamber by a factor of two indicating that our proposed method can be further used for the production of ultrafine aerosol nanoparticles.

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2FM.6

Crystallizing Amorphous Silicon Nanoparticles with a Double Plasma Configuration. NICOLAAS J. KRAMER, Rebecca J. Anthony, Aloysius A. Gunawan, K. Andre Mkhoyan, Uwe R. Kortshagen, *University of Minnesota*

The crystallization conditions for Silicon nanoparticles formed in a non-thermal plasma have been studied with a double plasma configuration. Amorphous Silicon nanoparticles with sizes from 4 up to 7 nm were formed [1,2] in a low power primary plasma and flown into a separate secondary plasma, which was operated with variable powers. Once a specific threshold power was reached in the secondary plasma, the silicon nanoparticles became fully crystalline, as was demonstrated with X-ray Diffraction (XRD), Raman spectroscopy and Transmission Electron Microscopy (TEM) measurements. Depending on the conditions in the primary plasma, the nanoparticle size remained either constant or increased in size when the power of the secondary plasma was increased.

To study the plasma properties under crystallizing conditions, Capacitance probe and Optical Emission Spectroscopy measurements were performed in the region where the crystallization occurs. From this the properties of the secondary plasma, such as electron temperature and ion density, were obtained for several conditions.

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2IA.1

Physical Characteristics of Particle Emission from Multiple Cooking Activities. YIJIA ZHAO, Mehdi Amouei Torkmahalleh, Iman Goldasteh, Alan Rossner, Philip K. Hopke, Andrea R. Ferro, *Clarkson University*

Since cooking is one of the major indoor sources of PM based on previous research, recently, cooking emissions have attracted greater attention from the public and in indoor air quality science. For cooking sources, frying results in the highest particle emissions, most of which are in the ultrafine particle (UFP) range. The purpose of the present study is to determine physical characteristics of the cooking aerosol corresponding to multiple factors during cooking. Experiments were designed to compare particle emissions from seven kinds of cooking oil as well as to investigate the effects of additives (salt, pepper, garlic powder, turmeric), and surface area of food on particle emissions. The oil was heated in a beaker in a laboratory hood and the resulting particle number concentrations, mass concentrations, mode diameters, and size distributions were determined for a range of oil temperatures. We also visually determined the smoke temperature for each oil. The particle concentration data were analyzed to estimate particle emission rates and emission fluxes from the surface of the oil. Consistent with previous studies, particle number emission rates ranged from 1011 to 1012 #. min^{-1} and PM2.5 emissions ranged from 103 to 104 µg.min^{-1}. Emission fluxes have not been previously reported in the literature. Fluxes for particle number and PM2.5 ranged from 1013 to 1014 #. min^{-1}.m^{-2} and 105 to 106 µg.min^{-1}.m^{-2}, respectively. Results indicate that there are large differences in particle emissions among cooking oils with soybean, canola, and safflower oils resulting in lower emissions than corn, coconut, olive, and peanut oils. The results show the changes in rates and size distributions of the particle emissions with the addition of spices and the food.

2IA.2

Critical Review of Particulate Matter Emitted from Biomass Cookstoves. YUNGANG WANG, Ashok Gadgil, *Lawrence Berkeley National Laboratory*

About 2.7 billion people worldwide currently reply on directly burning biomass for their primary cooking fuel. Emissions from biomass cookstoves have significant environmental, climate and health impacts. The particulate matter (PM) emission recently made headlines. It causes 1.6 million deaths mostly women and children per year. It also contributes to visibility degradation and global warming. In this study, we present a critical review on current available information from peer reviewed publications related to PM emitted from both traditional (Three Stone Fire) and improved biomass cookstoves. The review focuses on three key topics: (1) Measurement techniques; (2) Physical and chemical characteristics; and (3) Emission rates. The many studies conducted reveal a wide range of conclusions, even for the same type of cookstove. These divergences may be the result of using different sampling locations (laboratory vs. field) and measurement technologies. There is a shortage of field measurement data on the PM chemical composition, although recent work has begun to remedy this weakness. The conclusions include a number of recommendations for use in design of future studies.

2IA.3

Gravimetric Analysis of Dust Loading and Human Exposure Assessment. YAN MA, Lisa Bramwell, Andrea R. Ferro, *Clarkson University*

People can be exposed to settled dust on floorings through dietary and non-dietary ingestion as well as inhalation of resuspended dust, primarily via human activities. Typical activities, such as cleaning or simply walking around, have been implicated with approximately 30% of total human exposure to PM_{10} (Yakovleva et. al, 1999). In order to predict exposures to resuspended particles, size resolved settled dust floor loadings are critical. Literature values for floor loading vary widely and few size resolved data are available for particles in the inhalable range. We developed a new method to measure size-resolved floor loading, which combines the use of the ASTM Standard D5438 – 05 (Standard Practice for Collection of floor dust for chemical analysis) with a MOUDI^{TM}(MSP, Shoreline, MN) cascading impactor. Gravimetric samples were collected via the MOUDI^{TM} for six size bins:18-10, 10-5.6, 5.6-3.2, 3.2-1.8, 1.8-1.0, and 1.0-0.56 micrometers. Using this method,we collected and analyzed dust samples from 30 homes in St. Lawrence County, NY. These data formed an essential part of input files used within NIST's multizone ventilation and mass transport software CONTAM 3.0a. Manipulating CONTAM 3.0, equipped with a deposition with resuspension source/sink element, enabled the generation of distributions of exposures to resuspended particles on different flooring types.

2IA.4

Characterizing Particulate Formation and Filtration in Hookah smoke. Jessica Annonio, Mac Gilliland, Timothy Oh, Jeff Baker, CINDY DEFOREST HAUSER, *Davidson College*

Hookah smoking has been practiced in India for over 400 years but is just now increasing in popularity in North America, especially among youth. Hookah is a type of flavored and sweetened tobacco smoked through a waterpipe, and marketed as an alternative to cigarette smoking. The detrimental health effects of cigarette tobacco smoke have been well documented; and the particulate and gas phases of cigarette smoke are well-characterized. Previous studies of hookah smoke have characterized the gas phase but less is known about the particulate component. Evaluation of the health effects of hookah smoke will benefit from increased knowledge regarding the particulate component. Here, we investigate the processes involved in particulate formation and filtration through varying temperature, inhalation rate, and the chemical properties of the filtration media, while characterizing particle number density, size and composition.

2IA.5

Applications of Real-Time Quantitative Polymerase Chain Reaction in Assessing the Pseudomonas Aeruginosa in Air Environment. MIAO-CHING CHI, *Chang Gung University of Science and Technology, Taiwan*

Nosocomial infection has become a great public-health problem worldwide. Nosocomial infection in health care setting is among the major causes of and increased mortality among hospitalized patient. Because of the increased length of stay for infected patients, the economic costs are considerable. Therefore, the purpose of our current study was to build up the optimal conditions of real-time qPCR method to analyze Pseudomonas aeruginosa. Real-time qPCR was applied to evaluate the concentration of Pseudomonas aeruginosa in air environments. The result showed that the lowest detect limit of this method could be 5.7 copies/micro-liter, with a correlation coefficient value of 0.999. In evaluating the extraction time of bacteria form filter, there were the most cultural concentrations for shaking 1 min. Moreover, the activity and DNA of Pseudomonas aeruginosa storaged in low temperature would be damaged. Therefore, the results suggested that the samples should be immediately analyzed after air sampling. In air sampling, the concentrations of Pseudomonas aeruginosa in indoor air were from 2.34×10^3 copies/m^3 to 3.70×10^3 copies/m^3. This study indicated that Pseudomonas aeruginosa can exist in air environment. In the future, it is necessary to monitor the activity of Pseudomonas aeruginosa for estimating the route of transmission of nosocomial infection.

2IA.6

Initial Results of Testing for Ultrafine PM from Hardcopy Devices as per ECMA-328 and ISO/IEC 28360. Stephany Mason, HORNER ELLIOTT, *UL - Air Quality Sciences*

One recognized potential source of fine particles (FP) and ultrafine particles (UFP) in the indoor environment is office equipment with printing capabilities. The industry association, ECMA International, has acknowledged this issue and in 2012 UFP testing was added to its standard "Determination of Chemical Emission Rates from Electronic Equipment" (ECMA-328 and ISO/IEC 28360). A variety of printers was tested for UFP emissions following this methodology, using a butanol-based condensation particle counter (CPC) and/or an engine exhaust particle sizer (EEPS). The emission characteristics of particles in the size range of 7 – 300 nm were evaluated. The data reviewed to date show emission rates ranging from not quantifiable to greater than 1.8E+13 particles/hour. Assessments were made for correlations between particle emission rates, sizes and counts against printer speed, toner type, and other device characteristics. Reproducibility of results between repeat runs of the same unit were also evaluated.

2IA.7

Calibration of the Aerodynamic Particle Sizer using an Ink Jet Aerosol Generator (IJAG). JANA KESAVAN, Jerold Bottiger, Deborah Schepers, Andrew McFarland, *US ARMY ECBC*

The aerodynamic particle sizer (APS) measures the aerodynamic diameter and size distribution of aerosols in real time. The APS needs to be calibrated periodically and before each official test to ensure accurate results. The objective of this test was to characterize the counting efficiency of the APS as a function of particle size using solid, liquid and bio particles generated by an ink jet aerosol generator (IJAG). This is an easier method compared to the other methods listed in the literature. The output of the IJAG was positioned directly above the inlet of the APS for successful capture of all particles. The particle sizes used in this test ranged from 0.95 to 13.26 micrometers. The test results showed that the counting efficiency was 97.7% for 0.95 micrometer particles and reached 100% for the 1.3 micrometer particles. The counting efficiency showed slight decrease for particle sizes larger than 10 micrometers and reached 99.04% for 13.26 micrometer particles. The primary droplet volume of the IJAG was determined in this study using the fluorescence particles, and the results showed that the volume is 142.7 pL which corresponds to a 64.7 micrometer diameter particle. The accuracy of IJAG particle generation was checked by collecting bio particle output from the IJAG on a slit to agar sampler and culturing and counting them. The results showed that the particle generation efficiency of the IJAG is 98.1% based on the culture results.

2IA.8

Adverse Human Health Effects Associated with Particulate Matter of Indoor Air. ALFRED LAWRENCE, Nishat Fatima, Suryakant Tripathi, *Isabella Thoburn College, Lucknow, India*

The largest exposure to health-damaging indoor pollution probably occurs in the developing world, not in households, schools, and offices of developed countries where most research and control efforts have been focused to date. Most of the ill health effect due to indoor air pollution seems to occur among the poor and most vulnerable population of developing countries. Very little is known about the air pollution indoors in this part of the World. Lucknow is the capital of Uttar Pradesh, the most populated state of India. It is the second largest city in northern and central India. According to World's Bank's survey in 2004, Lucknow ranks 7th in the world regarding air pollution. Keeping this in mind, we surveyed patients of various respiratory diseases from Chhatrapati Sahuji Maharaj Medical University. According to the survey results, 5 different monitoring sites were established in Lucknow. Concentration of CO2, CO, NH3, SO2, NO2 and RSPM: - PM10 and PM2.5 were monitored simultaneously from January 2012 to April 2012. Preliminary analysis reveals that levels of PM10 and PM2.5 are 2 to 3 times above the permissible limits (NAAQS limits) and the levels of gaseous pollutants increases from well-planned residential colonies to roadside houses. Few occupants also reported irritation of eyes, lungs, throat, and sinuses along with increased severity of existing lungs diseases like asthma, pneumonia, emphysema, bronchitis, and risk of heart attacks. Long term exposure to such kind of indoor pollutants may lead to chronic obstructive airway disease (COAD), lung disease, chronic bronchitis, and increase risk of cancer and cardiovascular disease. In absence of complete data we cannot make any definitive conclusions but the preliminary observations suggest a higher level of Pollutants are present indoor. Long term database of pollutants levels of urban Lucknow will be useful to state and federal regulatory agencies, the researchers, consultants and the general public.

2IA.9

Numerical Study of Thermophoresis Effects on Particle Dispersion in a Turbulent Channel Flow Using the V2F Turbulence Model. Mohammad Majlesara, Mazyar Salmanzadeh, GOODARZ AHMADI, *Shahid Bahonar University of Kerman*

A computational model for simulating the instantaneous anisotropic velocities in a 2-D turbulent channel flow was developed. The V2F turbulence model of FLUENT code was used for evaluating the mean flow field and the anisotropic turbulence intensities. The Kraichnan method for generating continuous Guassian random field was extended and used for simulating the instantaneous anisotropic velocity fluctuations in the channel. The Lagrangian particle tracking approach was used for analyzing the particle movements. The Stokes drag, lift, Brownian, gravity, and thermophoretic forces were included in the particle equation of motion. The Brownian force was simulated using a white noise stochastic process model. The effect of anisotropic turbulence fluctuations and thermophoresis on the transport and dispersion of particles of different sizes emitted from point sources in the channel was studied. The simulation results showed that, when small particles are sufficiently close to the wall, the thermophoretic force significantly affects the particle motion.

2IA.10

Numerical Study of Various Parameters on Performance of Portable Air Cleaners in a Ventilated Room. Vahid Akbari, Mazyar Salmanzadeh, GOODARZ AHMADI, *Shahid Bahonar University of Kerman*

In recent years, the use of portable air cleaners (PACs) has attracted considerable attention for indoor air quality improvement. These PACs provides the flexibility in that it can be placed and operated on demand. Variables such as particle size, pollutant source location, air cleaner technology, air exchange rate, and the location of the air cleaner in a room influence the air cleaner effectiveness. The common rating used by the manufacturers for evaluating the performance of portable air cleaners is the Clean Air Delivery Rate (CADR). CADR, however, is a measure of the performance for an entire room space under well-mixed conditions; thus, it does not account for the effect of room air movement. In this study a computational fluid dynamics model was used to investigate the impact of the ventilation system, pollutant source characteristics and position of the PAC in a ventilated room on its effectiveness. The k-e turbulence model and Lagrangian particle tracking was used in these analyses

2IA.11

Development of Deodorizing and Sterilizing Filter. YOUNGJIN SEO, Seong Jin Yun, Sang Hyeon Kang, Sun Yong Lee, Gi Chun Lee, Sang Bock Lee, Il Seouk Park, *The Environment Technology Institute, Coway Co., Ltd.*

There has been a research activity whose ultimate goal was to extract all unwanted odors and bacteria out of faecal in a toilet and also to remove them using a novel filter. This paper presents development of a filter module that was comprised of a brush ionizer and balls coated with catalyst materials. The brush and the balls were made of a bundle of carbon fibers and alumina, respectively. Three catalyst materials such as a combination of manganese and phosphorus, ferrum, and ruthenium were experimented. The filter was cylindrical shape and 2 cm in diameter by 5 cm long. The overall size was decided to fit into a toilet seat. The ionizer was prepared in front of the catalyst for the purpose of regeneration of the balls.

Experiments were conducted to evaluate the effect of the filter module on deodorization and sterilization. Three representative gases such as ammonia, hydrogen sulfide, and methyl mercaptane were used to investigate the performance of deodorization. E. coli was used for sterilizing efficiency. A bacillus size of E. coli was approximately 1.5 µm wide by 3.5 µm long. The flow velocity through the filter was approximately 0.75 m/s. Deodorization efficiency was varied upon the catalyst material. A combination of manganese and phosphorus yielded the highest removal efficiency. The efficiency was maintained 100 % for one hour, forty minutes, and ten minutes with ammonia, hydrogen sulfide, and methyl mercaptane, respectively. The catalyst material did not affect on sterilization efficiency. The efficiency was over 99 % for over three hours. These astonishing results were obtained by single-pass experimentation and the novel filter developed here could provide real-time removal of odor and bacteria out of faecal in a toilet.

2IA.12

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

Airborne ultrafine particulate has been shown to cause adverse health effects when inhaled. This has led to an increased interest in the filtration of these particles by fibrous filters such as those commonly used in building HVAC systems. The characteristics of particle agglomerates have been shown to affect the evolution of flow resistance and filter efficiency but little is known about the characteristics of nanoparticle agglomerations within commercial filter media.

This work provides a comparison of dust accumulation and particle agglomerates from nanoparticles (mean diameter 100nm) within commercial HVAC filter media. The media compared utilizes an electrostatic charge on the fibers to improve filtration efficiency. Tests were performed on the media for both the charged condition and discharged condition; where the charge was removed by immersion in isopropyl alcohol (IPA). Analysis of SEM images of the loaded filters was used to compare particle agglomerates and dust holding properties of the charged and discharged filter media.

Particle agglomerates on the discharged fiber surfaces were found to have a more dense, collapsed structure when compared to the agglomerates on charged fiber surfaces, which grew as thin dendrites. The discharged filter media was also found to be proportionally more heavily loaded with particulate on the upstream side of the filter, which resulted in less dust holding capacity to a given increase in flow resistance. A comparison of the degree of filter loading after an added pressure drop due to dust loading of 4x the original clean filter pressure drop showed that the discharged filter contained ~20% less dust by mass. The degree of fiber surface coverage on the upstream side of the filter was found to be higher for the discharged filter media (12%) compared to the charged filter media (7%).

2IA.13

The Indoor Environment Within Green-Renovated Homes. KANISTHA CHATTERJEE, Tiina Reponen, Chris Schaffer, Eric Kettleson, Reshmi Indugula, Sergey A. Grinshpun, Gary Adamkiewicz, Stephen Vesper, *University of Cincinnati*

Green buildings are designed and constructed to have a minimal negative impact on the environment; however the indoor environmental quality (IEQ) inside these buildings has not been attested. We assessed the indoor air in 20 green-renovated and 20 control houses in Cincinnati, OH, USA as part of the Green Housing Study. The assessment of each home included 5-day measurements of temperature, relative humidity and concentration of fine particles. Temperature and relative humidity were collected using HOBO® continuous data loggers (Onset Computer Corporation). Particles ≤ 2.5 micro-meter (PM2.5) were sampled on 37 mm, 2.0 micro-meter pore-size PTFE membrane filters using single-stage Personal Modular Impactors (SKC, Inc.), and their mass concentration was determined. In addition, on the first day of the PM2.5 sampling, real-time number concentrations of ultrafine particles were assessed with a P-Trak condensation nucleus counter (TSI Inc.) operating during 45-60 min. Floor dust collected by vacuuming was analyzed for Environmental Relative Moldiness Index (ERMI). Information on the home characteristics was collected using questionnaires that inquired about the type of the building, heating and cooling, furnishings, cleaning regimens, presence of pests and pets, environmental tobacco smoke and reports of dampness. Preliminary data obtained from homes immediately after renovation shows that the geometric mean for the number concentration of fine particles was 27,000 $cm^{-}3$ in green-renovated homes and 40,000 $cm^{-}3$ in control homes (p=0.196). The relative humidity was significantly higher (p=0.03) in green-renovated homes (43.5%) than in the control homes (36.6%). However, the moldiness measured using ERMI, was lower (p=0.06) in renovated homes (4.0) than in control homes (6.7). Sampling the indoor environment at 6 and 12 months after the renovation will determine the development of the indoor air quality within the green-renovated homes over time.

2IM.1

How Many Replicates Are Sufficient for Characterizing Cookstove Emissions: A Case Study Using the Berkeley-Darfur Stove and Three Stone Fire. YUNGANG WANG, Ashok Gadgil, Thomas Kirchstetter, *Lawrence Berkeley National Laboratory*

One third of the world’s population uses biomass cookstoves. The emissions from this source have been linked to adverse health effects and climate change. A large number of “improved cookstoves” with higher energy efficiency and lower emissions compared to the traditional three stone fire (TSF) have been designed and are being promoted across the world, e.g. Berkeley-Darfur Stove (BDS). The stove emissions are commonly characterized and compared using an average obtained from a number of replicates of lab-based water boiling test (WBT). Inconsistent WBT results were reported from different laboratories, and even the number of replicates varies widely. In this study, results of statistical analyses are presented to answer the above question, using statistical sampling from a number of replicate tests of the BDS and the TSF. Our results suggest that cautions should be exercised in the interpretation based on averaging only a few replicate tests of cookstove emissions.

2IM.2

Comprehensive Single Particle Analysis by Aerosol Mass Spectrometry with Different Desorption and Ionisation Techniques. MARKUS OSTER, Matthias Bente-von Frowein, Jürgen Schnelle-Kreis, Ralf Zimmermann, *Helmholtz Zentrum München*

Laser mass spectrometry is commonly used for on-line investigation aerosols on single particle basis (SP). Lasers are often applied for ionisation in several ways. A laser pulse with high power density (~10^9W/cm^2) generates ions via a one-step laser desorption/ionisation (LDI), that can be analysed and detected with a mass spectrometer. A reduced power density (~10^7W/cm^2) produces gas phase neutrals (laser desorption, LD). Another method is thermal desorption (TD), where particles impinge on a heated metal surface. Neutrals produced by LD or TD can be ionised by several techniques like single- or multiphoton-ionisation. The choice of desorption and ionisation method delivers different information of the particles. While LDI mainly provides information of inorganic compounds and carbon clusters, two-step desorption/ionisation allows the detection of fragile organic molecules.

A system is presented, that uses a differentially pumped inlet system to generate a particle beam from aerosols. Laser velocimetry provides information about the aerodynamic diameter and velocity of individual particles. A CO_2-laser is used for LD, and a KrF-excimer laser for resonance-enhanced multiphoton-ionisation (REMPI), that selectively ionises polycyclic aromatic hydrocarbons (PAH) and alkylated PAH. Alternatively, LD can be replaced by TD, and instead of a two-step desorption/ionisation, the KrF-laser can also be used for a one-step LDI. The produced ions are subsequently analysed and detected by a reflectron time-of-flight mass spectrometer. By choosing adequate trigger settings for the lasers according to particle velocities, the LD-REMPI, TD-REMPI and LDI-mode can be performed with the same experimental setup.

With existing approaches, it is not possible to investigate inorganic and fragile organic components on single particle basis. To close this gap, in future work the LD-REMPI-mode will be combined with a subsequent LDI-process. By means of this method, besides collecting information of organic (specially PAH/alkylated PAH) components, inorganic compounds will be detected by recording a second mass spectrum of the same particle.

2IM.3

Comparison of the Ion Mobility Spectra of Four Different Bipolar Chargers. PETER KALLINGER, Gerhard Steiner, Wladyslaw Szymanski, *University of Vienna*

Well-defined charge conditioning of nanoparticles is a prerequisite for a number of particle measuring techniques. We investigated two different soft X-ray devices (TSI Advanced Aerosol Neutralizer and a custom-built unit), an AC-corona discharge device (MSP Corp. Electrical Ionizer), and a radioactivity based Am-241 charger as a reference. Electrical mobility size distributions of negative and positive ions produced in chargers due to different processes in a particle-free dry (below 2 % RH) air were measured with a high resolution DMA (Vienna Ultra-DMA operated at about 6.5 lpm aerosol flow and 550 lpm sheath air flow). The mobility spectra of the positive ions were found to be quite comparable for all chargers with a dominant peak at about 1.1 nm in terms of the equivalent electrical mobility diameter, whereas the spectra of the negative ions show a rather complex morphology. We did find that under certain conditions the commercial chargers need a warm up period of about 20 minutes to reach a stable negative ion mobility distribution. Nevertheless, the experimental results of nanoparticle charging show that charge conditioning by means of the AC-corona and soft X-ray created ions is very comparable to the charging results by radioactivity caused ions allowing the postulation that in all cases the Boltzmann-Fuchs charge equilibrium was obtained. Consequently both charger types can be used for charge conditioning of nanoparticles as an alternative to the radioactivity based nanoparticle charging devices.

2IM.4

Development of Thermal Desorption – Comprehensive Two-Dimensional Gas Chromatography Coupled with Tandem Mass Spectrometry (TD–GC×GC–MS/MS) for Determination of Trace Polycyclic Aromatic Hydrocarbons and Their Derivatives in Diesel Exhaust and Atmosphere. AKIHIRO FUSHIMI, Shunji Hashimoto, Teruyo Ieda, Nobuo Ochiai, Yoshikatsu Takazawa, Yuji Fujitani, Kiyoshi Tanabe, *National Institute for Environmental Studies*

We developed a highly sensitive method for determination of polycyclic aromatic hydrocarbons (PAHs) and their derivatives (oxygenated, nitrated, and methylated PAHs) in trace particulate samples by using thermal desorption followed by comprehensive two-dimensional gas chromatography coupled with tandem mass spectrometry (TD–GC×GC–MS/MS) with a multiple reaction monitoring mode. The sensitivity of TD–GC×GC–MS/MS was greater than that of TD–GC–high-resolution MS and TD–GC×GC–quadrupole MS by one or two orders of magnitude. The quantification limits were 0.09–0.8 pg (PAHs), 0.1–0.8 pg (oxygenated PAHs), 0.1–0.4 pg (nitrated PAHs), and 0.04–0.3 pg (methylated PAHs). For small amounts (10–20 µg) of standard reference materials (SRMs 1649a and 1650b, urban dust and diesel exhaust particles, respectively), the values measured by using TD–GC×GC–MS/MS agreed with the certified or reference values within a factor of two. Major analytes were quantified successfully by TD–GC×GC–MS/MS from diesel exhaust nanoparticles (18–32 nm) and accumulation-mode particles (100–180 nm).

This work was supported by the Environment Research and Technology Development Fund of the Japanese Ministry of the Environment (S2–06).

2IM.5

Improving the Resolution of Low Pressure Impactor. ANSSI ARFFMAN, Jaakko Yli-Ojanperä, Jorma Keskinen, *Tampere University of Technology*

Low pressure impactors in a cascade configuration are widely used to measure the aerodynamic particle size distribution of aerosol sample. Besides the particle size measurement, LPIs have been used for example in studying agglomerate particle bond strength by impacting nanoparticles in the LPI and observing the degree of disintegration as a function of particle impaction energy. In both applications it is beneficial to have an LPI with steep collection efficiency curve. Steep collection efficiency provides possibility to bring stage cutpoints closer to each other without interference of successive stages in the size distribution measurement. It also provides uniform impaction conditions and impaction energies for particles in the whole jet domain.

We studied experimentally and with numerical simulation methods the critical LPI parameters that affect the resolution or the steepness of the collection efficiency curve. Two LPI geometries, rectangular slit and round nozzle with 25nm cutpoint were investigated. Based on the simulation results, a new impactor stage with exchangeable nozzle throat length and jet-to-plate distance was designed, built and tested. The impactor was calibrated with four different configurations using monodisperse dioctyl sebacate aerosol. A good agreement between the simulated and the experimental resolutions and cutpoints was found. The best observed resolution was achieved with the slit type LPI that had very small nozzle throat length to width ratio. Compared to corresponding impactor stages of commercially available LPIs, the resolution of the new stage is by far the highest.

2IM.6

Practical Implementation of a New Coincidence Correction Technique. AARON COLLINS, William Dick, Francisco Romay, Lin Li, *MSP Corporation*

With urban and roadway aerosol concentrations considerably exceeding 20,000 particles/cm^3, it can be a challenge to accurately measure the total particle number concentration using a single-particle counter. A common counter used for ultra-fine particle measurement, the condensation particle counter (CPC), typically has an upper concentration limit of 10^4 to 10^5 particles/cm^3 in the single-particle counting mode. This upper limit is the result of a systematic reduction in counts caused by coincidence.

In this work we introduce a new coincidence correction technique to solve for the theoretical CPC counting rate. Modeling the system as a Poisson process results in a mathematical equation for coincidence that cannot be solved analytically in closed form. Using the Lambert W function to solve this equation allows for real-time correction, as well as post-measurement correction, of CPC count data for coincidence. There is, however, a clearly defined limit to the maximum amount of correction possible because the resulting solution is double-valued.

An experimental verification of this technique was performed using count data collected from MSP 1110, MSP 1120 and TSI 3785 CPCs over their respective valid ranges of correctable concentration. This paper explores the practical limitations of the coincidence correction method as well as issues associated with high concentration measurements. Additionally, correction of CPC count data from the literature demonstrates that this is a suitable method for post-correction of previous experimental data.

2IM.7

Scattering Phase Function Measurements of PSLs and Ammonium Sulfate Particles. PAUL KEBABIAN, Timothy Onasch, Joda Wormhoudt, Andrew Freedman, *Aerodyne Research, Inc.*

We present detailed measurements of the scattering phase function and the resultant particle asymmetry factor, g, for four sizes of polystyrene latex particles (200nm, 350 nm, 600 nm, and 800 nm) using a newly developed instrument which measures scattering from all angles simultaneously. The agreement with Mie scattering calculations for the asymmetry parameter (which varies between ~0.3 and 0.7 in this size range) agreed to within ±0.03 . We also present results from a polydisperse distribution of ammonium sulfate. Measurement of the size distribution of the ammonium sulfate at diameters greater than 1 micron was necessary to achieve proper closure with the measured value of 0.68. A discussion of the upgrades required to achieve sufficient sensitivity to measure g at scattering intensity levels found in the ambient environment will be presented.

2IM.8

Application of Ambient Ion Monitoring in the Athabasca Oil Sands Region. YU-MEI HSU, *Wood Buffalo Environmental Association*

A semi-continuous ambient ion monitor (AIM, URG-9000D, URG) is being used to monitor low ambient concentrations of inorganic gases (NH_3, HCl, HNO_2, HNO_3 and SO_2) and water-soluble aerosol species in the Athabasca Oil Sands Region (AOSR) of northeastern Alberta. The AIM includes two ion chromatography systems for cation and anion analyses, a parallel denuder plate with H_2O_2 solution for absorbing gases, and a cyclone with steam DI water for collecting aerosols. For field application, the AIM has been modified to include: (1) N_2 to control the flowrate of H_2O_2 solution passing through the denuder plate; (2) a carbonate removal device to reduce carbonate concentration in the water used for anion analysis.

The ambient ion monitor has collected hourly data at the Fort McKay community air monitoring station surrounded by the industrial areas from 2010 to 2011, including a forest fire episode. A Dynacalibrator has been applied to generate the known concentrations of SO_2, NH_3 and HNO_3 to examine the collection efficiencies and response time.

Preliminary results indicate that inorganic aerosol species and gas species concentrations are low at this community station. The collection efficient for SO_2 is higher than 90%. The correlation coefficient for ambient average-hourly SO_2 concentrations measured by the ambient ion monitor and a continuous monitor was 0.81. The relation of particulate sulfate concentrations between AIM and an annular denuder sampling system was good. During the forest fire, elevated particulate ammonium and nitrate concentrations were observed.

2IM.9

Prediction of Balloon-Borne Impactor Collection Efficiency at Different Altitudes. Gyuho Kim, SE-JIN YOOK, Kang-Ho Ahn,*Hanyang University*

For the analysis of particles airborne in the atmosphere, it is important to collect those particles efficiently. Inertial impactors are commonly used for sampling atmospheric aerosol particles. The inertial impactors have advantages in miniaturization owing to simple geometry and easy operation, and therefore are appropriate for being loaded on balloons. However, impactor cut-off size can vary according to altitude, since the atmospheric pressure and temperature change with increasing altitude. In this study, a numerical simulation technique was developed for predicting collection efficiency of inertial impactors, and validated at low as well as normal pressure levels by comparing the numerically obtained collection efficiencies with the experimental data of previous studies. Balloon-borne inertial impactors, having cut-off sizes of 1, 2.5, and 10 micrometers, were designed. A simple equation was suggested for predicting the sampling flow rate required for keeping the impacotor cut-off sizes constant at different altitudes. When the sampling flow rate was adjusted as predicted, the cut-off sizes of the balloon-borne inertial impactors were estimated to remain unchanged even at different altitudes in the troposphere.

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2IM.10

Calibration of a Condensation Particle Counter by Aerosol Particle Number Concentration System with Uncertainty Analysis. GUO-DUNG CHEN, Ta-Chang Yu, *Center for Measurement Standards, ITRI, Taiwan*

The measurement of aerosol particles number is important for environmental studies, clean room technology, human health, and environment safety. Therefore, the calibration of particles counter must be addressed. In this study, calibration of a commercial particles counter, such as condensation particle counter (CPC), by aerosol particle number concentration system was described. The system setup and measurement procedure were briefly introduced. The system consisted of electrospray aerosol generator, differential mobility analyzer (DMA), and Faraday-cup aerosol electrometer (FCAE). The electrospray generated aerosol particles from the liquid solution. Then, the particles were charged and classified by a differential mobility analyzer (DMA). Downstream of the DMA, the monodisperse aerosol was diluted in a mixing tube and equally flowed to the condensation particle counter (CPC) under calibration and Faraday-cup aerosol electrometer (FCAE). The Faraday-cup aerosol electrometer (FCAE) was calibrated by a traceable standard current source which was produced from voltage source (mV) and a nominal 100G ohm resistor. Both the voltage source and resistor properties were calibrated from National Measurement Laboratory, R.O.C. Besides, we generated the concentration with well-controlled flows and nominal size 100 nm polystyrene latex (NIST SRM 1963a) for calibration. The main contributions to the total uncertainty of the system included the uncertainty of the current measurement by Faraday-cup aerosol electrometer (FCAE), the uncertainty in splitting ratio at flow splitter, the uncertainty of difference in losses in tubes, and the variation of concentration due to instability. The measurement accuracy of the system are further identified and improved through uncertainty analysis. In our study, the expanded relative uncertainty of the concentration system was 10 % for particle concentrations of approximately 10^3 particles / cm^3.

2IM.11

Atmospheric Aerosol Measurement Using All-in-One Balloon Particle Sampler System. Kang-Ho Ahn, HONG-KU LEE, Hee-Ram Eun, Gun-Ho Lee, Dong-Hyun Yoo, *Hanyang University*

It is very important to measure atmospheric aerosols and analyze the characteristics of them since they have great effect on environment and human body. Satellite, aircraft, radio sonde have usually been used to measure vertical distribution of aerosols and its conditions such as temperature, humidity and atmospheric pressure. The common method of aircraft sampling takes that extracts collected particle on sampler filter and carries chemical analysis. Although, the method is favorable to measure the distribution of atmospheric aerosol, problems caused by fast flight speed; fragmentation of aerosol droplet and dispersion of collected particle, legal limit; flight altitude, prohibited airspace and flight time, and economical limit; frequency of sampling, have been restricted the measurement. These restrictions can be resolved by our all-in-one balloon system applying custom-made polyurethane balloon controlled by electrical winch. The system is composed of developed mini-impactor of 56g weight, several sensors, pump and its data processing board. It can not only collect atmospheric aerosol depending on each altitudes and particle sizes at low cost, but also monitor the atmospheric conditions; temperature, humidity, wind velocity, atmospheric pressure, GPS data, during the measurement.

In this research, we performed the atmospheric aerosol measurement using all-in-one balloon particle sampler system at altitude of 300m and 900m.

2IM.12

Ultrafine Particle Monitor (TSI 3031) Measurements and Evaluation in New York City. JAMES SCHWAB, G. Garland Lala, Kenneth Demerjian, Brian P. Frank, H. Dirk Felton, Oliver Rattigan, Robert Anderson, *University at Albany, SUNY*

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. The TSI 3031 UFP monitor attempts to address this need for a routine, long-term measurement of ultrafines. It combines a diffusion charger to increase the charge on the particles, a differential mobility analyzer to achieve size separation, and an electrometer to detect the size selected charged particles.

We have operated the 3031 UFP monitor at two sites on Long Island: Queens College in the New York City borough of Queens, and Eisenhower Park in East Meadow. We have comparison data at the Queens College site from a pair of SMPS systems for a roughly month-long period in 2009, and an FMPS (Fast Mobility Particle Sizer) for nearly six months in 2012. We have numerous other measurements at the Queens College site useful for evaluating ultrafine particle measurements as well. This poster will highlight the findings from these studies.

2IM.13

A Hi-Volume Dichot Sampler to Collect Fine and Coarse Particulate Matter for Chemical Composition. Guan Zhao, Philip K. Hopke, Paul A. Solomon, SURESH DHANIYALA, *Clarkson University*

Accurate sampling and measurement of size-classified particulate mass is necessary from a regulatory perspective and also for studies on health effects of ambient aerosol. For sensitive and high-resolution composition measurements, instruments sampling large volumetic flowrates are required. A high volumetric (hi-vol) instrument was investigated for sampling $PM_{2.5}$, and $PM_{10-2.5}$. For sampling fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) particles, different single-nozzle high flow dichotomous sampler designs were numerically and experimentally analyzed. To establish the role of turbulent dispersion on particle separation characteristics of a virtual impactor, the performance of hi-volume VIs was experimentally established as a function of Reynolds number. A new design criterion for hi-vol dichotomous samplers operating in turbulent regime was established.

For complete compositional characterization, particles must be collected on a range of substrate types. For particle capture downstream of the VI on multiple substrates, a plenum-based flow-splitter is designed to trifurcate the sample flow and collect particles uniformly on three open-face filters. Numerical modeling results are used to optimize the design of the collector section, minimizing particle loss in the section. The integrated collector-VI setup is evaluated experimentally in the laboratory. The development of this sampler will enable a near-complete mass balance of the coarse and fine fractions of the collected particles and will be suitable for use in monitoring networks for coarse particle chemical speciation and highly useful for PM-related health effects research.

2IM.14

The Low Cut Point Viable Bioaerosol Collector: Viability of E. coli Samples Collected at 300 L/min and Archived for 15 Days. MARIA D. KING, Ray Pierson, Asmaa Kassab, *Texas A&M University*

The low cut point 300 L/min Viable Bioaerosol Collector (LCP-VBAC) with an aerosol-to-hydrosol collection efficiency of 63% for 0.49 micrometer PSL particles and ~100% for particles >1 micrometer, was tested in a laboratory with fresh vegetative bacterial cells at the pressure drop of 55”.

Single E. coli cells were nebulized using the Collison 6-jet nebulizer and collected with the LCP-VBAC using 0.01% Tween-20 as collection liquid for 10 min collection periods. To 0.45 mL aliquots of the samples Phosphate Buffer Saline (PBS) was added to 10% final concentration immediately after collection. The third type of sample was collected in 0.01% Tween-20 for five minutes into tubes containing PBS to 10% final concentration. As reference sampler, the SKC Biosampler was used at 12.5 L/min with 20 mL of 0.01% Tween-20. The samples were divided into two equal volumes and stored at room temperature (RT) and 4ºC, respectively, for a period of 15 days. During archiving the culturability of the samples was monitored by plating; and for the samples stored at 4ºC, the DNA intactness was analyzed by real-time PCR. The samples archived at 4ºC for 48 hours in the presence of PBS show 14X recovery in culturability compared to 3X for the samples in Tween-20. Amending the samples with PBS seems to enhance the recovery of culturability; however, at 4ºC it has no significant effect whether the samples are amended with 10% PBS after or during collection. Real-time PCR analysis shows that the cell counts based on DNA content of the as-collected samples are 100X higher than expected based on colony forming units. As time progresses, the difference between DNA-based total cell counts and culturable cell counts decreases to 2X, very likely due to the role of PBS in the restoration of osmotic stress induced cell damage and viability.

2IM.15

Intercomparison of Particle Sizing Between AMS, SMPS and FMPS. BERTO LEE, Yong J. Li, Chak K. Chan, *Hong Kong University of Science and Technology*

Among the most commonly used particle sizing instruments are the Scanning Mobility Particle Sizer (SMPS), a combination of a Differential Mobility Analyzer (DMA) and a Condensation Particle Counter, and more recently the Fast Mobility Particle Sizer (FMPS). Instrumental comparison studies (Jeong et. al, 2009 and Asbach et. al, 2009) of both instruments have so far focused on the comparability of the particle number concentrations and have found significant counting discrepancies. From a comparison of field data acquired at a suburban site in Hong Kong during springtime 2011, a significant sizing discrepancy between the species mass size distribution from a High-Resolution Time-Of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and the volume size distribution from a collocated Fast Mobility Particle Sizer (FMPS) was observed. Subsequent experimental sizing verifications with various polydisperse inorganic aerosol and PSL particle solutions employing the HR-ToF-AMS, FMPS and a SMPS yielded good agreement between AMS and SMPS measurements, but a consistent mode diameter underestimation by the FMPS up to 40% in terms of volume size distribution was found. Using a simple correction method, the initial sizing underestimation was reduced to within a discrepancy of ~10%.

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2IM.16

Development of Near Continuous Sampling Methods for On Line Measurement of Chemical and Toxicological Properties of Size Fractionated PM. PAYAM PAKBIN, Constantinos Sioutas, Nancy Daher, Dongbin Wang, *University of Southern California*

Since PM components driving toxicity have diverse temporal variation and spatial distribution in the atmosphere, ambient measurements in high time resolution become critical to identify the toxicologically relevant PM species and further refine our understanding of atmospheric processes regulating their chemistry. Conventional quantitative analysis of PM chemical composition and toxicological properties is typically performed off-line, on particles collected on filter substrates, followed by extraction. In order to overcome the limitations of conventional sampling methodology a versatile online analyzer is being developed to allow hourly in-situ measurement of size-fractionated ambient aerosol trace elements and metals, water soluble organic carbon and offering great flexibility for other PM chemistry measurement. The toxicological significance of these chemistries will be established by concurrent macrophage-based ROS measurements.

The field evaluation of the sample collection module was conducted to demonstrate its adaptability and versatility for potential applications in long-term air quality monitoring with high resolution (i.e. hourly) of temporal variation of health relevant PM species. The chemical and oxidative characteristics of concentration-enriched PM2.5 samples simultaneously collected by filters, and the inertial impactor designed for the online sampler are compared. The deployment of these tools with on-line sampling and analysis methods will avoid artifacts associated with collection of PM on filter and impactor substrates and will allow the investigation of temporal changes in PM components and chemistry that is expected to change with sources, atmospheric aging and redox cycling.

2IM.17

Constraining Particle Bounce in an Impactor. ADAM BATEMAN, Scot Martin, *Harvard University*

Recently, it has been inferred from measurement of particle bounce in an impactor that secondary organic aerosol (SOA) particles are solid. This is based on the assumption that solid particles will bounce during impaction, while liquid particles will not. This assumption is investigated using custom made impactors designed to study particle bounce. During impaction, many particles have enough inertia to not only impact with the plate, but also to escape from the plate i.e. “bounce”. It has been observed by many early impaction studies attempting to quantify the mass fraction of aerosols in the atmosphere and laboratory that solid particles will bounce in an impactor while liquid particles will not. However, these observations are qualitative at best. A wide range of bounce behavior has been observed as a function of particle composition and relative humidity (RH), warranting further research into the bounce behavior of particles in an impactor. A variety of particles, both solid and liquid, as well as SOA particles generated from a flow tube and the Harvard Environmental Chamber (HEC) were studied as a function of RH in an attempt to constrain the assumption that if a particle bounces during impaction then it must be a solid, while if it does not bounce, then it is a liquid.

2IM.18

Neutralization of Electrosprayed Particles via Photo-ionizer. QIAOLING LIU, Da-Ren Chen, *Washington University in St. Louis*

Because of the capability of producing monodisperse particles when operated at the cone-jet mode, electrospray technology has been widely proposed to apply in many areas such as nano-material synthesis, drug delivery, particle encapsulation and thin film/particle film deposition. Particles generated from electrospray are highly charged and easily deposited on walls due to the electrostatic effect. Charge reduction is often the necessity to keep the particles airborne for transportation. Reduction of charges on electrosprayed particles has been done via either radioactive or AC-corona-based neutralizers. To ensure the minimal charges on particles AC-corona-based neutralizers require the careful monitoring of balanced bipolar ions. At the same time, tight safety regulation limits the use of radioactive material as neutralizers. It is thus needed to search for an alternative to generate bipolar ions for the charge reduction of electrosprayed particles. In this study we investigated the photoionizer (i.e., a soft X-ray source) as an alternative to neutralize electrosprayed particles. For this investigation we had designed a single-capillary electrospray aerosol generator with the charge reduction chamber in which the photoionizer was used as the bi-polar ion source. To evaluate the performance of the particle neutralization in the above-described generator, a custom-made scanning mobility particle sizer (SMPS), in which the polarity of high voltage power supply can be switched, was used to measure the size and charge distributions of electrosprayed particles exiting from the generator. The fluorescence particle method was also applied to quantify the fractions of neutral and positively/negatively charged particles exiting from the generator. We further investigated the effect of photoionizer’s intensity and position on the spray current when electrospray was operated at various spray modes. The detail of this study will be presented in this talk.

2IM.19

An Aerosol Detection Technique for Diesel Fuel Contaminants. KAI XIAO, Jacob Swanson, Lin Li, Tsz Yan Ling, David Kittelson, David Pui, *University of Minnesota*

The High Pressure Common Rail (HPCR) fuel injection systems are designed to increase combustion efficiency and reduce particle emissions for modern Diesel engines. However, these systems are more sensitive to particle contaminants in the Diesel fuel due to higher pressures and smaller clearances. Damage to the injection system can be caused by submicron particles. However, the current detection standard only regulates particles larger than 4 microns, leaving an uncertainty in the concentration of smaller particles in the supply fuel. This standard is based on direct optical measurements of particles using a liquid particle counter. A limitation to easily extend this technique while retaining general procedure is due to the fact that contaminants in the fuel have similar refractive index as the fuel itself, which makes it difficult to distinguish smaller particles from the fuel.

A new aerosol-based detection technique was developed to characterize particle contaminants in Diesel fuel. The Diesel fuel, diluted by highly volatile hexane, is vaporized by a constant output atomizer. The atomized Diesel fuel was passed through a catalytic stripper that was used to separate the solid contaminants from the fuel and diluent. A water trap and a diffusion dryer were connected after the catalytic stripper to collect the generated water droplets and vapor. Remaining solid particles were measured using an aerodynamic particle sizer (APS), which provides information on the contaminant particles' size distribution and total concentration. This technique is an effective means to transfer the liquid-borne particles into the gas phase and thus increase the distinction between particles and the background. Results reported include a comparison between this method and the current technique as well as fuel filter sample analysis. Results showed that the lower size limit of the aerosolization method can go down to as small as 0.5 microns.

2IM.20

High-Time Resolution Measurement of Particulate Matter Mass and Chemical Speciation. CHEOL-HEON JEONG, Krystal J. Godri, Greg J. Evans, *SOCAAR, University of Toronto*

Continuous high-time resolution measurements of particle mass and chemical composition, collected over an extended time course are needed to provide important links between sources and exposure in rapidly changing environments. New instruments are facilitating such measurements but their capabilities and limitations need to be explored and understood so as to properly use the valuable data they can provide. An Aerosol Chemical Speciation Monitor (Aerodyne ACSM) and a range of PM instruments were deployed in downtown Toronto, Canada at a near- roadway site in December 2011-March 2012. The ACSM measured non-refractory chemical composition of PM1, i.e., organics, nitrate, sulphate, ammonium, and chloride with 30 min resolution. Total mass concentrations were measured with a Filter Dynamics Measurement System-Tapered Element Oscillating Microbalance (FDMS-TEOM), a Synchronized Hybrid Ambient Real-time Particulate Monitor (SHARP) and DustTraks. Particle number and size distributions were measured by a Fast Mobility Particle Spectrometer (FMPS) and an Aerodynamic Particle Sizer (APS). Carbonaceous species mass concentration and optical properties were detected by a Sunset Lab OCEC analyzer and a Photo Acoustic Soot Spectrometer (PASS). In order to characterize the performance of the instruments, an equivalence study was performed. Particulate matter mass closure estimated by integrating ACSM chemical speciation data and elemental carbon was compared to mass concentrations measured by the FDMS-TEOM and the SHARP as well as estimated mass concentrations converted from the FMPS and APS integrated size distributions. Differences between these multiple measurements were identified and these, along with factors influencing the performance of the instruments, will be discussed.

2IM.21

Calibration of an Optical Particle Counter for low concentrations of 3 µm particles using a Wafer Surface Scanner. LIN LI, Laura Windmuller, George Mulholland, Miles Owen, David Pui, *University of Minnesota*

Optical particle counters (OPCs) are widely used to measure aerosol size distribution and number concentration in the size range of approximately 0.1 to 30 micro-meter by means of light scattering from single particles. They are applied to low concentration measurements such as clean room or ambient PM monitoring, and to high concentration industrial aerosols, e.g. industrial filtration. The US Army has a requirement to calibrate an OPC at low concentrations of 3 micro-meter particles with traceability to SI units realized by the National Institute of Standards and Technology (NIST) in support of fielded and future biological agent detectors. Most of the previous studies were focused on the particle sizing accuracy for particles of different size, shape, and refractive index. The OPC number concentration has been measured by comparison with a Condensation Particle Counter (CPC) for particles small than 1 micro-meter, an Aerodynamic Particle Sizer (APS), or a reference OPC. Limited study was conducted concerning OPC calibration at low concentrations.

In this study, we proposed a method for OPC calibration with 3 micro-meter PSL particles at the concentration from 10 to 100 #/L using a Wafer Surface Scanner (WSS) as reference. To have stable NIST traceable calibration for OPCs at low concentration, we nebulized a suspension of NIST traceable 3 micro-meter PSL spheres, evaporated the droplets leaving 3 micro-meter spheres, used a virtual impactor to concentrate the 3 micro-meter particles, and then used a differential mobility analyzer (DMA) to remove residue and select 3 micro-meter particles only. The aerosol stream exiting the DMA was split into two: half was deposited on a wafer and half sent to the OPC. By depositing a controlled number of particles on the wafer surface using a settling chamber, we calibrated the OPC based on the WSS analysis of the deposited particles. The details of this study will be given during the conference.

2IM.22

Characterization of Insoluble Submicrometer Particles in Seawater for Studying on Primary Marine Aerosol Formation.JIYEON PARK, Miji Kim, Seung hee Han, Kihong Park, *Gwangju Institute of Science and Technology*

A direct measurement of insoluble submicrometer particles in seawater (i.e., before aerosolization) is essential to better understand their role in marine aerosol formation. In this study, we applied the membrane filtration-differential mobility analyzer (MF-DMA) technique (Park et al., 2011) and the membrane filtration- quadruple aerosol mass spectrometer (MF-QAMS) technique to determine the number and chemical composition of insoluble submicrometer particles (20-450 nm) in seawaters sampled at different locations of coastal areas in Korea, in different seasons, and with varying tidal levels. Also, the effects of Asian dust storm and industrial sources on the number of insoluble submicrometer particles in seawaters were examined. To determine elemental composition of insoluble submicrometer particles collected on ultrafiltration (UF) membrane surface (Pore size: ~5 nm), a laser induced breakdown spectroscopy (LIBS) was also used. Simultaneously, biological properties of seawaters (concentrations of bacteria (20-450 nm), virus (20-200 nm), and chlorophyll-a (>700 nm)) were measured for all samples to find any link between the amount of biological materials and the number of insoluble submicrometer particles in seawaters. Significant increases of the number concentration of insoluble submicrometer particles were found in seawater sampled from Taean (i.e., East Sea of Korea), during spring period, and with maximum tidal variation (i.e., spring tide) in clean coastal environments. Also, the number concentration of insoluble submicrometer particles in seawater was strongly correlated with biological materials in seawater, suggesting that the biological materials were probably one of the major sources of insoluble submicrometer particles in seawater. When the site was heavily affected by industrial sources, it also led to an increase of the number concentration of insoluble submicrometer particles in seawater. Chemical and elemental analysis of insoluble submicrometer particles in seawater is in progress.

2IM.23

Determination of Polycyclic Aromatic Hydrocarbons and Their Oxidation Products in Particulate Matter Using Pressurized Fluid Extraction. RICHARD COCHRAN, Nagaraju Dongari, Haewoo Jeong, Josef Beranek, Alena Kubatova, *University of North Dakota*

Although secondary gas-phase mechanisms that produce oxidation products of polycyclic aromatic hydrocarbons (PAHs) have been studied extensively, the knowledge regarding heterogeneous oxidation mechanisms is limited. In order to determine these mechanisms an analytical method that allows for the analysis of the wide range of polar PAH products needs to be developed. In this study pressurized fluid extraction (PFE) was compared to the currently used Soxhlet extraction method for the quantification of PAHs and their oxidation products in wood smoke PM. Solid phase extraction (SPE) was used to fractionate PAHs and their oxidation products based on their polarities to improve the sensitivity of their analysis. GC-MS methods employed both electron ionization and negative ion chemical ionization. MS detection was performed in selected-ion-total-ion scanning mode, enabling both high sensitivity and identification abilities.

2IM.25

Smoke Test Chamber Part II: CFD Smoke Transport Simulation. TATEH WU, Chao-Hsin Lin, Jacob Swanson, David Pui, Sheng-Chieh Chen, *The Boeing Company*

A computational fluid dynamics simulation has been conducted to analyze smoke transport inside a test chamber. The test chamber is configured with two inlets on opposite walls and single outlets on opposite walls, with the inlet and outlet walls opposing each other. The test chamber can be ventilated at different conditions by controlling supply air inlet and exhaust outlet flow rates. The CFD model is built on the actual geometry of the test chamber. In addition to simulating air flows based on the ventilation configuration, the CFD smoke modeling simulates the smoke plume generation process that involves smoke injection, jet impingement, and buoyancy created by heaters inside the smoke generator.

The CFD model is a three dimensional turbulent compressible flow with species transport and both steady state and transient CFD cases are analyzed. Smoke particle transport is simulated by using a Lagrangian discrete phase approach. Convection, conduction, and radiation heat transfer are included in the CFD model. CFD predictions of air velocity above the smoke generator exit and below the test chamber ceiling are compared with the PIV test data. Time-averaged steady state and transient velocity model results are compared with PIV experimental data. In addition, transient smoke concentration distribution predicted by the CFD model is compared with the ELPI test data at several locations inside the test chamber in this study.

2IM.26

Method Development and Field Evaluation of an Acidic Ultrafine Particle Detector. Da-Wei Wang, Hai Guo, KALAM CHEUNG, Chak K. Chan, *Hong Kong Polytechnic University*

A simple and novel method, involving the use of an iron nanofilm detector, was developed for the enumeration and size measurement of acidic ultrafine particles. To obtain morphological information of acidic and non-acidic ultrafine particles on the designed iron nanofilm detectors, both types of particles were generated and collected on the detectors. The reaction spots were examined using Atomic Force Microscopy (AFM) to establish the correlations between the diameter of the particle and the size of the reaction spot. A field evaluation was conducted in Hong Kong from September to November 2010 to validate this method. A scanning mobility particle sizer (SMPS), in tandem with a condensation particle counter (CPC), was used to measure the size-resolved number concentration of ambient particles in the range of 5.5–350 nm at 4-min scan intervals. On the other hand, a SMPS + electrostatic precipitator (ESP) system was used to collect particles smaller than 350 nm on the iron nanofilm detectors, which were subsequently examined using AFM. Measurements obtained from these two sampling methods were compared for validation. The results indicated that the particle number concentrations obtained from the AFM scanning of the exposed detectors, collected via the SMPS + ESP system, were comparable to those derived from the SMPS + CPC measurements ($p > 0.05$). The average geometric mean diameter of particles at peak measured by the SMPS + CPC and the detectors scanned by AFM was 52.3 ± 6.9 nm and 51.9 ± 3.1 nm, respectively, demonstrating good agreement. The influence of temperature, relative humidity, and gaseous pollutants on the surface structure of the detectors was also examined. It is concluded that the iron nanofilm detectors developed in this study could be a reliable tool for the measurement and analysis of acidic particles in a wide range of ambient conditions.

2IM.27

Evaluation of the Classification Performance of the New Centrifugal Particle Mass Analyzer. JONATHAN SYMONDS,*Cambustion*

The CPMA (Olfert and Collings, 2005) classifies particles by their mass to charge ratio, by applying opposing electric and centrifugal forces between two rotating cylindrical electrodes between which a potential difference is applied. Unlike the Aerosol Particle Mass (APM) Analyzer (Ehara et. al, 1996), the CPMA's inner electrode spins slightly faster than the outer electrode, which allows the centrifugal and electrical forces to balance across the entire classification region. This stable system of forces has previously been shown to give a higher transmission efficiency for otherwise equivalent geometries and setpoints.

An evaluation of the newest implementation of the CPMA classifier, in terms of mass accuracy and penetration efficiency is presented. Mass accuracy is determined by comparison with the effective mass calculated for DMA classified PSL and NaCl particles (taking into account dynamic shape factor where necessary). The two methods show consistent agreement to within <5%, across a wide range of particle sizes (20–200 nm), with no systematic loss of accuracy observed for either the smallest or largest particles. Error analysis indicates that the uncertainties in the CPMA measurement are much less than the uncertainties in the DMA equivalent mass technique. In terms of penetration, once static diffusive losses are taken into account, dynamic particle loss is generally low, though some increase in loss is seen at the very highest rotational speeds.

2IM.28

Quantification of Carboxylic Acid and Carbonyl Functional Groups in Organic Aerosol Infrared Absorbance Spectra.SATOSHI TAKAHAMA, Anita Johnson, Lynn Russell, *Scripps Inst. of Oceanography; EPF Lausanne*

This work describes and evaluates the algorithm introduced by Russell et al. 2009 for apportionment and quantification of oxygenated (carbonyl and hydroxyl) functional groups in organic aerosol from Fourier Transform Infrared Spectroscopy (FTIR) analysis of the condensed phase. The procedure for spectra interpretation and quantitative analysis is described through the context of an algorithm in which contributions of background and analyte absorption to the infrared spectrum are apportioned by the superposition of lineshapes constrained by laboratory measurements. For the absorption profile of carboxylic COH, which is particularly broad, an average lineshape is extracted from profiles of a fatty acid series using a statistical decomposition method.

Our algorithm for quantifying carboxylic COOH is applied to a multifunctional compound, and to a multifunctional mixture with <30% average prediction error. The ketonic C=O in pinonic acid is detected by our method by the amount of carbonyl in molar excess of carboxylic COH, and estimated within 25% of actual values. Aldehydic compounds are observed to form diols in aqueous solution in agreement with expectations; excess carbonyl detected in atmospheric samples are also likely to be ketonic rather than aldehydic C=O. This algorithm has been applied to the analysis of ambient particles collected on Teflon substrates during field campaigns between 2006 and 2010. The reproducibility introduced through its implementation leads to improved precision in the FTIR measurements, and provides an explicit framework by which additional constraints can be used to reduce the uncertainty in this analysis technique.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., Bates, T. S., 2009. Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the R/V Ronald Brown during TEXAQS/GoMACCS 2006. Journal of Geophysical Research-Atmospheres 114, D00F05.

2IM.29

Validating a Centrifugal Particle Mass Analyzer and Differential Mobility Spectrometer System for Mass-Mobility Measurements. Tyler Johnson, Jonathan Symonds, JASON OLFERT, *University of Alberta*

Many different methods measure the mass mobility of individual nano-particles such as the Aerosol Particle Mass (APM) analyzer and Centrifugal Particle Mass Analyzer (CPMA). However, the traditional setup of these instruments with a Differential Mobility Analyzer (DMA) and Condensation Particle Counter (CPC) require each mass setpoint to be scanned, limiting their application to steady state measurements.

This limitation can be overcome by using a Differential Mobility Spectrometer (DMS), replacing the DMA-CPMA-CPC with a CPMA-DMS system. Since the DMS measures real-time aerosol size distributions, transient mass mobility measurements can be completed for each CPMA mass setpoint.

This concept was verified by measuring the mass mobility of aerosolized lube oil using both a DMA-CPMA-CPC and a CPMA-DMS system. To increase sizing accuracy the DMS was modified by disabling the aerosol charger and lowering the sample and sheath flow rates. In a normal DMS the uncertainty, largely due to charging efficiency and its dependence on particle morphology, would have been 10% in particle size or 31% in effective particle density. By size calibrating the modified DMS with a DMA and applying a post-processing algorithm to correct the DMS results for multiply charged particles an uncertainty of 4-5% in particle size or 13-17% in effective particle density was achieved. These values were calculated using a 8% CPMA mass setpoint uncertainty and a 3% DMA mobility size uncertainty. Using the above values a 12% uncertainty in effective particle density for the DMA-CPMA-CPC system was determined.

The lube oil effective density results from the DMA-CPMA-CPC and CPMA-DMS systems were found to agree within error. Therefore, the CPMA-DMS can be used for mass mobility measurements, but at the cost of higher uncertainties compared to a DMA-CPMA-CPC system.

2IM.30

Investigation of Beta Attenuation Monitor Filter Rolls for Particulate Matter Speciation. SURESH RAJA, Philip K. Hopke, Xia Xiaoyan, Sriraam Ramanathan Chandrasekaran, Lin Lin, Kalliat Valsaraj, Jon Klassen, James W. Sweet, *Providence Engineering and Environmental Group*

Traditional FRM $PM_{2.5}$ samplers have been typically used throughout California for ambient PM_2.5 mass measurements. Recently monitors in the San Joaquin Valley were changed to non-traditional PM systems, such as the Beta Attenuation Monitor (BAM) (Model BAM-1020, manufactured by Met One Instruments, Incorporated) because there is a need for real-time $PM_{2.5}$ data. These units provide a filter tape with a series of 1-hour samples. In this work, speciation methods were developed and tested to investigate the use of BAM filter rolls for chemical speciation of PM collected on BAM filter spots. A total of 22 BAM samples (each comprising of 24 1-hour spots) from 12 sites were analyzed for ions and black carbon (BC). Additionally, 336 1-hour spots from the Hanford and Madera City monitoring stations were used to analyze for organic molecular markers (MM). Measurements of ions and BC in each site appear to have been underestimated likely due to volatilization losses. MM measurements in the 336 BAM filter spots from Hanford and Madera City indicate speciation of BAM filters for MM could be a viable method for measuring useful marker species.

Statistical analysis was conducted by grouping particles into one with mass concentrations greater than 80 micrograms/m^3, and another with mass concentrations less than 80 micrograms/m^3. Analysis of delta-C concentration (i.e., delta-C = BC370 nm - BC880 nm) in these two groups of samples revealed that most of the high $PM_{2.5}$ concentration days ($PM_{2.5}$ greater than 80 micrograms/m^3) were likely not impacted by biomass combustion particles. A major portion of the samples analyzed in this work with high concentrations of $PM_{2.5}$ are likely to be inorganic species such as ammonium sulfate, ammonium nitrate and other ions.

Results from this work suggest that handling and storage of BAM filter samples play a critical in the quality of results.

2IM.31

Development of a Special Dust Feeder for Long-Term Aerosol Generation from Poor Flow Dust Materials. STEPHAN GROSSE, *Topas GmbH*

A wide range of scientific and industrial aerosol applications requires submicron airborne dust particles due to their very special property profile. This includes filtration, pharmaceutical and polymer industry as well as surface treatment, environmental and occupational safety applications. But because of the special characteristics of submicron particles most of the common feeding and aerosol generating instrumentations do not show a reliable continuous operation anymore especially at low feeding rates. A proper material handling is strongly affected by adhesion effects which are significantly increasing at decreasing particle size. This poster will present a new patented concept of generating aerosols from submicron dust particles such as aluminium oxide, titanium dioxide and soot. As a closed cycle feeding technique is applied a continuous non-stop operation with a constant particle output rate is realised. The feeding rate is adjustable by certain instrument settings in a range between milligrams per hour up to several grams per hour. Because the material is not impacted feeding fluctuations from different levels of dust impaction are avoided a priori. The feeding behaviour of different particle materials depends only on bulk properties as there is a loose bulk feeding. Furthermore this instrument has been designed with a minimum of contact surfaces to minimise adhesion effects and attrition. The main focus of this poster will be validation of this new aerosol generating technique for testing cleanable filter media according to new ISO 11057 standard.

2IM.32

Two Sources of Errors in Determination of the Particle Concentration Reduction Factor of the Volatile Particle Remover Used in Legislated Vehicle Emission Measurement. HIROMU SAKURAI, Keizo Saito, Tsuyoshi Taishi, Tetsuji Koyama, *AIST*

We investigated sources of errors in determination of the particle concentration reduction factor (fr) of the volatile particle remover (VPR) used in legislated vehicle emission measurement. Sodium chloride and soot are two of the most frequently used materials of particles used in the fr evaluation. We identified two sources of errors that are associated with the use of these materials: One is the variation of the detection efficiency of condensation particle counters (CPCs) against sodium chloride particles, which was found to depend on the preheated temperature of the particles. The other is the size shrinkage of soot particles generated with a propane flame burner that are not thermally pre-treated, when the particles were heated at temperatures typically set at the evaporation tube of VPRs. These two sources of errors have presumably caused disagreement of fr values obtained with particles of the two materials. We found that, by selecting appropriate CPCs and also by sufficiently pre-heating the particles, disagreement due to these errors could be eliminated. As a result, consistent fr values were obtained between measurements with the two different particle materials, i.e., sodium chloride and soot.

2IM.33

Evaluation of a Personal Diffusion Battery. DONNA VOSBURGH, Timothy Klein, Maura Sheehan, T. Renee Anthony, Thomas Peters, *University of Wisconsin-Whitewater*

A four-stage personal diffusion battery (pDB) was constructed to measure submicron particle size distributions. The pDB consisted of a screen-type diffusion battery, solenoid valve system, and electronic controller. A data inversion spreadsheet was created to solve for the number median diameter (NMD), geometric standard deviation (GSD), and particle number concentration of unimodal aerosols using stage number concentrations from the pDB combined with a handheld condensation particle counter (pDB+CPC). The limitations of the pDB+CPC inversion spreadsheet were determined by calculating simulated distributions.

The pDB+CPC with inversion was challenged with propylene torch exhaust and incense exhaust using timings of 80 seconds per measurement cycle and 240 seconds per measurement cycle. The pDB+CPC with inversion measured five of the 12 polydispersed aerosol runs with the acceptable criteria. Three of the runs that did not fall within the acceptable criteria were below the lower limit of the pDB+CPC with inversion. They successfully solved the NMD to 16 nm, a NMD constraint, alerting the operator to the issue. The ratio of the nanoparticle portion of the aerosol (RNano) was calculated for the twelve runs to determine the ability of pDB+CPC with inversion to measure only the nanoparticle portion of the aerosols. The RNano was from 0.87 to 1.01 when the inversion did not solve to a constraint and from 0.06 to 2.01 when the inversion did solve to a constraint. Future work is needed to evaluate the pDB+CPC response to multimodal aerosols.

2IM.34

Development of a Mobile Atmospheric Reaction Chamber with Precision Thermodynamic Control for Generation of Complex Urban Air Mixtures. JONATHAN KRUG, Michael Lewandowski, John Offenberg, Tadeusz Kleindienst, M. Ian Gilmour,*U.S. Environmental Protection Agency*

A mobile atmospheric reaction chamber was developed by the United States Environmental Protection Agency (EPA) at its facility in Research Triangle Park, NC. The goal was to develop a reaction chamber capable of generating complex urban air mixtures that can simulate various pollutant conditions (e.g., Code Orange and Code Red levels with different multi-pollutant chemistry: high ozone/low PM, high PM/Low ozone, high SOA/low ozone, high carbonyls/high ozone). With integration of the reaction chamber to in vitro and in vivo equipment, studies of exposure to gas and particle phase constituents of complex urban air mixtures, aged combustion emissions, or SOA from direct injection of hydrocarbons will be possible.

The atmospheric reaction chamber, clean-air supply, and basic instruments are fully contained in a 24’ long, 12’ high trailer enabling the chamber to be moved to different combustion sources and exposure facilities. Temperature control is handled by a pair of 2-ton continuous load air conditioners that allow thermodynamically stable photochemical aging between 15 and 45 degrees C with a typical steady state deviation of less than ±0.5 degrees C. The chamber features 14 cubic meter total volume and can support 4-6 hour exposures in batch mode as well as continuous exposures in continuous stirred tank reactor mode with photochemical residence times up to 8 hours. A detailed description of the mobile reaction chamber components and principles of operation will be presented in addition to select results from laboratory evaluations of the chamber performance.

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

2MB.1

The Effect of the Dust Samples Collected From Moisture Damaged Schools on the Immunological Cells: Results of HITEA-Study. KATI HUTTUNEN, Martin Täubel, Juha Pekkanen, Anne Hyvärinen, Dick Heederik, Jan-Paul Zock, Maija-Riitta Hirvonen,*University of Eastern Finland, Kuopio, Finland*

Exposure to moisture and mold damaged materials is known to cause adverse health effects ranging from unspecific symptoms to chronic respiratory diseases. The relative potential of a material or dust sample to cause immunotoxicity in experimental conditions can be studied with cell lines.

In this work we studied the in vitro -effects of dust samples collected from moisture damaged schools in three European countries. The effects of samples from moisture damaged schools were compared to the samples collected from reference schools. A mouse macrophage cell line was exposed for 24 hrs to the settled dust collected from Finnish, Dutch and Spanish schools. After the exposure, the concentrations of four inflammatory mediators: nitric oxide, tumour necrosis factor (TNF) alpha, interleukin (IL-) 6, macrophage inflammatory protein MIP) 2 were measured from the cell culture medium. In addition, the viability of the cells was assessed with propidium iodide (PI)-exclusion and (3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) -tests.

According to the preliminary results, the samples collected from the moisture damaged schools in the Netherlands and Spain induce stronger inflammatory response compared to samples of the reference schools, whereas the responses caused by the Finnish samples are overall lower and differences between schools are smaller.

2MB.2

Effect of Small Scale Mechanical Vibrations on Fungal Bioaerosol Concentrations Within Confined Environments and Comparison of the Concentration With Ambient Fungal Bioaerosol Concentrations.

BYUNG UK LEE, *Konkuk University, Seoul, Republic of Korea*

There are various reasons of mechanical vibrations in urbanized life. Falling of big objects in upstairs, strong wind, nearby passing trains and trucks, and earthquakes cause various scale vibrations. When vibrations occur, they may affect not only human beings' life but also microorganisms which stay on walls and ceilings of buildings. It was reported that when big vibrations happened, some microbial diseases spread. We have suspected that vibration may increase the concentration of bioaerosols in air environments. In this study, we developed an artificial mechanical vibration system and measured bioaerosol concentrations after vibration incidents. We also compared the concentration with ambient fungal bioaerosol concentrations. Experimental results show that small scale artificial vibration can increase the concentration of fungal bioaerosols with moderate scale.

This work was supported by a National Research Foundation of Korea (NRF) grant ('Measurement of airborne microorganisms in public facilities and development of control methods against airborne pathogenic microorganisms', No. 2012-0002857) funded by the Ministry of Education, Science, and Technology.

2MB.4

Coupling a Viable Bioaerosol Collector (VBAC) with Pyrosequencing to Characterize a Dynamic Bioaerosolization Event.

Juan Pedro Maestre, Andrew Hoisington, Sungwoo Bae, Maria D. King, KERRY KINNEY, *The University of Texas at Austin*

Short-term, dynamic bioaerosol events can be difficult to capture in conventional bioaerosol sampling units that have low sampling rates and potentially poor microbial recovery. This difficulty is compounded by culture-based analysis of the recovered organisms which can greatly underestimate the diversity of the microorganisms actually present. In the current work, a high flow (100 L/min) Viable Bioaerosol Collector (VBAC) was used to capture the bioaerosols generated over a 15 minute period in an operating shower stall. The VBAC was also used to collect 15-minute bioaerosol samples prior to and following shower operation to investigate how the airborne microbiome changed in response to the short term event. To provide a basis for comparison, an impinger-based bioaerosol sample and a filter sample of the bioaerosol were also collected simultaneously. All the collected samples were quantitated by traditional culturing on agar media and real-time PCR, using universal ITS primers and also specific oligonucleotides developed by EPA for the analysis of the most frequently occurring indoor fungal strains.

DNA extraction of the microorganisms recovered in the VBAC coupled with pyrosequencing analysis indicates that a diverse range of fungi were present in the bioaerosol generated during the 15-minute shower event. The dominant fungal species identified in the shower aerosol was Alternaria alternata, which is usually considered a potent outdoor asthma trigger. Sequencing of the microorganisms captured in the impinger and filter samplers yields a much less diverse community which suggests that these sampling techniques have difficulty capturing short-term, dynamic events. Pyrosequencing of the bacteria captured in the bioaerosol samplers will provide a valuable comparison to the fungal results collected to date. In addition, the presence of potential bacterial pathogens in the bioaerosol and the likely source of the microorganisms (e.g., water distribution line, shower biofilm) will be investigated.

2MB.5

Selectively Detecting Influenza Viruses in Exhaled Breath in Minutes Using Silicon Nanowire Sensor: A New Arena for Flu Diagnosis. Fangxia Shen, Jindong Wang, Zhenqiang Xu, Yan Wu, Qi Chen, Xiaoguang Li, Jie Xu, Li Lidong, MAOSHENG YAO, Xuefeng Guo, Zhu Tong, *Peking University*

Influenza epidemics worldwide result in substantial economic and human costs annually. However, rapid and reliable flu diagnosis method is significantly lacking. Here we have demonstrated the selective detection of influenza A viruses down to 29/μL in clinical exhaled breath condensate (EBC) samples (diluted by 100-fold) within minutes using silicon nanowire (SiNW) sensor devices. In all cases, we have observed that EBC samples tested positive or negative by gold standard method RT-qPCR generated corresponding positive or negative SiNW sensor responses. High selectivity of SiNW sensing was also demonstrated using H1N1 viruses, 8 iso PGF 2a and inert nanoparticles. Finally, magnetic beads were shown capable of enhancing SiNW sensing directly for low level viruses and 8 iso PGF 2a. When calibrated by virus standards and EBC controls, our work suggests that SiNW sensor device can be reliably applied to the diagnosis of flu in a clinical setting with 2-order magnitude less time compared to gold standard method RT-qPCR.

2MB.6

Thermal Inactivation of Bioaerosol during Filtration. HSING-WANG LI, Elizabeth Gomez, Brian Damit, Chang-Yu Wu,*University of Florida*

The spread of airborne pathogens as well as the intentional release of biological agents for terrorism in recent years have raised the public’s concerns about bioaerosol and the urge for its effective control. Filtration is the most common method for removing aerosol; however, an appropriate treatment for the filter that has collected microorganisms is critical to preventing reaerosolization and formite transmission.The objective of this study was to develop a novel technology to estimate inactivation efficiency of bioaerosol collected on filter. In this study, joule heating was used to inactivate the collected microorganisms.

The activated carbon filter was challenged with Escherichia coli (E. coli), a gram negative bacterium with a primary particle size around 0.8 μm, in a parallel filtration system. Biosamplers were used downstream to collect the sample, and the filter was tested at ~22oC and ~50% relative humidity. Experimental results showed that the average surface temperatures on the filter measured by pyrometer reached around 31, 63, and 104oC at 1, 3 and 4V, respectively. The bioaerosol removal efficiency of activated carbon filter only and heated activated carbon filter were 90.0% and 92.0%, respectively. In addition, the inactivation efficiency on the filter surface due only to heating was 99.7%. The results demonstrate that the heated filter is safer for handling.

2MB.8

The Floor Dust-Indoor Air Continuum: A Microbial Community Perspective.

DENINA HOSPODSKY, William Nazaroff, Jordan Peccia, *Yale University*

Humans spend approximately 90% of their time indoors, where inhalation of microbial constituents is a significant exposure route. Through combining indoor air modeling efforts with molecular biology-based microbial population assessments, previous research has suggested that human occupancy shapes the indoor air microbiome, mostly through resuspension of bacteria contained in floor dust. The goal of this study is to examine how independent parameters including human activity, air exchange rate, floor dust load, and relative humidity, influence the contribution of floor dust bacteria to the bacterial species found in indoor air.

Floor dust and indoor aerosols were sampled in six classrooms in the US (1), Europe (3), and China (2) during times of occupancy. Phylogenetic libraries based on the 16S universal bacterial gene were produced for floor dust and air samples using 454 pyrosequencing technology. Retrieved sequences were assigned to phylotypes and the differences between floor dust and air populations were quantified via their weighted UniFrac distance metric. A low (near zero) distance metric indicates that the floor dust and air populations are identical (i.e., demonstrating a strong floor dust source contribution). We investigated linear correlations between this UniFrac distance metric and independent parallel measured variables including air exchange rate [h-1], relative humidity [%], floor bacterial load [genomes m-2], and the intensity of occupants' activities [W m-2 h-1].

Results demonstrate that an increase in floor dust contribution (lower UniFrac distance) was strongly correlated with increased human activity (Pearson correlation, r = -0.67) and bacterial floor dust load (r = -0.57), and moderately correlated to increased relative humidity (r = -0.39). Decreased source strengths of the floor dust were moderately correlated with increasing air-exchange rate (r = 0.43). Multivariate statistics analysis will be presented to identify the combination of building parameters that most confidently predicts the resuspension of microbial communities from the floor to the air.

2MB.9

Potential for Metabolic Activity of Bioaerosols.

Valdis Krumins, GEDIMINAS MAINELIS, Lee Kerkhof, ValaRae Partee, Donna Fennell, *Rutgers, The State University of New Jersey*

While many microorganisms have been identified and enumerated in ambient air, there has been very little exploration of microbial activity and potential for growth in natural bulk air. Natural air contains oxygen, water, and substrates in the form of volatile organic compounds (VOCs) that potentially allow for microbial growth while airborne. The objective of this study is to determine whether bacteria present in ambient air are active or growing.

Bioaerosols from 1 m^3 air samples were collected from four sites across New Jersey using filters (Supor, Pall, Port Washington, NY) and by liquid impingement using Biosamplers (SKC, Eighty Four, PA). The liquid samples were divided into four aliquots and enriched in minimal media supplemented with 1 mM of one of the following VOCs: methanol, ethanol, acetic acid, and acetone. The prokaryotic and eukaryotic components of the microbial communities of the enrichments were analyzed by denaturing gradient gel electrophoresis.

Enrichment cultures were aerosolized into rotating bioreactors which can maintain bacteria-sized particles airborne for several days. The reactors are made from 0.32 m^3 stainless-steel drums equipped with temperature, pressure and humidity sensors. The bioaerosols in the drums were supplied with ^{13}C-labeled or unlabeled acetic acid (240 ppbv) or ethanol (20 ppmv) and incubated for two days at room temperature. Stable isotope probing of the 16S rRNA gene was used to explore whether new DNA had been synthesized.

Sphingomonas aerolata, a psychrotolerant bacterium previously isolated from indoor air, was also tested in bioreactor incubations. Increased ribosomal RNA content of ethanol-fed compared to starved bioaerosols suggests metabolic activity in the presence of the volatile substrate. A proteomics approach is also being used to assess activity.

2UA.1

Monitoring of Air and Soil Pollution from Tailings and Mass Transport of Deposited Aerosol in Mitrovica - Republic of Kosovo. AFRIM SYLA, Fatbardh Syla, Rizah Hajdini, *University of Prishtina Kosovo*

In December 2008-2011 we undertook a detailed air and soil sampling programme at Mitrovica. Three potential sites have been identified by Departament of environment, with the favoured site on the north and south bank of the Ibar at Mitrovica . However, a pilot soil survey (using portable XRF) by a International Company Mercy Corps at this site revealed very high metal levels (especially Pb) in the soils, and questions were therefore raised about the suitability of this site.

Following discussions between University and Municipality of Mitrovica, a series of objectives were identified relating to the three proposed development sites:

1. What are concentrations of Pb and other metals/metalloids in air,surface and sub-surface soils?
2. Are the Pb concentrations typical or atypical of soil Pb concentrations found elsewhere in Mitrovica city?
3. What is the bioaccessibility of soil Pb to the residents of Mitrovicë/a?
4. What is the source of the lead, and is the source still "active"?

To address Objectives 1 and 2, soil and mining/industrial waste samples were collected from from sites in and around Mitrovica . All samples were collected, the WGS84 UTM coordinates of all sample sites were recorded using a Garmin 60CSx GPS unit. In January 2009 University submitted a report to Municipality that addressed objectives. Following the completion of Pb isotope and human bioaccessibility analyses this report addresses objectives 1-4 and thus completes the assessment of air and soils in Mitrovica. The main body of this study provides a summary of the principal findings of, and recommendations arising from, the bioaccessibility and Pb source identification work.

2UA.3

Characterization of Organic, Metal and Trace Element PM Species and Derivation of Freeway-based Emission Rates in Los Angeles, CA. JAMES LIACOS, Winnie Kam, Ralph Delfino, James Schauer, Constantinos Sioutas, *University of Southern California*

Particulate matter from two major Los Angeles freeways (I-710 and Route 110) was collected during March-April 2011 using a novel on-road sampling method. Freeway-based emission rates (ERs) – mass per kilometer of freeway per hour – were calculated using mass concentrations, fuel characteristics, and traffic flow rates. These ERs are presented such that freeways could be treated as line sources of emissions for use in predictive models of population exposure for nearby communities. I-710 is a major route for heavy-duty diesel vehicles (HDDVs) traveling to and from the Ports of Long Beach and Los Angeles, while Route 110 has a much lower HDDV fraction – 3.9% versus 11.4%. Two sets of samples were collected for each freeway, each set representing approximately 50 hours of on-road sampling. Concurrent fixed-site sampling in downtown Los Angeles provided estimates of urban background levels. Chemical analysis was performed for elemental carbon (EC), organic carbon (OC), polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes, and trace metals and elements. Concentrations and ERs were generally lower (or comparable) on Route 110 than on I-710, with EC and pyrene being notably lower on Route 110, findings consistent with that freeway’s lower HDDV fraction. EC ERs were lower than those reported in previous studies, suggesting that efforts to reduce HDDV emissions at the Ports of Los Angeles and Long Beach have been successful. While ERs for organic tracers were largely within the range of values reported by previous studies, the present study found much higher ERs for trace metals and elements. This suggests the sampling methods employed in this campaign are more efficient at capturing particles from sources such as resuspended road dust and wear from tires and brakes, which are usually not included in traditional sampling methodologies for assessing vehicular emissions (e.g. dynamometer studies).

2UA.4

Trends in the Mass and Chemical Species Concentrations of Coarse Particulate Matter in the Los Angeles Basin and Relation to Sources and Air Quality Regulations. KALAM CHEUNG, Martin Shafer, James Schauer, Constantinos Sioutas,*University of Southern California*

To assess the impact of air quality regulations on coarse particles, the concentrations of CPM mass and its chemical constituents were studied in the Los Angeles Basin (the Long Beach, Los Angeles and Riverside area) from 1987 to 2009 using data acquired from peer-reviewed journals and regulatory agency database. Overall, PM_{10} mass concentration has decreased by approximately half from 1988 to 2009 at the three sampling sites examined. Annual CPM mass concentrations - calculated from the difference between daily PM_{10} and $PM_{2.5}$ from 1999 to 2009 when both measurements were available - showed that high CPM episodes driven by high wind speed / stagnant condition caused year-to-year fluctuations in the $99^{th}/98^{th}$ percentile CPM levels. In addition, the reductions of average CPM levels were lower than those of PM_{10} in the same period, suggesting that the decrease of PM_{10} level was primarily driven by reductions in the concentrations of fine particles. This is further confirmed by the significant decrease of combustion related emissions of Ni, Cr, V, and EC in the coarse fraction after 1995, consistent with the implementation of $PM_{2.5}$ standard in 1997. On the other hand, the contribution of secondary formation and sea salt to CPM was not significantly reduced, as demonstrated by the comparable concentrations of several inorganic ions (sulfate, chloride and to a lesser extent nitrate). Levels of Cu, a tracer of brake wear, either remained similar or decreased at a smaller rate compared with elements of combustion origins after 1995, suggesting that the contribution of brake wear to CPM has become more significant despite the overall reduction of CPM mass concentrations in the same period. In summary, our results suggest that past and current regulations may have been more effective in reducing fugitive dust and combustion emissions rather than coarse particles from vehicular abrasion, secondary formation and sea salt.

2UA.5

Seasonal and Spatial Variations of Individual Organic Compounds of Coarse Particulate Matter in the Los Angeles Basin.KALAM CHEUNG, Michael Olson, Brandon Shelton, James Schauer, Constantinos Sioutas, *University of Southern California*

While the organic content of ultrafine and fine particulate matter (PM) is well studied, the organic composition of coarse particles has remained largely uncharacterized. To improve our understanding on the sources and formation mechanisms of coarse PM-bound organic species, coarse particles were collected once a week from April 2008 to March 2009 at 10 sampling sites in the Los Angeles Basin. Samples were composited into two seasons: summer (June 2008 to September 2008) and winter (November 2008 to February 2009), and were analyzed for the levels of individual organic constituents using gas chromatography-mass spectrometry. Our results reveal that the predominant organic constituents in the coarse size fraction, namely n-alkanoic acids and medium molecular weight (MW) n-alkanes (C25 to C35), were well correlated with crustal materials. Polycyclic aromatic hydrocarbons (PAHs) and hopanes (both in low concentrations), and high MW n-alkanes (C37 and C38), were associated with traffic-related emissions. In summertime, when onshore winds were strong, the downwind/rural sites had higher levels of PAHs, n-alkanes and n-alkanoic acids. At the urban sites, an opposite trend was observed - the levels of PAHs, n-alkanes and n-alkanoic acids were higher in winter, when the low wind speed limited long range transport of particles. The mass fraction of organic compounds to coarse PM was higher in winter, due to the lower concentrations of other coarse PM components (such as sea salt, secondary ions) and/or the increasing source strengths of organic compounds, the latter of which is supported by traffic-induced re-suspension of mineral and road dust in cooler months, when both wind speed and atmospheric dilution were low. Overall, our results suggest that soil and the associated biota represent the major source of organic constituents in coarse particles, with a more pronounced influence in the downwind semi-rural/rural areas in summer.

2UA.6

Size-segregated Composition of Particulate Matter (PM) in Major Roadways and Surface Streets. WINNIE KAM, James Liacos, James Schauer, Ralph Delfino, Constantinos Sioutas, *University of Southern California*

A sampling campaign was conducted to assess on-road particulate matter (PM) composition for three size fractions ($PM_{10-2.5}$,$PM_{2.5-0.25}$, and $PM_{0.25}$) on three representative roadways in Los Angeles: 1) the I-110, a high-traffic freeway composed mostly of light-duty vehicles (LDVs), 2) the I-710, a major freeway for heavy-duty vehicles (HDVs) travelling to and from the Ports of Los Angeles and Long Beach, and 3) Wilshire/Sunset Boulevards, two major surface streets. Concurrent sampling was conducted at the University of Southern California (USC), which was used as an urban background site. Two sets of PM samples were collected for each roadway, and were analyzed for inorganic ions, elemental carbon (EC), organic carbon (OC), water-soluble OC (WSOC), and trace elements and metals. Results showed that the $PM_{0.25}$ fraction is heavily influenced by on-road vehicular emissions, as indicated by average roadway PM concentrations that were 48.0±9.4% higher than those observed at USC ($p<0.05$), while the $PM_{10-2.5}$ fraction is mostly influenced by resuspension of road dust and the $PM_{2.5-0.25}$ fraction is mainly composed of secondary species. Overall, the composition of inorganic ions (%) was relatively consistent across the three roadway environments. With very low EC levels in $PM_{10-2.5}$, the most notable difference among the three roadway environments was the $PM_{2.5}$ EC levels observed on the I-710, which are 2.0±0.2 micro-gram/m^3 and 4.1 times greater than USC, while levels on the I-110 and Wilshire/Sunset were 1.0±0.2 micro-gram/m^3 and 0.6±0.01 micro-gram/m^3 and 2.1 and 1.2 times greater, respectively. Results from this study have major public health implications for passengers who commute frequently on high-traffic roadways. Finally, a comparison of EC levels to previous studies conducted at fixed sites near the I-110 and I-710 showed substantial decreases in EC concentrations over the past years, which may be a result of the recent Port of Los Angeles Clean Truck Program.

2UA.7

Process Analysis and Sensitivity of Air Quality to Emissions in Pearl River Delta of China using CMAQ Model. QI FAN, Wei Yu, Shaojia Fan, Jing Lan, YeRong Feng, *Sun yat-sen University*

In this study, a modeling system consisting of Mesoscale Model (MM5), Sparse Matrix Operator Kernel Emissions (SMOKE) and Community Multiscale Air Quality (CMAQ) model has been applied to an aerosol episode in Pearl River Delta, China. Sulfur dioxide (SO2), nitrogen dioxide (NO2), ozone (O3) and particulate matter (PM2.5) concentrations modeled with the finest horizontal grid resolutions (4km) were evaluated against available ground-level observations from PRIDE-PRD2004 campaigns for the period of 09-12 Oct 2004. Both MM5 and CMAQ show reasonable performance for major meteorological variables (i.e., temperature, relative humidity, wind direction, planetary boundary layer height) with normalized mean biases (NMBs) of 4.5–38.8%. The temporal variations of surface concentrations SO2, NO2, O3 and PM2.5 were captured well by CMAQ model. Relatively poor performance was found in the simulated maximum concentrations of all pollutants, the CMAQ systematically underpredicted the mass concentrations. The process analysis (PA) results showed that emissions, horizontal and vertical transport were the most important processes for PM2.5 and its secondary components. The contributions of horizontal and vertical transport processes were different during the period, but in all, these two processes contributed to the removal of air pollutants. Besides, the contributions of the same physical process were different for various pollutants, the dry deposition was vital to the removal of PM10. NOx was affected by the transport process obviously. Guided with PA results, sensitivity experiment excluding the emissions in Guangzhou city was conducted to identify the contributions to PM2.5 from local and non-local emissions.

2UA.8

Development and Evaluation of Air Pollution Model into a Horizontal Wind Flow in Kosovo.

AFRIM SYLA, Fatbardh Syla, Erik Solbu, *University of Prishtina, Kosovo*

Kosova is a mountainous farm region which at past was in the process of industrialization because of its reach coal and mineral resources. The problem of air pollution in the surroundings of Power Plants appeared as early as 1954 when Thermal Power Plant of Kosova has started work in Obiliq.

The city of Obiliq, approximately 5 km north of Prishtina-capital of Kosova, is the site of one the largest air pollution. Coal - related industries have been a major element of the economy of Kosova, but created extensive health risk due to environmental pollution with PM and a variety of other substances. A field study was conducted at the Kosovo Central Power and North part of Kosovo, from 15 February 2011 to 15 March 2012.

The downwash algorithms in the Industrial Source Complex (ISC3) model, currently recommended for regulatory application, were largely developed with data that represented neutral stability, moderate to high wind speeds, winds perpendicular to the building face, and non-buoyant or low buoyancy plumes. Some of the limitations of the ISC3 downwash algorithms are (1) the location of the stack is not considered (if the stack is determined to be within the general region of influence of the building, the stack is always treated as though it were at the center of the lee wall of the building), (2)streamline deflection is not considered (ascent of the mean streamlines upwind of and over the building and descent in the lee of buildings), (3) there are no effects on plume rise due to the velocity deficit in the wake or vertical wind speed shear, (4) there is no linkage between plume material captured by the near wake and far wake concentrations, (5) there are discontinuities at the interface between the two downwash algorithms, (6) there are no wind direction effects for squat buildings, and (7) large concentrations predicted during light wind speed, stable conditions that are not supported by observations.The PRIME model includes several advances in modeling building downwash effects including enhanced dispersion in the wake, reduced plume rise due to streamline deflection and increased turbulence, and a continuous treatment of the near and far wakes. All of these effects consider the location of the plume within the wake. Comparisons of the model with wind-tunnel and field data have shown improved performance over the current ISC3 model. The model is implemented within the ISC3 model code, but can be implemented in other refined or screening air quality models.

2UA.9

Quantification of Ultrafine Particles with Electric Charges in On- and Near-freeway Environments.

EON LEE, Bin Xu, Yifang Zhu, *University of California, Los Angeles*

Previous studies have reported the presence of ions and charged particles in motor vehicle exhaust. However studies characterizing electric charges on particles on and near traffic emissions are limited. This study presents the fraction of charged particles measured on and near two major freeways in Los Angeles. A tandem Differential Mobility Analyzer (DMA) system was used to evaluate the fraction of ultrafine particles (UFPs) carrying different number of charges across a broad range of electrical mobility diameters (30, 50, 80, and 100 nm). We first attempted to characterize the fraction of charged particles on two distinctively different freeways: a gasoline-vehicle dominated freeway (I-405) and a diesel traffic dominated freeway (I-710 i.e., up to 20 % diesel traffic). We found that the fraction of charged particles was higher on I-710 than on I-405, and the fractions on both freeways were significantly higher than the background. We also found that the background UFPs carried only up to two charges but traffic-induced particles could carry up to three charges across the tested electrical mobility diameters. Downwind from the I-405, we found the decay rates of charged particles were generally slower than that of total cluster ions but faster than that of particle number concentration. Particles with higher charges had the faster decay; that is, the fastest decay for triply charged particles and the slowest decay for singly charged particles. Further investigation on bipolar charged particle distributions showed strong net positive charges on nucleation mode particles. In comparison with Boltzmann steady-state charge equilibrium theory, we found that charged particles (especially, those in nucleation mode) might not necessarily reach the charge equilibrium distributions in the near-freeway environments.

2UA.10

Measurement of Aerosol Number Concentrations in Houston, TX. YU JUN LEONG, Longwen Gong, Robert Griffin, Barry Lefer,*Rice University*

The adverse health effects of exposure to high mass concentrations of particulate matter smaller than 2.5 micron (PM2.5) have led to the establishment of the National Ambient Air Quality Standard for PM2.5 by the United States Environmental Protection Agency. Recent work has shown that ultrafine particles also have a significant impact on public health due to their ability to penetrate tissues and enter the blood stream. These tiny particles contribute very little to the overall mass concentration but may account for a large fraction of total aerosol number concentration. The aim of this project is to collect a one-year, continuous, high time-resolution data set of ambient aerosol number concentration in the Houston urban area. The measurements are being conducted atop the North Moody Tower on the University of Houston main campus because the location is influenced by various pollutant sources including power plants, motor vehicles, and the industrial facilities of the Houston Ship Channel. Since February 2012, a condensation particle counter (CPC) has been deployed at Moody Tower for continuous measurement of particle number concentrations. An array of complementary data is also available at this location (meteorology, gas-phase pollutants, etc.). The continuous data set measured by the CPC will be used with these complementary data to identify factors (secondary formation, direct emission from a variety of sources) that influence aerosol number concentrations in this large urban setting.

2UA.11

Non-Refractory Submicron Aerosol and Black Carbon Measurements in Background, Industrial and Traffic Sites in Santiago, Chile. FELIPE REYES, Paula Reyes, Marcela Castillo, María A. Rubio, Ernesto Gramsch, Pedro Oyola, *Universidad de Santiago de Chile*

Santiago, Chile’s capital is one of most polluted megacity (5.5 million of people) of the world. Currently, PM2.5 annual concentration is over 2.2 times the Chilean standard.

In order to characterize the contribution from mobile and industrial emission sources in Santiago Metropolitan Region, a winter campaign will be implemented during 2012.

Continuous measurements of non-refractory (sulphate, nitrate, ammonium and organics aerosol) components and black carbon will be obtained using an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.) and Absorption Coefficient Monitor System (SIMCA, Santiago University), respectively. In addition, PM2.5 measurements will be carried out with a Dust-track (TSI). Meteorological data will be obtained from the air quality network operated by the environmental authority.

The traffic site will be placed near at Santiago major avenue/Alameda, at street level. The industrial site will be located at Cerrillos, an area with chemical and metallurgical industries. A large residential area (72 000 inhabitants) is located close to this industrial region. Urban background measurements will be implemented at the Santiago University Campus (USACH), 25 m over the ground level.

Measurements will get to the Chilean environmental authorities the possibilities to implement a decontamination plan to reduce the concentration of PM2.5.

2UA.12

Characteristics of Carbonaceous Compounds for PM2.5 Aerosols in the Gyeongsan Area, Korea. INJO HWANG, Yeong-Jin Jeong, Min-Jae Jeong, *Daegu University*

Carbonaceous compounds such as elemental carbon (EC), organic carbon (OC), and a small quantity of carbonate carbon (CC) constitute a significant portion (10 ~ 70 % of the mass) of the atmospheric aerosol mass in the various areas. Carbonaceous compounds play a major role in serious atmospheric pollution such as visibility degradation and climate chance, and these compounds has adverse human health effects. Elemental carbon originates from incomplete combustion processes of fossil fuel. On the other hand, organic carbon directly emitted in particulate matter (primary OC) or formed in the atmosphere from products of gas phase photochemical reactions (secondary OC). The objective of this study was to estimate the trend and characteristics for carbonaceous compounds concentration of PM2.5 in the sampling area during the sampling period. In this study, PM2.5 samples were collected by PM2.5 sampler from September 2010 to December 2011 at the Daegu University, Gyeongsan-si, Korea. The PM2.5 samples were collected on Teflon, nylon, and quartz filters every 3 days. The quartz filters were used for analysis of OC/EC by TOR method. TOR method following the IMPROVE protocol using the DRI analyzer (DRI Model 2001 Thermal/Optical carbon analysis). Detailed estimation of characteristics of carbonaceous compounds for PM2.5 will be presented.

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2UA.13

Chemical Characteristics of Submicrometer Aerosols at Urban Gwangju in Korea Measured with Aerosol Mass Spectrometer. Kihong Park, Jiyeon Park, Seungyong Lee, HEE-JOO CHO, Minsoo Kang, *Gwangju Institute of Science and Technology*

Size-resolved chemical composition of submicrometer non-refractory particles was measured with quadruple aerosol mass spectrometer (QAMS) at urban Gwangju in Korea in fall (8/30/2011-9/19/2011) and winter (12/19/2011-12/30/2011) with varying air masses. It was found that organics was dominant chemical species (~50%) of submicrometer non-refractory aerosol mass. Average mass concentrations of organics were 4.7±1.8 μg/m³ and 6.3±1.8 μg/m³ in fall and winter, respectively. The ratio of m/z 44 to organics and sulfate increased significantly in the afternoon, suggesting that intense photochemical activity led to produce oxidized organics and sulfate in the afternoon. The average sulfate concentration was 1.8 μg/m³, which was the lowest among sites in other East Asia countries due to few SO_2 emission sources around the sampling site. The nitrate concentration in winter was ~4 times higher than those in fall (2.45 versus 0.62 μg/m³). The low temperature and strong temperature inversion might lead to the significant increase of nitrate concentration in winter. It was observed that sulfate, nitrate, and chloride were fully neutralized by the ammonium in winter, while these anions were not fully neutralized by ammonium in fall. Size distribution data showed that sulfate had only one peak at Dva of 500-600 nm, regardless of season, while organics had one peak (500-600 nm) in fall and bimodal distribution (100-200 nm and 500-600 nm) in winter. The absence of the first mode (i.e., Dva<200 nm) in organics in fall suggests that oxidized organic species would be more dominant than hydrocarbon-like organics, which is consistent with the higher ratios of m/z 44 to organics in fall (0.10±0.02) than winter (0.07±0.01). Air-mass dependent concentrations of species showed that northwest air mass (i.e., long-range transported from industrial areas in China) and southeast air mass (i.e., transported from industrial area in Korea) were mainly responsible for high loadings of organics and sulfate.

2UA.14

Diurnal Variation of On-road Black Carbon Pollution on the Motor Express Ways in Seoul. SEUNG-BOK LEE, Bo-Eun Park, Dong-Hun Lee, Seung-Jae Lee, Dae-Kwang Woo, Hyoun-Cher Jin, Gwi Nam Bae, *Korea Institute of Science and Technology*

Air pollution phenomena caused by vehicle exhaust are known as hot spot pollution because of frequent high concentration peaks of traffic-related air pollutants. On-road measurement is needed to examine the source emission intensity of vehicles and to understand the exposure level of hazardous pollutants to drivers nearby busy roads. Traffic-related air pollutants have been monitored regularly on the Motor Express Ways such as Naebu and Gangbyeon in Seoul in the morning and afternoon since 2009 to monitor the on-road air pollution level that is expected to be reduced by continuous effort of traffic-related environmental policies. In this study, the on-road black carbon concentration on the Motor Express Way was intensively measured with an aethalometer at daybreak and in the morning rush hour, afternoon, evening rush hour, and late evening using a mobile laboratory for four days in March, 2011. The total length of the driving route was about 40 km and average vehicle speed was in the range of 35-65 km per hour. The average black carbon concentration of each driving ranged from 4 to 22 microgram per cubic meter. The diurnal variation of the on-road black carbon concentration is analyzed together with other pollutant concentration, traffic volume and meteorological conditions.

2UA.16

Characterization of Rural and Urban PM2.5 and PM10-2.5 Mass Concentrations in Colorado from 3 Years of Continuous Monitoring. NICHOLAS CLEMENTS, Jana Milford, Shelly Miller, Jennifer Peel, Michael Hannigan, *University of Colorado at Boulder*

The Colorado Coarse Rural-Urban Sources and Health (CCRUSH) study is investigating the health impacts of $PM_{10-2.5}$ in arid rural and urban environments. $PM_{10-2.5}$ was measured continuously from 2009 to 2012 at six monitoring sites, 4 urban (Denver, CO) and 2 rural (Greeley, CO). Four of these sites used TEOM 1405-DF continuous dichotomous monitors. Two urban sites, operated by the Colorado Department of Public Health and Environment, provided collocated PM_{10} and $PM_{2.5}$ TEOM data, measuring $PM_{10-2.5}$ through subtraction. Temporal and spatial trends of total mass concentrations and concentrations of semi-volatile loss are characterized for $PM_{2.5}$ and $PM_{10-2.5}$. Nonparametric smoothing kernels reveal general spatial trends associated with the influence of wind direction on particulate concentrations, as well as any nearby point sources. This method is also used to compare relationships between mass concentrations and other meteorological factors such as wind speed and humidity. These regressions can reveal characteristics of particle sources, such as the resuspension of deposited particles and geogenic dust. Due to instrument problems, large gaps in the time series exist, so a spatially predictive statistical model is developed to fill in these gaps.

2UA.17

Characterization of Metal and Ion Concentrations in Rural and Urban PM2.5 and PM10-2.5 in Colorado. Nicholas Clements, JENNY EAV, Allison Moore, Kelly Albano, Jana Milford, Shelly Miller, Michael Hannigan, *University of Colorado at Boulder*

The Colorado Coarse Rural-Urban Sources and Health (CCRUSH) study is investigating the health impacts of $PM_{10-2.5}$ in arid rural and urban environments. To compliment the health study, one year of sixth-day 24-hour samples were collected with a dichotomous medium-flow filter sampler at four locations in Colorado. Two sites are located in urban Denver, CO and are characterized as industrial-residential and urban-residential. One site, Alsup Elementary, is near the intersection of 4 major roadways and adjacent to a gravel pit operations. The other two sites are located 50 km northeast of Denver in Greeley, CO, a rural city near major agricultural operations, including multiple animal feeding operations. These sites are classified as rural-residential. Monthly composite groups of $PM_{2.5}$ and $PM_{10-2.5}$ samples collected on Teflon filters were analyzed by ICP-MS for metals, water-soluble metals, and ions. Species concentrations are analyzed spatially for correlations and heterogeneity. Crustal enrichment factors are calculated to assess influence of anthropogenic emissions on the crustal signature of the air. PCA is also used as a tool to identify particulate sources.

2UA.18

Spatially Resolved Elemental Air Pollution Concentrations in Southern California. SCOTT FRUIN, Fred Lurmann, Ed Avol,*University of Southern California*

As part of the Southern California Children's Health Study, a longitudinal study of children's respiratory health, we conducted an ambitious particulate sampling campaign to investigate the near-source, within-community spatial variation in particulate air pollution due to traffic sources. 30 sites per community (24 residences, 5 schools, and an existing central site monitor) were selected to capture high and low predicted traffic emissions impacts from arterial roads and freeways, respectively, using the CALINE line source dispersion model. We used four cascade impactors at each site to collect three PM sizes, <0.2, 0.2 to 2.5, and 2.5 to 10 um, along with NO2 and NOx via passive monitors. Samples were collected during two consecutive 2-week sampling periods, in each of two seasons. Elemental analyses included elemental and organic carbon (EC/OC), total and water soluble elements, water soluble organics (WSOC), ions, and nitrate. Primary pollutants such as NO, EC0.2, EC2.5 and copper (form brake wear) showed the largest differences by predicted traffic impact while PM2.5 or WSOC, pollutants with significant contributions from photochemistry, showed little or no traffic impact pattern. Traffic impacts were also more distinct in the cool season (Oct 1 through Mar 31). Principal components analysis (PCA) of the elemental concentrations showed correlated clusters of elements indicative of brake wear (Cu, Ba, Sb) and catalytic converters (Pt, Rh) in the fine and coarse size fractions PCA also showed clusters indicative of regional scale ship emissions (S, V, Ni) and sea salt (Na).

2UA.19

Quantifying the Uncertainty of Particulate Matter in Regional Air Quality Models in the Presence of Uncertain Emission Inventories. WENXIAN ZHANG, Marcus Trail, Alexandra Tsimpidi, Yongtao Hu, Athanasios Nenes, Armistead Russell, *Georgia Institute of Technology*

Particulate matter (PM) is regulated as one of the criteria pollutants in NAAQS due to its adverse effects on human health and public welfare. As part of the air quality management process, regional air quality models are widely used to evaluate control strategy effectiveness. As such, the accuracy of the model simulations is of concern since a number of factors may introduce uncertainties in the simulation, such as uncertain emissions, chemical reaction rates, meteorological inputs, and initial/boundary conditions. This study focuses on quantifying how uncertain emission rates impact simulated PM concentrations in the Community Multi-scale Air Quality (CMAQ) model, and the assessment of pollutant responses to emission controls. The uncertainty is computed using a reduced-form model with Monte Carlo simulation. The reduced-form model is constructed using first- and second-order sensitivity coefficients obtained from a single CMAQ-HDDM/3D simulation. It represents the pollutant-precursor response and requires much less computational effort than applying the original model for uncertainty propagation. A case study has been conducted for an episode in Houston region. The uncertainties of NOX, SO2, NH3, and primary PM emissions, domain-wide and from specific sectors (e.g., point, area, on-road and non-road mobile), are considered. The uncertainties of simulated particulate matter species are quantified. The variation of the uncertainty due to different emission control strategies is also analyzed.

2UA.20

Variations in Aerosol Size and Number During DISCOVER-AQ. EDWARD WINSTEAD, Lee Thornhill, Andreas Beyersdorf, Charles Hudgins, Luke Ziemba, Bruce Anderson, *NASA Langley Research Center*

The Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) mission is a multi-year campaign designed to improve the use of satellites to monitor surface-level air quality. DISCOVER-AQ is addressing its goals by conducting a series of coordinated ground-based and flight experiments over urban areas with well-established air quality issues to obtain vertically resolved measurements of trace gas and aerosol components. The first flight mission consisted of 14 science flights over the Washington D.C. - Baltimore metropolitan area during July, 2011. A large suite of aerosol instruments were flown onboard a NASA P-3B aircraft to measure the microphysical, optical and chemical properties of aerosols during spirals over the ground sites and during low level flights over Interstates 95 and 695 connecting Washington and Baltimore. This presentation examines the variability of aerosol size and number in both time and space over the Baltimore metropolitan region.

Within the atmospheric boundary layer between 0.3 and 1 km, particle number densities and size distributions varied considerable over short time periods and across horizontal distances as short as 1 km. High CN values typically occurred at times when aerosol scattering and hence surface area was relatively low. Values also tended to increase during the day as gas phase precursors were photochemically oxidized to form less volatile species, which in turn condensed to form new particles. Accumulation mode number concentrations often increased during the day, as the nucleation mode particles coagulated and aerosol surface increased to the point where deposition of low volatility precursors on existing particles was favored over new particle formation. Particle number concentrations and size also varied considerably from site to site across the 100-by 30-mile study area. This presentation examines the causes of the variability in more detail.

2UA.21

Overview of ClearfLo Detling Site: Study of Aerosol Sources and Processing at a Rural Site Southeast of London. LEAH WILLIAMS, Scott Herndon, John Jayne, Andrew Freedman, William Brooks, Jonathan Franklin, Paola Massoli, Edward Fortner, Puneet Chhabra, Mark Zahniser, Harald Stark, Timothy Onasch, Douglas Worsnop, Felipe Lopez-Hilfiker, Claudia Mohr, Joel A. Thornton, Nga Lee Ng, Lu Xu, Matthew Kollman, Berk Knighton, Mavendra Dubey, Allison Aiken, Kyle Gorkowski, Timothy Martin, Richard Coulter, *Aerodyne Research, Inc.*

Clean Air for London (ClearfLo) is a large, multidisciplinary study of the London urban atmosphere aimed at understanding the relationships between surface meteorology, gas-phase composition and particulate matter at a city street site, a city background site (away from local traffic sources) and at a rural location that samples the outflow from the London urban area. We deployed a suite of instruments at a rural site approximately 50 km southeast of London in Detling, UK during January-February, 2012. Measurements included aerosol chemistry and microphysics, gas-phase tracers, secondary organic aerosol (SOA) precursors, and radiative and meteorological conditions. During the six week campaign, we sampled air masses from several distinct sources. Winds from the southwest passed over a large road 200 m from the site and brought air masses characterized by highly variable CO, indicating local sources, high black carbon, and hydrocarbon-like aerosol chemical composition. When the wind was from the east and northeast, we sampled outflow from the European continent. The gas-phase composition indicated an aged air mass, and particle composition was predominately oxygenated organics, nitrate and sulfate. Although the goal of the site was to sample outflow from London, we sampled air masses from the northwest on only a few occasions. In addition to regional air quality, the winter time studies provided information on gas and particle emissions from home heating solid fuels. Here we present a summary of the different sources observed at Detling.

Funding was provided by the US Department of Energy Atmospheric System Research Program and the UK National Centre for Atmospheric Science.

2UA.22

Numerical Study of Dust Deposition and Accumulation at the Entrance of Electrostatic Precipitators with a Bend. Sadegh Naderinejad, Mazyar Salmanzadeh, GOODARZ AHMADI, Mohammad Yavarzadeh, *Shahid Bahonar University of Kerman*

Dust deposition at the entrance of electrostatic precipitators (ESP) with a bend at its entrance is studied. Some industrial electrostatic precipitators have a bend in their inlet that could cause accumulation of particles in the wake region after the bend before entering the ESP. On occasions, the amount of deposition could be to the extent that reduces the bend outlet cross section. In this study, dust movement and deposition in duct bends was studied using a computational modeling approach. The airflow was simulated using the k-e turbulence model. The particle trajectories were analyzed using the Lagrangian particle tracking method. The effects of bend curvature and airflow velocity on the deposition in the bend were studied. It was shown that particle deposition could occur in some unexpected regions.

2UA.23

European Air Pollution Hot Spot in Winter 2012: Middle Scale PM2.5 Variability. JAN HOVORKA, Michal Grégr, Martin Braniš, Petra Pokorná, Alexandra Baranová, *Charles University in Prague*

During monthly campaign (25 Jan.-21 Feb. 2012), aimed to characterize comprehensively atmospheric aerosol in city of Ostrava, Northern Silesia, the Czech Republic, highly-time resolved PM2.5 were determined by a set of laser nephelometers – DustTraks (DT). Five minute integrates of PM2.5 were recorded by seven DTs in a line arrangement. Inter-DT distances ranged from 260 to 2300 meters. Multiple-site PM2.5 measurement helped to evaluate position of the monitoring station for representative air quality measurement and influence of sparsely distributed local-heating sources.

There were not significant (alpha=0.05) differences for PM2.5 among the DTs according to Wilcoxon signed-ranks test for 2 dependent samples even though two distinct periods were distinguished during the campaign. The first period, smog spanning for 20 days, characterized low average temperature (-15 ^{0}C), and high PM2.5 median and maximum (140 and 310 micrograms per m^3 respectively). In the second period average air temperature raised near to zero, two snow storms were occurred and as result, PM2.5 median and maximum were much lower (35 and 100 micrograms per m^3 respectively). Based on results of this multiple-site measurement, we may conclude that placement of the monitoring station is representative for this urban area and local-heating sources, contrary to expectations, do not contribute significantly to the air pollution at the locality.

2UA.24

European Air Pollution Hot Spot in Winter 2012: Distribution of PAH with Aerosol Particle Size. JAN HOVORKA, Jan Topinka, Jan Bendl, Alexandra Baranová, Petra Pokorná, Martin Braniš, *Charles University in Prague*

During monthly campaign (25 Jan.-21 Feb. 2012), aimed to characterize comprehensively atmospheric aerosol in city of Ostrava, Northern Silesia, the Czech Republic, size segregated aerosol samples were analyzed for 13 types of Polycyclic Aromatic Hydrocarbons – PAH. Daily samples were collected by a high-volume cascade impactor (BGI 900), which classifies the particles into coarse (1-10 dae), upper (0.5-1 dae), and lower (0.17-0.5 dae) accumulation, and ultrafine (smaller 0.17 dae) size fractions of aerodynamic diameter dae (in micrometer). The coarse and accumulation fractions were collected on polyurethane foam (PUF) while the ultrafines on Teflon-coated ultrafilters. Also additional PUF were placed below back-up ultrafilter to evaluate sampling artifact. Positive sampling artifacts were in the ranges of 6-30% for Phenanthrene, 7-37% for Anthracene, 1-6% for Fluoranthene, 0.5-2.8% for Pyrene and 2-8% for Benz(a)anthracene while for other low-vapour PAHs, carcinogenic PAH (c-PAH) was negligible. Total c-PAH concentrations went over 100 nanograms per m^3 during the smog episode. c-PAHs were predominantly bond to upper accumulation size fraction. At the peak days of the smog c-PAH were also enriched in coarse size fraction. Proportionality of different PAH did not vary significantly among size fractions but concentrations of higher-vapor PAHs tend to follow modality of particulate surface size distribution. Alarmingly high concentrations and enrichment in fine aerosol of PAH or c-PAH represent a serious health threat to residents of the city of Ostrava.

2UA.25

Spatial Distribution of Black Carbon, Polycyclic Aromatic Hydrocarbons and Volatile Organic Compounds During the Wintertime in Greater Pittsburgh Area.

YI TAN, Rawad Saleh, Eric Lipsky, Albert A. Presto, Neil Donahue, Allen Robinson,*Carnegie Mellon University*

Pittsburgh's air quality is affected by a complex combination of local industrial and commercial sources, motor vehicles, topography (e.g. river valleys) and regional transport. To better understand the temporal-spatial distribution of air pollution in Pittsburgh, we developed a mobile measurement platform to characterize a suite of air pollutants (black carbon, particle-bound polycyclic aromatic hydrocarbons, benzene, and toluene). During the 2011/2012 winter, 42 mobile sites were sampled in three different sessions (afternoons/evenings, mornings, and midnights): 38 sites were randomly sampled for one hour in each session and 4 sites were sampled multiple times only in the mornings. One fixed site was continuously monitored for 5 days. CMU campus was monitored for the rest of the time. Pollutant concentrations were influenced by the combination of meteorology, terrain (e.g. valleys), traffic (e.g. buses) and industrial sources. Meteorology conditions and point sources controlled background concentrations at sampling sites, while local traffic caused strong spikes. Highest concentrations were observed in the mornings due to the combination of meteorology and traffic. Measurements were compared with 2005 NATA predictions. Predicted concentrations were generally within a factor of 2 of measured values except for PAH. PAH concentrations near industrial facilities were significantly over-predicted by NATA, possibly caused by large changes in emissions. However, predictions (census tract level) did not capture the measured spatial variation of pollutants. Large spatial variations within census tracts potentially contributed to this discrepancy.

2UA.26

Characterization of Carbonaceous Particle Emissions by Mobile Sources in Sao Paulo (Brazil).

Maria de Fatima Andrade, Adalgiza Fornaro, Beatriz Oyama, Rita Ynoue, PIERRE HERCKES, *Arizona State University*

Emissions from mobile sources (cars, trucks) account for a substantial fraction of ambient particulate matter and are of interest from an air quality and climate perspective. Emissions within megacities might have substantial impacts beyond the city, on a regional scale. While many studies addressed particulate matter emissions from vehicles in the northern hemisphere, less is known in the southern hemisphere.

In this work, size resolved particulate matter samples were collected during two tunnel studies in the City of Sao Paulo (Brazil) to investigate the emission of carbonaceous aerosol by mobile sources. A first tunnel, within the center of the city was characterized by mainly light-duty vehicle traffic, some of which used alcohol as fuel. In this tunnel organic carbon accounted for the largest fraction of particulate mass, while elemental carbon (soot), was substantial but not a dominant fraction of the particulate matter and hence the emissions. A second tunnel, strongly impacted by heavy duty trucks, showed substantial concentrations of particulate matter with a dominant fraction being elemental carbon. The results of the tunnel studies will be discussed in terms of variability by vehicle types, particulate matter size and in terms of analytical measurements to assess soot (Elemental carbon vs black carbon).

2UA.27

Seasonal Variation of Organic Aerosols at Urban Gwangju, Korea Measured With Aerosol Mass Spectrometer.SEUNGYONG LEE, Jiyeon Park, Kihong Park, *Aerosol Technology and Monitoring Lab., GIST*

Atmospheric aerosols are strongly associated with earth’s radiation budget, cloud formation, human health, and visibility impairment. Organic aerosols constitute a significant mass fraction of the submicron aerosols, and understanding of organic aerosols is necessary to reduce the largest uncertainties in aerosol effects on radiative forcing and cloud formation and to better control the air quality. In this study, seasonal and diurnal variations of organics in the submicron particles was determined by using an Aerosol Mass Spectrometer (Aerodyne Inc, USA) in fall (8/30/2011-9/19/2011), winter (12/19/2011-12/30/2011), spring (5/16/2012-5/24/2012), and summer (7/23/2012-8/6/2012) at urban Gwangju, Korea. Furthermore, the organic aerosols were further classified into hydrocarbon-like organic aerosol (HOA), less-volatile oxygenated organic aerosol (LV-OOA), and semi-volatile oxygenated organic aerosol (SV-OOA) components by using a Positive Matrix Factorization (PMF) method (PMF2 software) (Paatero, 2004a; Paatero 2004b). It was found that organics were the most dominant chemical species in the total aerosol mass loadings at the urban Gwangju, and the average mass concentrations of organics were 4.7 +- 1.8 µg/m3, 6.3 +- 1.8 µg/m3, 4.0 +- 1.8 µg/m3, 4.9 +- 1.8 µg/m3 in the fall, winter, spring, and summer, respectively. The HOA was the most dominant in the organic aerosols in winter, while the OOA was the highest in summer. The LV-OOA was somewhat higher than SV-OOA in summer. Diurnal variation showed that the HOA had a pronounced diurnal pattern with increased concentration in the morning and evening times, while the OOA increased in the afternoon. More data analysis is in progress, which will be discussed in the presentation.

3AC.1

Comparison of Laboratory Generated Secondary Organic Aerosol from Oxidation of Biogenic Volatile Organic Compound Mixtures and Remote Ambient Samples Using High Resolution Mass Spectrometry. IVAN KOURTCHEV, Stephen Fuller, Juho Aalto, Robert Healy, Taina Ruuskanen, Willy Maenhaut, John Wenger, Markku Kulmala, Markus Kalberer, *University of Cambridge*

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric chemistry and give rise to secondary organic aerosols (SOA), which have effects on climate and human health. Laboratory chamber experiments have been performed during several decades in an attempt to mimic atmospheric SOA formation. However, it is still unclear how close the aerosol particles generated in laboratory experiments resemble atmospheric SOA with respect to their detailed chemical composition. To date, most laboratory experiments have been performed using a single organic precursor (e.g., alpha- or beta-pinene, isoprene) while in the atmosphere a wide range of precursors contribute to SOA, which results most likely in a more complex SOA composition compared to the one-precursor laboratory systems. The objective of this work is to compare laboratory generated SOA from oxidation of BVOC mixtures and remote ambient samples using ultrahigh-resolution mass spectrometry (UHR-MS) that allows detection of thousands of individual SOA constituents. We examined aerosol samples from a boreal forest site, Hyytiälä, Finland and determined that a dominant fraction of the detected compounds are reaction products of a multi-component mixture of BVOCs. In the subsequent smog chamber experiments, SOA was generated from the ozonolysis and OH initiated reactions with BVOC mixtures containing species (alpha- and beta-pinene, delta-3-carene, and isoprene) that are most abundant in Hyytiälä's environment. The laboratory experiments were performed at conditions (e.g., RH, aerosol seed, and VOC ratios) that would resemble those at the boreal sampling site during the summer period. The elemental composition of the complex mixtures from laboratory generated SOA samples were compared with field samples using statistical data analysis methods. The possible reaction mechanisms of the most abundant compounds identified in both type of samples are discussed.

3AC.2

Modeling Nanoparticle Growth in Biogenic VOC+Nitrate Radical Chamber Studies. KELLEY C. BARSANTI, Juliane L. Fry, Danielle C Draper, John Ortega, Steven Brown, Peter Edwards, Michael J. Lawler, Paul M Winkler, Peter McMurry, James N. Smith, *Portland State University*

New particle formation (NPF) in the atmosphere may contribute to the formation of cloud condensation nuclei if the newly formed particles grow faster than they are scavenged. Research over the last twenty years has shown that relatively rapid growth of nanometer-sized particles (> 2-3 nm) cannot be explained by condensation of sulfuric acid alone and that organic compounds clearly play a role. It has been suggested that relatively volatile/low molecular weight compounds may contribute to NPF via organic salt and/or accretion product formation; relatively non-volatile/high molecular weight compounds may condense directly to contribute to NPF. Much work is currently being done to elucidate the key mechanisms by which organic compounds contribute to NPF, and to identify the critical species involved. Parallel efforts are underway to represent such processes in models capable of predicting NPF in laboratory studies as well as in the atmosphere. In this work, process-level modeling was used to evaluate particle growth in chamber experiments of individual monoterpenes with nitrate radical. Comparisons of measured and modeled growth rates and secondary organic aerosol yields were used to describe the limitations in available biogenic volatile organic compound (VOC)+nitrate radical parameterizations and to explore the potential species, including organonitrates, contributing to NPF in these chamber experiments.

3AC.3

An Evaluation of the Mixing and Evaporation of Organic Aerosol Components. CHRISTINE LOZA, Matthew Coggon, Jill Craven, Wilton Mui, Katherine Schilling, Rebecca Schwantes, Lindsay Yee, Xuan Zhang, Richard Flagan, John Seinfeld, *Caltech*

Ambient secondary organic aerosol (SOA) is a mixture of oxidation products of various anthropogenic and biogenic precursors. The nature of these mixtures and their phase behavior has been modeled theoretically using assumptions about gas-particle partitioning equilibrium and mixing ideality, but the some of these assumptions remain to be validated experimentally. We present results of experiments performed in the new Caltech dual 17-m^3 chambers designed to probe the evaporation behavior of aerosol mixtures. SOA mixtures were formed from low-NO_x oxidation of unlabeled alpha-pinene and labeled toluene under dry and humid conditions and were subjected to dilution and heating. A high-resolution time-of-flight aerosol mass spectrometer was used to separate the different aerosol types. A comparison of SOA mixing under dry and humid conditions and SOA evaporation behavior will be presented.

3AC.4

Laboratory Measurements of Organic Aerosol Chemical Composition: Primary Emissions and Secondary Formation from Biomass Combustion. BRENT WILLIAMS, Raul Martinez, Peter Mellott, Dhruv Mitroo, Yaping Zhang, Pratim Biswas, Andrew Lambe, Kenneth Christian, William Brune, Thorsten Hohaus, Manjula Canagaratna, John Jayne, Douglas Worsnop, *Washington University in St. Louis*

Biomass combustion contributes substantially to the atmospheric loading of organic trace gases and particles. Organic gases undergo atmospheric photooxidation to produce secondary organic aerosol. Atmospheric primary and secondary organic aerosol causes source-specific impacts on climate and is detrimental to human health. Of the major contributing sources to atmospheric fine particle mass, the direct emissions and secondary aerosol formation potential of biomass burning remains one of the least understood. This is largely due to the complexity in combustion conditions and the wide variety of biomass fuel types.

We have begun an investigation, utilizing fully automated high time resolution instrumentation and novel laboratory methods, to characterize the chemistry and particulate burden of biomass burning emissions under variable combustion and photooxidation conditions and for various biomass fuel types. Instrumentation includes the thermal desorption aerosol gas chromatograph (TAG) for individual organic compound analysis combined with a high resolution time-of-flight aerosol mass spectrometer (AMS) for total organic, sulfate, nitrate, ammonium, and chloride mass concentrations as well as elemental ratios of O:C, H:C, N:C to determine oxidation state and nitrogen content. Laboratory setup includes both an emissions/combustion chamber and a drop tube furnace coupled to a potential aerosol mass (PAM) flow tube reactor to mimic atmospheric photochemical processing of gas-phase emissions and heterogeneous reactions on primary aerosol. Results from combustion of several plant species and plant fractions will be presented.

3AC.5

Effect of Temperature, Humidity, and Background Aerosol Concentrations on Organic Aerosol Emissions from Gasoline and Diesel Fueled Motor Vehicles. Toshihiro Kuwayama, Isabel Faria, Peter Green, MICHAEL KLEEMAN, *UC Davis*

Experiments were conducted using a dilution air sampler combined with a dynamometer system to explore the effects of temperature, humidity, and background aerosol concentrations on primary organic aerosol (POA) emissions from both gasoline and diesel fueled motor vehicles at realistic ambient concentrations. Successive tests were conducted on the same fleet of 6 on-road vehicles under different control conditions. Temperature was adjusted from ambient to 100 degrees Celsius, RH was adjusted between ambient to 85%, and background EC concentrations were adjusted between 0 to 20 micro gram per m^{-3} above ambient. All majority of tests diluted exhaust by a factor of ~100 with a residence time of ~60 sec while a subset of tests varied both dilution factor and residence time to determine the effect of these conditions on the evolution of POA.

Aerosol samples were collected with a denuder-filter-PUF sampling train designed to separately capture gaseous and particulate compounds. Primary PM samples were analyzed for elemental carbon (EC) and organic carbon (OC) to characterize the PM mass emissions. All samples were further analyzed for detailed molecular composition using derivatization by PFBHA followed by analysis using GC-MS.

Predictions from absorption and adsorption models for POA partitioning will be compared to measured partitioning results. The volatility of primary organic aerosol at atmospherically relevant concentrations will be evaluated. Previous observations of significant concentrations of small oxygenated compounds in the condensed phase will be analyzed in this context. Significant gaps in the ability of state-of-the-science models for partitioning of POA will be highlighted.

3AC.6

The Role of the Precursor's Volatility and Structure on Secondary Organic Aerosol Formation: From Experiments to Models. SHANTANU JATHAR, Marissa Miracolo, Daniel S. Tkacik, Peter Adams, Allen Robinson, *Carnegie Mellon University*

Photo-oxidation experiments were conducted using a smog chamber on unburned evaporated fuel to investigate the influence of the precursor's volatility and structure on secondary organic aerosol (SOA) formation. We perform experiments on gasoline, two Fischer-Tropschs (Sasol and Shell), two JP-8s and six diesels; they span a modest range of volatility and structure. We find that for a unit amount of fuel reacted, diesel forms the most SOA followed by JP-8, FT-Shell, gasoline and FT-Sasol. Both JP-8s exhibit the same SOA potential while all diesels exhibit very similar SOA potential. Chemically, the SOA from our experiments is lightly oxygenated (O:C~0.2-0.4) and looks similar to semi-volatile oxygenated organic aerosol (SV-OOA). A traditional SOA model (SAPRC07 lumping, Murphy and Pandis (2010) yields) results in a reasonable model-measurement comparison (fractional error = 76%, fractional bias = 26%) for the JP-8, FT-Shell and diesel experiments. The model over-predicts SOA in the FT-Sasol experiments because it is not configured to account for branched alkanes which have lower yields compared to straight/cyclic alkanes and which mostly constitute FT-Sasol (88%). The model over-predicts SOA in the gasoline experiments probably because the Murphy and Pandis (2010) yields for single-ring aromatics are biased too high. When we add a branched alkane and multi-ring aromatic model species to SAPRC07 and adjust yields for the traditional SOA model, we improve the model-measurement comparison significantly (fractional error = 54%, fractional bias=-2%). On using a volatility-based model that does not account for differences in the precursor's structure, we find that the model (when fit) is marginally better than the traditional SOA model (fractional error = 73%, fractional bias=13%). This implies that the SOA formation across these precursor fuels can reasonably be explained by differences in their volatility alone. Since the volatility-based model runs on only 4 parameters compared to SAPRC's 30 parameters, it would be much more efficient to use in computationally expensive chemical transport models.

3AE.1

Paper-Based Microfluidic Devices for Aerosol Exposure Assessment. David Cate, Josephine Cunningham, Mallory Mentele, Wijitar Dungchai, Yupaporn Sameenoi, Kirsten Koehler, Charles Henry, JOHN VOLCKENS, *Colorado State University*

Aerosols present health hazards in a variety of settings ranging from manufacturing to the production of food and energy. In U.S. occupational settings alone, an estimated 5 to 8 million air samples are collected annually to assess human exposure to aerosol hazards. However, our ability to associate aerosol exposure with occupational disease is hampered by limitations in existing sampling technology, especially with cost and timeliness. For example, particulate metals exposure assessment requires an 8-hour filter sample followed by analysis using inductively coupled plasma (ICP) at a cost of hundreds of dollars per sample. Furthermore, sample handling and processing times for such samples vary from days to weeks, reducing the efficiency of the risk communication process. Here, we address the need for improvements in the cost and timeliness of personal exposure assessment through the use of microfluidic paper-based analytical devices (mPAD for short). In mPADs, wax-based hydrophobic barriers are patterned onto hydrophilic filter paper to create channels for directed flow to be directed from a central sample reservoir to multiple unique detection zones. The resulting device use only small amounts (~10 microliters) of eluent, making measurement of low levels of many analytes reasonable. Finally, because the devices are made from filter paper, wax, and inexpensive chemical reagents, assay costs are less than a dollar per sample. Here we will present the development of mPADs for the analysis of aerosolized metals from welding fumes and aerosol oxidative load using filters obtained from personal exposure monitors. The mPADs we have developed allow for detection limits of 1 microgram of total mass for metals and 1 nmol of DTT consumption for oxidative activity. Furthermore, these devices are designed for sample collection and analysis in the field, providing immediate results for a given exposure assessment.

3AE.2

An Aerosol Sampler to Estimate Regional Deposition within the Human Respiratory Tract. KIRSTEN KOEHLER, John Volckens, *Colorado State University*

This work describes the development of an aerosol sampler to mimic regional particle deposition in the human respiratory tract. The motivation for this research is to improve our ability to estimate inhaled aerosol dose. Current methods for aerosol measurement and exposure/risk assessment are based on particle aspiration (i.e., inhalable PM) or on penetration to various regions of the respiratory system (i.e., PM10). However, a large proportion of inhaled aerosol is subsequently exhaled and does not contribute to the dose. Furthermore, regional deposition can also drive the incidence of certain health outcomes (e.g., sinusitis vs. bronchitis vs. pneumonia). Therefore, the goal of this work was to develop an aerosol sampler capable of estimating particle deposition to three regions of the human respiratory tract. The International Commission on Radiological Protection (ICRP) has developed a model that estimates particle deposition, as a function of particle aerodynamic diameter, to three main regions: head airways, tracheobroncial, and alveolar. We developed a semi-empirical model to design substrates capable matching the ICRP-defined deposition to these regions. These substrates, made from polyurethane foam and mesh screen, have specific dimensions (i.e., length, diameter, fiber size) and operating conditions (e.g., face velocity) necessary to reproduce the aerodynamics of aerosol deposition in the human respiratory tract. The substrates are placed in series within a sample holder that operates at 16.7 liters per minute of flow. Performance of the sampler was evaluated using test aerosols ranging in size from 0.01 to 10 microns. These results show good agreement with the ICRP convention for regional lung deposition. Comparing two direct-reading PM10 mass samplers, one with regional deposition sampler placed upstream and the other as total PM10 reference, we evaluated the overestimation of lung deposition as a function of time for ambient aerosols. Substantial differences between PM10 intake and deposition were observed.

3AE.3

Evaluation of Real-time Instruments Used to Monitor PM in a Green Building. ZUOCHENG WANG, Gediminas Mainelis, Leonardo Calderon, Clinton J. Andrews, Richard Wener, Jennifer Senick, MaryAnn Sorensen-Allacci, *Rutgers, The State University of New Jersey*

Studies show that exposure to elevated concentrations of airborne particulate matter (PM) poses a significant human health risk. Traditional exposure monitoring methods employing filter-based samplers are robust and can provide accurate results. However, continuous real-time PM monitors are advantageous due to their ability to provide time-resolved data. To be confident of the data provided by real-time PM monitors which use a variety of methods to measure PM concentration these instruments should be evaluated in a wide range of environments, including indoor environment.

In our ongoing study of indoor air quality (IAQ) in a green residential high rise building we measured various PM fractions by using a PMI2.5 impactor (PM2.5; SKC, Inc), a DRX monitor (PM2.5, PM4, PM10, total PM; TSI 8534), a pDR-1500 monitor (real time and gravimetric PM2.5; Thermo Scientific), and an Optical Particle Counter (OPC, TSI 8820). The measurements were performed in 17 homes and repeated 3 times in different seasons. In each home, DRX and OPC sampled for 60 minutes, while PMI2.5 and pDR-1500 sampled for 24 hours. 37 mm Teflon filters were used for PMI2.5 and pDR-1500. Here we compare data obtained with different instruments.

The results indicate that the filter-based measurements of PMI 2.5 and pDR-1500 were highly correlated (R^2=0.9639) and the result was similar between the pDR-1500 real-time reading (24 hr average) and pDR-1500 filter mass (R^2=0.8438). The PM2.5 readings of DRX (1 hour average) and pDR-1500 (average of the first hour) were also highly correlated (R^2= 0.7137). The airborne particle number concentration from OPC was used to estimate particulate mass (PM2.5) by assuming that particles are spherical and have density of 1.65 g/cm^3. The estimated mass concentration by the OPC were well correlated with DRX readings (R^2=0.6390). This comparison will be useful for investigators performing PM measurements using different instruments and methods.

3AE.4

Real-Time Measurements of Direct and Catalytic Aerosol Oxidative Activity. Yupaporn Sameenoi, Meghan Mensack, Kirsten Koehler, Jeff Shapiro, Jeffrey L. Collett, John Volckens, CHARLES HENRY, *Colorado State University*

Anthropogenic particulate matter significantly impacts human health, most likely through the generation of oxidative stress. Because of the chemical complexity of atmospheric aerosols, multiple pathways exist for generating oxidative stress, including both direct oxidation and catalytic oxidation where reactive oxygen species are generated by the reaction of the particulate matter with biological oxidants such as peroxide. At present, the dithiothreitol (DTT) assay is the most common method to measure direct aerosol oxidative activity. In this assay, reduced DTT is oxidized to its disulfide by particulate matter; the remaining DTT is then reacted with Ellman's reagent and quantified by UV spectroscopy. The traditional DTT assay requires long sampling times (hours to days) such that sufficient mass is collected for analysis. Thus, many of the most reactive (and short lived) species may not be present at the end of the sampling period. The DTT assay is only capable of quantifying direct catalytic processes and does not provide the ability to measure catalytic oxidative activity. To address these problems, we have developed two novel electrochemical sensors to measure direct and catalytic aerosol oxidative activity in real time. The direct oxidative activity sensor electrochemically measures the remaining DTT present after reaction with particulate matter collected using a Particle Into Liquid Sampler (PILS). The system provides the ability to make measurements at atmospherically relevant particulate matter concentrations with high time resolution (~3 min). Measurements of oxidative activity for two laboratory-generated aerosols (fly ash and urban dust) show a strong correlation between oxidative activity and aerosol concentration. The catalytic sensor measures an aerosol's ability to generate hydroxyl radicals by mixing particulate matter with H_2O_2 and a radical trapping agent, salicylic acid. On trapping of the radical, the salicylic acid is converted to dihydroxy-benzoic acid that can be easily detected electrochemically.

3AE.5

Nanoparticle Characterization for Exposure Studies. KAARLE HAMERI, Joonas Koivisto, *University of Helsinki, Department of Physics*

The understanding of the occupational health and safety aspects of engineered nanoparticles and nanomaterials (ENP or ENM) is still limited because quantitative exposure levels are lacking and dose metrics are unclear. In this study, we present exposure measurements carried out in different occupational environments. Our aim is to compare different exposure scenarios during ENM synthesis and handling. We found that in nanoparticle (NP) synthesis with liquid flame spray process, the exposure and dose of NPs were defined by number. While in TiO2 ENM packing and carbon nanodiamond handling the exposure and dose were defined by mass. In NP synthesis, the dose of NPs 70% were deposited in alveolar region, while in ENM handling nearly all ENM particles were deposited in head-airways.

3AE.6

Facial Effect on Regional Deposition of Aerosols in Human Upper Airway System in Calm Air Condition. Arash Naseri, Pejman Farhadi Ghalati, Omid Abouali, GOODARZ AHMADI, *Shiraz University*

In most of earlier works in the filed of micro particle deposition in the upper airway, the aerosols are injected uniformly at the inlet of nostril. In present work it is aimed to investigate the effect of facial effect on regional aerosol deposition in the nasal airway system. For this aim a 3-D computational model of the airway system is combined with a 3-D model of mannequin. The computational domain includes the regions around the mannequin and the inside of the airway system. The simulation was performed for the calm air condition. Firstly the flow filed for the inhalation of a specified air flow rate is obtained by solving the Navier Stokes equations. Then the particles are released form the boundaries around the mannequin head and their motion are evaluated using a Lagrangian approach for solving the equations for dynamics of particles. The regional aerosols deposition is evaluated for different parts of the human air way system and the results compared with those for separate modeling of the airway system. The results depict that the importance of facial effect on the local deposition of inhaled particles in the airway system.

3AN.1

The vSANC – An Instrument for Basic Nucleation Studies and Ambient Measurements of Nanoparticles. TAMARA PINTERICH, Paul M Winkler, Paul E. Wagner, Aron Vrtala, *Universitaet Wien, Vienna, Austria*

Based on our experience with the Size Analysing Nuclei Counter, SANC (Wagner et al. (2003)), we developed a new versatile expansion chamber system. Well-defined uniform vapour supersaturation is obtained by adiabatic expansion. Subsequently aerosol particles, acting as condensation nuclei, cause heterogeneous nucleation and grow to visible droplets. An optical detection method, the CAMS method (Wagner (1985)), is applied utilizing multiple light scattering angles. Light fluxes at twenty different scattering directions as well as the transmitted light flux are monitored simultaneously. This enables automated determination of growth rates and absolute number concentrations ranging from ~50/cc to 10^7/cc, independent from the aerosol flow. Growth rate measurements allow precision determination of vapour saturation ratios.

The design of the flow plan enables both active and passive operation of the vSANC. In particular the latter is of advantage when performing measurements in combination with a uDMA. The connection between inlet and expansion chamber is thermostated in order to prevent evaporation losses. Connections were built straight and as short as possible using only stainless steel tubing and pinch valves with complete and true full bore. This minimizes particle losses and enables an unobstructed aerosol flow.

The vSANC was optimised to achieve high flexibility in investigating aerosol particles from diameters of 1-2nm upwards. Depending on the pre-sampling conditions either the aerosol is already humidified and is passed directly into the expansion chamber or it first passes through a humidifier. In fact two humidifiers were implemented allowing the simultaneous use of different vapour compounds. Accordingly, information on different particle properties such as solubility or wettability can be obtained.

We present first measurement results providing precision determinations of heterogeneous nucleation probabilities and allowing evaluations of sizes of molecular clusters.

Wagner, P.E. (1985), J. Colloid Interface Sci.105, 456.
Wagner, P.E. et al. (2003), Phys. Rev. E67, 021605.

3AN.2

Evidence for Surface Freezing in Supercooled n-Alkane Nanodroplets. VIRAJ MODAK, Harshad Pathak, Mitchell Thayer, Sherwin Singer, Barbara Wyslouzil, *The Ohio State University*

Crystallization from the melt is a fundamental process that plays a central role in semiconductor processing, chemical separations, pharmaceutical production and purification and material science and metallurgy. In many cases, the transition to the most stable solid phase can proceed via an intermediate metastable phase. For example, n-alkanes (C_nH_{n+2}) of intermediate chain length (n>15) can form a series of rotator phases. Moreover, in contrast to most other molecules that pre-melt at temperatures below the bulk melting point Tm, intermediate chain length n-alkanes ($16 \leq n \leq 50$) form an ordered surface monolayer up to 3 K above Tm. Our experiments strongly suggest that even the short chain alkanes, n-octane and n-nonane appear to freeze at the surface of supercooled liquid droplets prior to the initiation of bulk freezing. In our experiments we create liquid nanodroplets in highly non-equilibrium states in a continuous flow supersonic nozzle. We characterize the flow using axially resolved static pressure measurements, and study the droplets using spatially resolved Small Angle X-ray Scattering (SAXS) and Fourier Transformed Infrared Spectroscopy (FTIR). In addition we complement our experiments with molecular simulation studies at the united atom level to develop molecular level insight into homogeneous liquid-solid nucleation and strengthen our interpretation of the experimental results.

3AN.3

Monomer, Clusters, Liquid: An Integrated Study of Methanol Condensation. BARBARA WYSLOUZIL, Hartawan Laksmono, Shinobu Tanimura, Heather Allen, Gerald Wilemski, Mark Zahniser, Joanne Shorter, David Nelson, J. Barry McManus, *The Ohio State University*

Particles or droplets form by nucleation and condensation in many ambient settings, and particle production is thought to occur via a series of intermediate clusters. For most materials, cluster concentrations are too low to observe these intermediates in the transition from the vapor to the liquid. Methanol is an important exception: the properties of vapor phase methanol can only be explained by invoking the presence of clusters. This talk will discuss our recent work to quantify the amount of methanol present in the vapor, cluster, and the liquid states as methanol condenses. When liquid first appears, cluster formation has already consumed up to 30% of the monomer. An energy balance suggests that a significant fraction of the cluster population is larger than the tetramer, while preliminary SAXS measurements suggest that these clusters contain, on average, 6 monomers.

3AN.4

Sulfuric Acid Nucleation: A Systematic Study of the Effect of Bases. WALKER GLASOE, Baradan Panta, Juliana Zollner, David Hanson, *Augsburg College*

Nucleation of particles composed of sulfuric acid, water, and nitrogen base molecules was studied using a continuous flow reactor. The particles formed from these vapors were detected with an ultrafine condensation particle counter, while vapors of sulfuric acid and nitrogen bases were detected by chemical ionization mass spectrometry. The effect of ammonia as well as several different amines were investigated. Enhancement of particle numbers when ammonia or amines were added indicates they have powerful effects on the nucleation properties of sulfuric acid vapor. Power dependencies for particle numbers on sulfuric acid and nitrogen bases will be presented. Particle detection efficiencies, the extent of particle growth, and cluster thermodynamics will be discussed with the help of computational fluid dynamics simulations of the flow and chemistry within the flow reactor.

3AN.5

DMA-MS Measurement of Water Vapor Uptake by Charged Clusters Under Sub-Saturated Conditions.

DEREK OBERREIT, Carlos Larriba, Peter McMurry, Christopher Hogan Jr., *University of Minnesota*

Vapor molecule uptake by charged particles in the nanometer size range is an important yet not well understood phenomenon observed in atmospheric chemistry, materials synthesis, and aerosol instrumentation. Existing methods used to study these effects for aerosols lack the sensitivity required for small particles. We use DMA-MS (Differential Mobility Analysis-Mass Spectrometry) to study water vapor uptake by charged particles/clusters by introducing controlled vapor concentrations to the DMA sheath gas. Electrical mobilities of charged salt cluster particles composed of Cs+(CsI)n, Rb+(RbI)n, K+(KI)n, and Na+(NaI)n are measured at varying saturation ratios of water vapor at different temperatures where the value for n ranges from 0 to 13 neutral cation-anion pairs. The charged salt clusters are generated using electrospray ionization with methanol as the solvent. The DMA is high resolution (R~60), parallel-plate DMA operated such that particles/clusters of a specified electrical mobility are constantly provided to the mass spectrometer inlet. The mobility range is decreased stepwise to obtain mass-mobility spectra. With a mass spectrometer as the detector, we can clearly distinguish between cluster ions of similar electrical mobility but different mass to charge ratio (singly versus doubly charged). From these measurements, we find that the electrical mobility of all clusters examined decreases with increasing water saturation ratios. The relative shift in electrical mobility varies for different numbers of neutral cation-anion pairs present in the original cluster and does not depend monotonically on dry cluster size. The measured electrical mobility of the clusters corresponds to their average size when equilibrium is established with the surrounding vapor; thus, electrical mobility shifts allow us to infer the equilibrium constants for water vapor uptake by clusters of controlled size and chemical composition.

3AN.6

The Roles of Gaseous Oxidation Products in Organic Nucleation from Ozonolysis of Atmospheric Terpenes.

JUN ZHAO, Paul M Winkler, John Ortega, Peter McMurry, James N. Smith, *National Center for Atmospheric Research*

New particle formation due to ozonolysis of atmospheric terpenes may represent an important source of atmospheric particles, particularly in forested areas. In this work, we present chamber and flow tube measurements of gas-phase oxidation products from ozonolysis of monoterpenes (e.g., α-pinene) and sesquiterpenes (e.g., β-caryophyllene) with the Cluster Chemical Ionization Mass Spectrometry (the Cluster CIMS) using both positive and negative ion detection schemes. In either mode of operation, the oxidation product compounds/clusters were broken up by applying high collision energy in the conical octopole region and the pattern of the oxidation products was thus obtained. A series of high molecular weight oxidation products/clusters that likely contain carboxylic groups were observed from ozonolysis of both α-pinene and β-caryophyllene. Positive Matrix Factorization (PMF) was used to study the temporal evolution and category of the oxidation products that are related to particle production. The possible roles of those products/clusters in the formation of new particles in the chamber and flow tube experiments will be discussed.

3CC.1

Causes of the Seasonal Variation of Cloud Effective Radii over Oceans. HANNELE KORHONEN, Anton Laakso, *Finnish Meteorological Institute*

We use the aerosol-climate model ECHAM-HAM to investigate the seasonal variation in cloud top effective radius over the oceanic regions as observed in MODIS satellite retrievals. The role of oceanic emissions, oxidants, removal processes as well as continental transport are quantified. For the latitude band 40-60S we show that the clear summer-time minimum in effective radius is caused for the most part by high DMS concentration in ocean water with with a smaller contribution from a faster formation rate of hydroxyl radicals in summer. However, the changes in mean surface wind speeds between the seasons also play an important role: in a theoretical case that the oceanic DMS concentration remained constant throughout the year, the seasonal cycle in effective radius would be reversed due to seasonal wind speed changes.

3CC.2

Using a Global Model Adjoint to Unravel the Footprint of Spatially-Distributed Emissions on Cloud Properties. VLASSIS KARYDIS, Shannon Capps, Daven Henze, Athanasios Nenes, *Georgia Institute of Technology*

Cloud droplets form upon pre-existing atmospheric aerosols, and their modulation has profound impacts on cloud radiative properties, the hydrological cycle and climate. Unraveling the complex relationship of cloud droplet number concentration (CDNC) to aerosol and aerosol precursor emissions is carried out with global climate models, often by activating/deactivating emissions. Although straightforward, this approach neglects the nonlinear dependence of aerosol concentrations on aerosol precursor emissions so that the resulting sensitivity reflects not only the actual CDNC response to an emissions change but also an altered size distribution and composition.

Adjoint modeling eliminates these issues by propagating an infinitesimal perturbation backwards through the model and, thus, elucidating the sensitivity of model output (e.g., CDNC) to the entire field of model parameters (e.g., emissions) without perturbing the model state. In this study, we reveal these relationships by developing the adjoint of the Kumar et al. (2009) CDNC parameterization (which considers the effects of soluble/insoluble particles on cloud droplet formation) and coupling it with the adjoint of the GEOS-Chem chemical transport model. This model framework is then used to determine the impacts of emissions of aerosol precursors on cloud droplet formation through adjoint gradients. Specifically, the adjoint model is applied to quantify the influences of global emissions on the predicted CDNC within the Midwest US, Southest US, California, and Central Europe.

The resulting sensitivity maps display the range of spatial, sectoral and seasonal variability in the susceptibility of CDNC to emissions changes. In particular, over US, SO2 and NOx emissions have a significant impact on CDNC during August, while NH3 emissions are the most important contributor to CDNC during February. Moreover, SO2 and NH3 emissions from East Asia have also a significant impact on CDNC over California. Finally, the CDNC over Central Europe is most sensitive to NH3 and NOx emissions during both seasons.

3CC.3

Evaluation of the Sectional Aerosol Model SALSA within the Aerosol-Climate Model ECHAM5-HAM. TOMMI BERGMAN, Veli-Matti Kerminen, Hannele Korhonen, Kari Lehtinen, Risto Makkonen, Antti Arola, Tero Mielonen, Sami Romakkaniemi, Markku Kulmala, Harri Kokkola, *Finnish Meteorological Institute*

Aerosols affect the radiative balance of the atmosphere directly by absorbing and scattering radiation and indirectly by altering the radiative properties of clouds. For estimating the changes and uncertainties in both direct and indirect effect, the number size distribution shape and total particle number concentrations are the key parameters to predict.

Global climate models generally describe the aerosol size distribution with modal or moment approaches. However, sectional models enable more flexibility in describing the aerosol size distribution and the particle size dependent chemical composition, which have implications in e.g. aerosols' ability to form cloud droplets.

We present the implementation of the sectional aerosol model SALSA (Sectional Aerosol module for Large Scale Applications) (Bergman et al. 2011, Kokkola et al. 2008) within the ECHAM5-HAM aerosol-climate model. The SALSA module describes the aerosol population from 3 nano-meter to 10 micro-meter with 10 size classes with parallel chemical compositions, thereby consisting of 20 sections in total. The SALSA considers five compounds: sulphate, organic carbon, black carbon, sea salt and dust. In addition to these compounds the water uptake is also included.

The average modeled surface concentrations of sulphate, organic carbon and black carbon at the IMPROVE sites are within a factor fo two of the observations, with the mean fractional bias showing underestimation of 19-25 %. The simulated number size distributions show concentrations lower than observed at continental sites. This suggests that the new particle formation and condensational growth is too low and should be improved with a condensable vapour e.g. organic vapour. Over the tropical oceans the aerosol optical depth (AOD) shows good agreement with satellite retrievals, while at high latitudes and very polluted regions the AOD is underestimated. Nevertheless, our study shows that even very few sections is enough to simulate the aerosol population in the global scale.

3CC.4

The Importance of the Cloud Processing of Aerosols in Predicting in Aerosol Nucleation, Growth and CCN. JEFFREY PIERCE, Betty Croft, *Dalhousie University*

Clouds are associated with large uncertainties in atmospheric models. Thus, any influence that clouds have on the evolution of aerosols may lead to uncertainties in aerosol predictions. In this presentation, we explore two influences of clouds on aerosols in the GEOS-Chem-TOMAS global aerosol microphysics model: (1) The aqueous oxidation of SO2 to form sulfate aerosol mass in activated aerosols as opposed to the gas-phase oxidation of SO2 to form H2SO4 vapors, and (2) the wet deposition of aerosols. The balance of aqueous oxidation versus gas-phase oxidation of SO2 plays a critical role in determining H2SO4 vapor concentrations and thus aerosol nucleation and growth rates. A 15% increase in the gas-phase oxidation rate of SO2 leads to a 7% increase in H2SO4 and a 2.5% change in CCN. Yet, there is large differences between models in the gas-phase/aqueous-phase oxidation split with gas-phase oxidation representing less than 1/4 to more than 1/3 depending on the model. We also tested the model sensitivity to a double of the aerosol wet removal rate. The wet deposition of aerosols directly removes CCN; however, it reduces the aerosol condensation sink allowing enhanced nucleation, growth and the formation of fresh CCN. Thus, changes CCN predictions are dampened to changes in aerosol wet-deposition rates.

3CC.5

Kinetics of Droplet Growth Observed in Recent Field Campaigns. FAN MEI, Jian Wang, *Brookhaven National Laboratory*

Atmospheric aerosols can indirectly influence global climate budget by changing the microphysical structure, lifetime, and coverage of clouds. While it is generally agreed that aerosol indirect effects act to cool the Earth-atmosphere system by increasing cloud reflectivity and coverage, the magnitudes of the indirect effects are poorly understood. The formation of cloud droplets from aerosol particles is kinetically controlled by the availability of water vapor, equilibrium water vapor pressure above the growing droplet surface, and both the gas phase and aerosol phase mass transfer resistances. It has been hypothesized that the formation of surface organic films or the delay in dissolution of solute could significantly delay the growth of cloud droplets. Such delay could lead to a higher maximum supersaturation within a rising cloud parcel, therefore higher droplet number concentration and smaller droplet size at constant liquid water content. When only a subset of the droplets experiences significant growth delay, the overall droplet size spectrum will be broadened, which facilitates the formation of precipitation.

During three recent field campaigns (CalNex-LA, CARES, and Aerosol Intensive Observation Period at Brookhaven National Laboratory), the CCN activity and droplet growth of size selected particles ranging from 25 to 320 nm were characterized by a CCN counter under supersaturations from 0.1% to 0.8%. The three campaigns allow us to examine the droplet growth for many representative organic aerosol types, including biogenic SOA, anthropogenic SOA, and organic aerosols from biomass burning. The droplet growth of size-selected particles inside the CCN counter is found to be influenced by particle critical supersaturation, heterogeneity in particle composition, and particle concentration. The potential impact of surface organic film on droplet growth is examined by comparing the droplet growth of size-selected ambient particles to that of ammonium sulfate particles with the same critical supersaturation, and the results will be discussed.

3CC.6

Eastern Pacific Emitted Aerosol Cloud Experiment (E-PEACE). LYNN RUSSELL, Armin Sorooshian, John Seinfeld, Bruce Albrecht, Athanasios Nenes, Lars Ahlm, Yi-Chun Chen, Matthew Coggon, Jill Craven, Richard Flagan, Amanda Frossard, Haflidi Jonsson, Eunsil Jung, Jack Lin, Andrew Metcalf, Rob Modini, Johannes Muelmenstaedt, Greg Roberts, Taylor Shingler, Siwon Song, Edwin Sumargo, Zhen Wang, Anna Wonaschutz, *Scripps Institution of Oceanography*

Aerosol-cloud-radiation interactions are widely held to be the largest single source of uncertainty in climate model projections of future radiative forcing due to increasing anthropogenic emissions. The underlying causes of this uncertainty among modeled predictions of climate are the gaps in our fundamental understanding of cloud processes. There has been significant progress with both observations and models on addressing these important questions, but quantifying them correctly is nontrivial and limits our ability to represent them in global climate models. The Eastern Pacific Emitted Aerosol Cloud Experiment (E-PEACE) 2011 was a targeted aircraft campaign with embedded modeling studies, using the CIRPAS Twin Otter aircraft and the Research Vessel Point Sur in July and August 2011 off the coast of Monterey, California, with a full payload of instruments to measure particle and cloud number, mass, composition, and water uptake distributions. E-PEACE included (a) using three emitted particle sources to separate particle-induced feedbacks from natural variability, namely (i) combustion particles from container ships with dry diameters between 50 and 100 nm, (ii) shipboard smoke-generated particles with dry diameters between 100 nm and 1 µm, and (iii) aircraft-based milled, coated salt particles with dry diameters between 3 and 5 µm; (b) comparing large eddy simulations and aerosol-cloud parcel modeling studies to measured plume dispersion and interactions to form the basis for interpreting the aircraft observations; and (c) analyzing satellite images of the effects of these emitted particles to quantify warm cloud microphysics.

3CO.1

Dynamic Changes in the Aerosol Composition and Concentration During Different Burning Phases of Wood Combustion.MICHAEL ELSASSER, Christian Busch, Jürgen Orasche, Hans Hartmann, Jürgen Schnelle-Kreis, Ralf Zimmermann, *Helmholtz Zentrum München*

Different on- and off-line mass spectrometry-based methods were applied to investigate changes in aerosol gas-phase and particle-phase composition during wood combustion in the different phases of the burning process. The experiments were carried out with a logwood boiler and a stove at the Technology and Support Centre (TFZ) for renewable resources in Straubing, Germany. Different fuel types (spruce and beech) and burning conditions (normal, overloaded feed, oxygen deficiency) were investigated. The aerosol particle phase of the non-refractory compounds was analysed by a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc.). Together with a Photo Ionisation (PI) Time-of-Flight Mass Spectrometer (ToF-MS), which detects selective aromatic organic compounds in the gas phase by Resonance Enhanced Multi Photon Ionisation (REMPI), it provides a useful tool to measure the dynamic of wood combustion.

This dynamic could be described and reflected in four different burning phases, during which the aerosol compounds and concentration changed strongly. For example, the first phase, which is of pyrolysic nature, shows the highest concentrations of organic mass, mass-to-charge ratio (m/z) 60 and guaiacol. The following “harsh combustion phase” provides an increase of the phenolic compounds in the flue gas, indicating the breakdown of the lignin backbone of the wood structure. Additionally, the contribution of organic mass to total non-refractory mass during these phases decreases from 99% to 91%. The wood combustion marker signal at m/z 60 also decreases. The subsequent “stable flaming phase” has the highest relative amount of sulphate and chloride, so the impact of inorganic compounds increases like in the second phase. The start of the char burnout is indicated by an increase of the carbon monoxide concentration in the gas phase. This contribution provides an overview of the impact of the dynamic phases of wood combustion. Additionally, it shows that burning conditions can significantly change the emission.

3CO.2

Polycyclic Aromatic Hydrocarbon Emissions in Transient Wood Combustion. Axel Eriksson, Erik, Z Nordin, Robin Nyström, Esbjörn Pettersson, Christoffer Bergvall, Roger Westerholm, Erik Swietlicki, Christoffer Boman, JOAKIM PAGELS, *Lund University, Lund, Sweden*

Polycyclic aromatic hydrocarbons (PAHs) have been denoted key components in particle related toxicology. Emissions of PAHs can under certain circumstances be high in residential wood combustion. However, previous attempts to identify the combustion conditions favouring high PAH emissions have typically been limited to averages over one to several combustion cycles. In this work we applied Aerosol Mass Spectrometry for highly time-resolved direct measurements of PAHs and total organics in residential biomass combustion.

Emissions from a conventional wood stove and a novel pellet reactor with possibility to control fuel and air supply were studied. The flue gas was diluted with particle free air of ambient temperature, the total dilution factor was 1:2000. A high resolution aerosol mass spectrometer (HR-TOF-AMS, Aerodyne Inc.) was used for size resolved composition of compounds vaporised at 600°C. The results were compared with off-line speciated PAH analysis using GC-MS.

In the wood stove the highest emission factors of total particle phase organics and PAHs occurred during the first 1-5 minutes after addition of new batches of logs on glowing embers, although PAHs constituted less than 1% of the total organics. Elevated PAH-emissions also occurred at hot air starved combustion in both appliances, when O2 levels in the flue gas were below 5%. In these cases, PAHs composed up to 30% of the total organics. A high burn rate under hot and air-starved combustion conditions, leads to thermal cracking of primary released oxygenated pyrolysis products (e.g. levoglucosan and methoxy-phenols). At higher temperatures mostly aromatic compounds and soot are stable enough to survive resulting in elevated PAH emissions.

It is well known that poorly insulated stoves, bad mixing and humid fuels lead to high organic emissions. This work illustrates the potential deterioration of emission levels caused by too high burn rates.

3CO.3

Particulate Matter and Other Criteria Pollutants Reduced by Algae Fuel in Marine Vessels. M. Yusuf Khan, William A. Welch, Robert L. Russell, David R. Cocker III, MARYAM HAJBABAEI, *UC Riverside*

Particulate matter (PM2.5) and other criteria pollutants from harbor craft significantly affect air quality in populated regions near ports and inland waterways. In an effort to reduce Particulate matter and dependency on fossil fuels, this study examined the use of Algae fuel in marine vessel. Emissions were measured from a 4-stroke, 600 kW Caterpillar D398 diesel generator used for propulsion in a Stalwart class (T-AGOS) ocean surveillance ship operated in the lake of Michigan. Base emissions were measured when ship operated on ultra-low sulfur diesel (ULSD) fuel following ISO 8178-4 D2 certification test cycle. Subsequently, fuel was switched to 50/50 blend of ULSD and Algae fuel (B50) to compare its emission profile with base fuel (ULSD).

Significant reduction (up to 35%) in PM2.5 was observed at 50% engine load and below on consuming B50. At higher loads (75% and 100%), PM2.5 was reduced by 6% and 7%, respectively. Overall a reduction of 25% was found for PM2.5. PM2.5 collected on quartz filter was speciated into Elemental carbon (EC) and Organic carbon (OC). PM2.5 was dominated by OC (77-94%) for both fuels. Substantial reduction (30-34%) in EC was observed across all loads except at 10% engine load where reduction dropped down to 6%. Overall a reduction of 30% in EC and 20% in OC was obtained on consuming B50 fuel. Other criteria pollutants such as Nitrogen oxides (NOx) and Carbon monoxide (CO) were reduced by 10% and 18%, respectively. The consumption of 50/50 blend also resulted in better fuel economy.

Impact of fuel properties on PM2.5 and other criteria pollutants will be discussed in the presentation.

3CO.4

Fate of Nanomaterials and Byproducts During Combustion. ERIC VEJERANO, Amara Holder, Linsey Marr, *Virginia Tech*

The widespread adoption of nanotechnology means that products containing nanomaterials will inevitably end up in waste streams, and some of these will be incinerated. Our objectives are to investigate how the combustion process affects the chemical and physical properties of nanomaterials and to determine how their presence in the waste stream affects formation of potentially toxic byproducts. Surrogate wastes containing polyethylene, polyvinyl chloride, and paper spiked with various nanomaterials such as silver, nickel oxide, titania, ceria, fullerene, iron, and quantum dots were incinerated at 850 oC with 1 lpm of air. Particle size distributions and concentrations from furnace exhaust were measured using a scanning mobility particle sizer and optical particle counter. Gaseous and particulate samples were collected in exhaust for analysis of the nanomaterial in question along with polycyclic aromatic hydrocarbons (PAHs) and dioxins. The most abundant PAHs found in exhaust were naphthalene, acenaphthylene, and fluorene. Preliminary findings suggest that nickel oxide and C60 fullerene generally enhanced PAH emissions, while ceria, titania, and silver produced both increases and decreases in emissions, depending on the type of waste and the specific PAH. It is evident that incineration of nanomaterials has the potential not only to affect the characteristics of the nanomaterials themselves but also the yields of toxic byproducts. The results of this study will enable us to understand how engineered nanomaterials and byproducts are transformed and controlled during incineration, leading to improved ability to predict their fate and impacts in the environment.

3CO.5

Detailed Characterization of Shape-Selected Fractal Soot Particles. ALLA ZELENYUK, Dan Imre, Josef Beranek, Paul Reitz,*Pacific Northwest National Laboratory*

Recently we developed a novel system to measure simultaneously individual particles compositions, mass, mobility, and vacuum aerodynamic diameters. In this system, a new-generation compact aerosol particle mass analyzer (APM) is used to generate particles with a narrow distribution of masses that are classified with differential mobility analyzer (DMA) to select particles with one charge and a narrow distribution of mass and shape. The compositions and vacuum aerodynamic size distributions of these particles are measured with single particle mass spectrometer, SPLAT II.

The combined APM/DMA/SPLAT or ADS yields particle size, composition, density/effective density, and dynamic shape factors (DSFs) in the transition and free-molecular regimes.

We applied the ADS to aspherical ammonium sulfate and NaCl particles and demonstrate that both are present in a wide distribution of shapes and that the ADS can be used to select particles of the same volume equivalent diameter, but with very different shapes. For each particle shape, we measure the DSFs in the transition and free-molecular regimes. This approach produces direct relationship between the dynamic shape factors in the two regimes as a function of particle size and makes it possible to separate in real time particles with different shapes for further analysis by SPLAT II or microscopy.

We then apply the ADS to characterize fractal soot particles produced by miniCAST soot generator. We show that in this case it is possible to determine fractal dimension of soot agglomerates, the average primary spherule diameter, number of primary spherules, and void fraction as function of particle size. We show that it is possible to separate soot aggregates of one mass, but with different shapes, and characterize their DSFs in the transition and in the free-molecular regimes. In addition, we demonstrate a new approach to determine the average primary spherule diameter based on the DMA/SPLAT measurements alone.

3CO.6

Pro-inflammatory Responses of Diesel Engine Exhaust Particles - Impact of Organic Compounds. ANNIKE IRENE TOTLANDSDAL, Alena Kubatova, Johan Øvrevik, Richard Cochran, Jan Inge Herseth, Anette Kocbach Bølling, Per E Schwarze, Flemming R Cassee, Edel Lilleaas, Magne Refsnes, Jørn A Holme, Marit Låg, *Norwegian Institute of Public Health, Norway*

Exposure to diesel engine exhaust particles (DEPs), representing a complex and variable mixture of components, has been linked to adverse cardiopulmonary effects. The biological mechanisms involved are currently not clarified, but inflammation is considered a key event. In this study we characterize and explore which components of DEPs that may initiate pro-inflammatory responses.

Human bronchial epithelial cells (BEAS-2B) were exposed to either native DEPs, corresponding methanol DEP-extract or residual DEPs, and investigated with respect to cytotoxicity and expression and release of multiple inflammation-related mediators. In order to further investigate the potency of different groups of organics to induce these pro-inflammatory responses, cells were also exposed to fractionated methanol extracts, which were prepared by using solid phase extraction with hexane and 20% dichloromethane (DCM) in hexane and methanol.

Both native DEPs and DEP-extract, but not residual DEPs, induced marked mRNA expression of COX-2, IL-6 and IL-8, as well as cytotoxicity and release of IL-6. However, CYP1A1 was primarily induced by the native and residual DEPs. Gas chromatography with mass spectrometry (GC/MS) analysis of DEP-extracts indicated that the majority of the analysed polycyclic aromatic hydrocarbons (PAHs) and PAH-derivatives were extracted from the particles, but that certain PAH-derivatives, possibly their carboxylic isomers, tended to be retained on the residual DEPs. Notably, certain cytokine-inducing components of the methanol extract may suppress CYP1A1 expression. Chemical analyses of fractionated extracts indicated that the methanol-soluble fraction containing hydroxy-PAHs may be responsible for the pro-inflammatory response induced by the DEP extracts. Interestingly, the same fraction seemed to be important for similar polarity fractions of wood smoke particles. These results suggest that hydroxy-PAHs may represent a group of compounds that may be of particular interest to study in further research of inflammatory responses induced by exposure to particulate air pollution.

3UA.1

Long-term Measurements of Aerosol Particle Composition with an Aerosol Chemical Speciation Monitor in Megacity Beijing, China. YELE SUN, Zifa Wang, Ting Yang, Xiaole Pan, Pingqing Fu, Huabin Dong, Jie Li, Ping Chen, John Jayne, *Institute of Atmospheric Physics, Chinese Academy of Science*

Air pollution is still a major environmental concern in China. Knowledge of sources and processes of particulate matter (PM) is of importance for improving air quality and reducing its harmful effects. In this work, we deployed an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) in megacity Beijing, China for a long-term measurement of non-refractory submicron (PM1) species, including organics, sulfate, nitrate, ammonium, and chloride. Here we present the results from a year-long (July 2011- July 2012) measurement at the Institute of Atmospheric Physics which is located between 3rd and 4th ring road in metropolitan area of Beijing. The seasonal variations, diurnal cycles, and evolution processes of organic and inorganic aerosols, as well as their association with meteorological variables are discussed. Particularly, the chemical characteristics of aerosol species in different environments, e.g., dust storm in spring, biomass burning in early summer, and coal combustion in heating season are explored. Positive matrix factorization is performed to ACSM organic aerosol (OA) mass spectra from different seasons. Various OA components, e.g., hydrocarbon-like OA (OA), cooking OA (COA), biomass burning OA (BBOA), and oxygenated OA (OOA) are identified, but not always consistent in different seasons. The sources and processing, seasonal and diurnal variations of primary and secondary OA are elucidated. Finally, HYSPLIT back trajectory and potential source contribution function analyses are used to further investigate the source regions associated with the high PM pollution in different seasons in Beijing, China.

3UA.2

Long-Term Aerosol Mass Spectrometric Measurements in Zurich. Francesco Canonaco, JAY SLOWIK, Andre Prévôt, Urs Baltensperger, *Paul Scherrer Institute*

Long-term monitoring of aerosol chemical composition provides a powerful tool for investigating aerosol sources and atmospheric processing, which are critical to understanding their effects on human health, climate, and visibility. We present year-long continuous measurements of submicron aerosol composition from an aerosol chemical speciation monitor (ACSM, Aerodyne Research, Inc.) deployed in downtown Zürich, Switzerland throughout 2011. The ACSM yields quantitative mass spectra of the non-refractory aerosol component with 15 minute time resolution. These long-term measurements show a number of seasonal cycles in aerosol components. For example, particulate nitrate is much higher during the winter than in warmer seasons. Additional trends are evident in the organic spectra. Significant secondary aerosol formation from biogenic VOCs during the spring and summer months is suggested by an increase in the fraction of organic mass occurring at m/z 43 ($C_2H_5O^+$ and/or $C_3H_7^+$ ions) relative to the organic mass fraction at m/z 44 (CO_2^+, proportional to the molecular O:C ratio). Interestingly, it was observed that photochemical activity does not always increase the aerosol oxidation state. The continuous nature of the measurements also enables sampling of aerosol from unique local events, such as high levels of cooking-derived aerosol from a local festival, which might not be captured by a shorter campaign. Particle sources and processes are further investigated using positive matrix factorization (PMF) and the multi-linear engine (ME-2), which both represent the organic mass spectral time series as a linear combination of static factor mass spectra and their time-dependent intensities. ME-2 allows constraints to be placed on the factor mass spectra, which is useful for distinguishing hard-to-resolve factors. These techniques are used to evaluate the year-long importance and seasonable variability of particle sources in Zürich.

3UA.3

PMF Analysis of Urban and Transported Aerosols in Fukuoka, Japan. AKINORI TAKAMI, Takao Miyoshi, Satoshi Irei, Keiichiro Hara, Masahiko Hayashi, Naoki Kaneyasu, *NIES*

Emissions in East Asia have been increasing due to the rapid economic growth. In spring time, transport of gas and aerosol from the Asian continent to Japan prevails due to the seasonal monsoon. Since Fukuoka is located at the west part of Japan with a large population, urban type and long-range transported type of aerosols are expected to be observed. To monitor them, we have set up an Aerodyne aerosol mass spectrometer (Q-AMS or ACSM) and a TEOM at Fukuoka (33.5N,130.3E).

Aerosol chemical species were measured using Q-AMS in spring 2010 and 2012 and using ACSM in summer 2011. The main species were sulfate and organics, while nitrate and chloride were minor.

Organic data obtained from both Q-AMS and ACSM were analyzed by the Positive Matrix Factorization (PMF) method using the PMF evaluation tool developed by Ulbrich et al. The PMF analysis showed that three factors were the most plausible to explain the spring data. The mass spectra (MS) of the first component shows the highest signal at m/z=44 (COO fragment), considered to be well aged organics. MS of the second one shows the relatively high signals at m/z=55, 57 (C_4H_7, C_4H_9 fragments), considered to be fresh organics. MS of the third one shows the relatively higher signal at m/z=43 (CH_2CHO fragments) with respect to m/z=44 signal. This is considered to contain the partly aged organics. The mass fraction of the third component to the total organic mass was about half, indicating that the middle range transport was dominant.

With the summer data, only one component was obtained. The mass spectra show that the m/z=44 signal is the highest. However, m/z=43 and m/z=55 are also clearly seen in the mass spectra. This suggests that aged and fresh organics are mixed during this observation period.

3UA.4

Chemical Characterization of Sub-micron Aerosol Particles with the ACSM in Santiago, Chile. SAMARA CARBONE, Sanna Saarikoski, Felipe Reyes, Paula Reyes, Marcela Castillo, Pedro Oyola, John Jayne, Risto Hillamo, *Finnish Meteorological Institute*

Chemical characterization of sub-micron particles close to real-time was accomplished in Santiago de Chile using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) and the Semi-continuous OC/EC analyzer (Sunset Laboratory Inc.). The instrumentation operated during three months, from August 15th to November 23rd, 2011 in an urban station located inside the University of Santiago de Chile. Meteorological conditions varied along the studied period due to the transition from winter to spring time. Atmospheric inversions during the first month of the experiment were responsible for sub-micron particulate matter levels up to 80 micro-grams per cubic meter, in an hour average, especially during the night time. The average concentration for the whole period was 29 plus-or-minus 25 micro-grams per cubic meter. The aerosol particles were composed mainly of organics 59 percent, followed by nitrate, ammonium, sulfate, black carbon and chloride with 14, 12, 8, 3 and 3 percent, respectively. With the source apportionment the organic fraction can be separated in at least two distinct types or organic aerosol, oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA). The first one comprised 60 percent of the organic fraction and correlates well with nitrogen dioxide, whereas the HOA corresponded to 40 percent of the organic fraction and correlates well with nitrogen oxide and carbon monoxide, mainly emitted by traffic. This result suggests important contribution by traffic emissions to the total particulate matter (PM2.5) in Santiago de Chile.

3UA.5

Characteristics of Ambient Aerosol at a Suburban Site in Hong Kong During Springtime Using Aerosol Mass Spectrometry.

BERTO LEE, Yong J. Li, Chak K. Chan, Jian Zhen Yu, Peter Louie, *Hong Kong University of Science and Technology*

As a part of the Pearl River Delta (PRD), the Hong Kong Special Administrative Region (HKSAR) has been experiencing aggravating air pollution problems over the past few decades. Measurements of ambient particulate matter (PM2.5 and PM10) in Hong Kong in the past have been almost exclusively based on filter sampling and off-line analysis. We present here the first time application of a real-time PM characterization instrument, a High-Resolution Time-Of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), at a suburban site in Hong Kong during spring 2011. Measured non-refractory PM1 (NR-PM1) concentrations are well below those observed in other areas of the Pearl River Delta Region (Huang et. al, 2011, He et. al, 2011) as well as other Chinese cities (Huang et. al, 2010, Sun et al., 2010). Sulfate and organics were identified as the dominant species, with the former contributing to more than 50% of NR-PM1 at the sampling site. Analysis of high resolution organic spectra by Positive Matrix Factorization yielded 3 distinct Organic Aerosol (OA) components, Hydrocarbon-like organic aerosol, Semi-volatile organic aerosol and low-volatile organic aerosol (HOA, SV-OOA, LV-OOA) with characteristic diurnal profiles. Back trajectory analysis indicates that elevated total NR-PM1 mass concentrations and contributions of organics during the sampling period were mainly associated with northerly continental and north-easterly coastal air masses. Instrumental inter-comparison with a collocated MARGA (Monitor for Aerosols and Gas in Ambient Air) operated by the Environmental Protection Department of the HKSAR government and a Sunset thermo-optical ECOC analyzer were performed, with good agreement for organics, sulfate and ammonium, while a considerable underestimation of nitrate by AMS as compared to MARGA was observed.

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3UA.6

Chemical Characterization and Redox Activity of Fine and Coarse Particulate Matter in Milan, Italy.

NANCY DAHER, Ario Ruprecht, Giovanni Invernizzi, Cinzia De Marco, Justin Miller-Schulze, Jong Bae Heo, Martin Shafer, Brandon Shelton, James Schauer, Constantinos Sioutas, *University of Southern California*

The correlation between health effects and exposure to particulate matter (PM) has been of primary concern to public health organizations. An emerging hypothesis is that many of the biological effects derive from the ability of PM to generate reactive oxygen species (ROS) within affected cells. Milan, one of the largest and most polluted urban areas in Europe, is afflicted with high particle levels. To characterize its ambient PM, fine and coarse PM (PM2.5 and PM2.5–10, respectively) samples were collected on a weekly basis for a year-long period. Samples were analyzed for their chemical properties and ROS-activity. Findings revealed that PM2.5 is a major contributor to ambient particle levels in Milan, averaging 34.5 ± 19.4 µg m−3 throughout the year. Specifically, secondary inorganic ions and organic matter were the most dominant fine PM species contributing to 36 ± 7.1% and 34 ± 6.3% of its mass on a yearly-based average, respectively. Highest PM2.5 concentrations occurred during December–February and were mainly attributed to poor atmospheric dispersion. On the other hand, PM2.5–10 exhibited an annual average of 6.79 ± 1.67 µg m−3, with crustal elements prevailing. ROS-activity measurements indicated that PM2.5-induced redox activity expressed per m3 of air volume is greatest during January (837 µg Zymosan equivalents m−3) and February (920 µg Zymosan equivalents m−3). Conversely, intrinsic (per PM mass) ROS-activity peaked in July (22,587 µg Zymosan equivalents mg−1 PM) and August (25,161 µg Zymosan equivalents mg−1 PM), suggesting the influence of specific components on oxidant properties of PM. A correlation analysis between ROS-activity and select PM chemical components showed that Ni, Cr, Cu and water-soluble OC are strongly associated with ROS.

4AC.1

Thermodynamic Properties and Evaporation Kinetics of DOP, DEHS, and Oleic Acid Aerosols. ALAN SHIHADEH, Sarah Safieddine, Rawad Saleh, Andrey Khlystov, *American University of Beirut*

Recent thermodenuder-based approaches to studying aerosol volatility have allowed for decoupled determinations of thermodynamic and kinetic properties governing the phase partioning behavior of semi-volatile aerosols. These techniques have been applied to little-studied solid-phase organic aerosols of relevance to atmospheric air pollution, but have not been validated against better characterized systems such as DOP, DEHS, and oleic acid, for which saturation pressure or surface tension data are available or attainable through independent means. In this study we report vapor pressures, enthalpies of evaporation, evaporation coefficients, and surface tensions of DOP, DEHS, and oleic acid particles as determined using the Integrated Volume – Tandem DMA (IV-TDMA) method and compare them to values obtained by earlier investigators using other means. Contrary to common assumptions, we find that these aerosol systems exhibit evaporation coefficients of order 0.1, indicating an energy barrier to evaporation despite their liquid state. As a result, these aerosol systems exhibit higher volatility than reported in previous thermodenuder studies, all of which assumed an evaporation coefficient of unity. We also find that surface tensions obtained using the IV-TDMA are consistent with those found using macroscopic methods.

4AC.2

The Importance of Relative Humidity and Particle Phase on the Oxidation of Unsaturated Compounds in Aerosols. PETER GALLIMORE, Francis Pope, Pattanun Achakulwisut, Jason Lee, Stephen Fuller, Vanesa Carrascon, James F. Davies, Alex Björkegren, David Spring, Markus Kalberer, *University of Cambridge*

Organic compounds constitute a major fraction of tropospheric aerosol. The atmospheric properties of aerosol particles are critically influenced by their chemical composition, which continually changes due to gas/particle partitioning, heterogeneous oxidation and reactions occurring within the particles.

This study illustrates the importance of relative humidity (RH) and particle phase on the ozonolysis of three unsaturated carboxylic acids used as model organic aerosols: oleic, maleic and arachidonic acids. It combines two experimental techniques: An Electrodynamic Balance (EDB) is used to levitate single particles and measure changes in mass, size and phase [1]. An aerosol flow reactor is coupled to ultra-high resolution mass spectrometry to identify in detail the compounds formed in the oxidised particles [2].

While the hygroscopicity of maleic acid and arachidonic acid increased significantly after aging at high RH, oleic acid aerosol shows minimal water uptake before and after oxidation. There is also a marked contrast in the secondary chemistry occurring in the particle phase. We interpret this in terms of the fate of the initial reactive intermediates formed during ozonolysis [3]. For oleic acid, their relative stability, combined with low aerosol water content, means they can act as building blocks for oligomer formation. For aqueous maleic acid aerosols, they are rapidly hydrolysed and acid-catalysed reactions between “stable” products form secondary esters and hydrates.

We also illustrate the complex interplay between ozonolysis and particle phase. Liquid arachidonic acid aerosols rapidly form an amorphous crust when oxidized at low RH. Oxidation of maleic acid dissolved in the surface water of solid aerosols promotes further water uptake and, through a positive feedback mechanism, complete dissolution of the crystalline core.

References:
[1]: Pope, F.D. et al. (2010), Environ. Sci. Technol., 6656-6660.
[2]: Gallimore, P.J., et al. (2011), Atmos. Chem. Phys., 12181-12195.
[3]: Lee, J., et al. (2012), Phys. Chem. Chem. Phys., submitted.

4AC.3

Ammonia Uptake by Pure and Secondary Organic Aerosol Particles: Dependence on Particle Phase. SCOT MARTIN, Mikinori Kuwata, Ronan Lebouteiller, *Harvard University*

Chemical aging of organic aerosol particles, which is induced by uptake of reactive molecules, is known to alter their important characteristics, including hygroscopicity and optical properties. Recent studies demonstrated that secondary organic materials (SOM) particles are likely semisolid, raising a question if the uptake process is restricted by slow bulk diffusion. In this study, phase dependent ammonia uptake by pure and secondary organic aerosol particles was investigated. Crystalline pure organic particles were generated using a newly-developed particle generator, and its phase was regulated by controlling water exposure history. Particles were exposed different concentration levels of ammonia in a mixing reactor, and the particle phase ammonium was subsequently quantified using a high-resolution time-of-flight aerosol mass spectrometer (AMS). In addition, comparison of the AMS data with mobility size distribution data provides qualitative information on particle phase and morphology. No measurable ammonia uptake was observed for crystalline particles of the pure organic test compounds, while ammonia uptake was observed for aqueous and semisolid particles. Ammonia uptake by semisolid particles was significantly smaller than that observed for aqueous particles, likely due to slow mass transfer processes. In addition, ammonia uptake by SOM particles originated from biogenic precursors, those are known for their solid-like mechanical properties, were generated using the Harvard Environmental Chamber (HEC). Ammonia uptake by biogenic SOM particles was not a fast process at low relative humidity (RH) condition, consistent with the result for solid and semisolid pure organic particles. Ammonia uptake was enhanced at high RH, likely due to decreased viscosity. The results presented here demonstrate that uptake of reactive species by semisolid SOM particles is limited by slow bulk diffusion.

4AC.4

Deliquescence, Efflorescence, and Phase Miscibility of Mixed Particles of Aqueous Ammonium Sulfate and Isoprene-Derived Secondary Organic Material. MACKENZIE SMITH, Allan Bertram, Scot Martin, *Harvard University*

The hygroscopic phase transitions of particles composed of laboratory-generated secondary organic material and ammonium sulfate were investigated using a dual arm tandem differential mobility analyzer. Organic material was generated via isoprene photo-oxidation at organic mass concentrations of 20 to 30 micro-gram m^{-3} and oxygen-to-carbon ratios of 0.67 to 0.74. We show that the organic material produced by isoprene photo-oxidation exerts a measurable influence on the hygroscopic properties of ammonium sulfate. Compared to an efflorescence relative humidity (ERH) of 30 to 35% for pure ammonium sulfate, efflorescence was eliminated for mixed aqueous particles having organic volume fractions epsilon of approximately 0.6 and greater. Compared to a deliquescence relative humidity (DRH) of 80% for pure ammonium sulfate, the DRH steadily decreased for increasing epsilon, approaching a DRH of 40% for epsilon of 0.9. Parameterizations of DRH(epsilon) and ERH(epsilon) and a new account of partial dissolution of ammonium sulfate for RH < DRH (i.e., initial deliquescence) are presented for these mixed particles.

These results imply that isoprene photo-oxidation products are miscible with the aqueous inorganic phase and are therefore able to alter the hygroscopic behavior of ammonium sulfate. This phase miscibility is in contrast to the liquid-liquid separation that occurs for some other types of secondary organic material (e.g., terpene dark ozonolysis products). The differences in phase miscibility are consistent with a parameterization predicting phase separation as a function of organic material oxygen-to-carbon ratio. In the context of previous work, these results show that the influence of secondary organic material on the hygroscopic properties of ammonium sulfate varies with organic composition and confirm that the degree of oxygenation of the organic material, including complex organic materials, is an important variable influencing the hygroscopic properties of mixed organic-inorganic particles.

4AC.5

Equilibration Time Scales of Secondary Organic Aerosol from Alpha-pinene Ozonolysis. RAWAD SALEH, Allen Robinson,*Carnegie Mellon University*

Most chemical transport models assume instantaneous equilibrium to represent gas-particle partitioning of atmospheric aerosols. Recently, this approach has been challenged by studies which suggest that biogenic secondary organic aerosol (SOA) cannot reach equilibrium within atmospheric timescales. The emergent hypothesis is that evaporation/condensation rates are limited by the mass transfer rate (diffusion) within the condensed phase, which is thought to be “glassy”. There are two issues that might bias these findings: 1) they are based on measurement of evaporation rates (not equilibration time scales), which are sensitive to the assumption on SOA volatility; and/or 2) the SOA loadings are much higher than typical atmospheric conditions (hundreds of micrograms/m^3) .

Here, we investigate the equilibration time scales of SOA from alpha-pinene ozonolysis by measuring the dynamic response to a step-change in temperature (14 C to 30 C). Upon heating, equilibrium is disturbed, and the particles evaporate to restore equilibrium at the new temperature, which is said to be attained when evaporation ceases. This method requires no prior knowledge of volatility. Experiments were performed in a flow-tube, with SOA loading of 40-50 micrograms/m^3, and in a smog chamber, with SOA loading of 5 micrograms/m^3. Both experiments exhibited dynamic responses consistent with an accommodation coefficient on the order of 10^{-1}. For a wide range of typical atmospheric conditions, this translates into equilibration time scales on the order of 10 minutes.

4AC.6

Novel Experiments Give Quantitative Measure of Atmospheric Particle Viscosities. LINDSAY RENBAUM-WOLFF, Allan Bertram, Adam Bateman, Mikinori Kuwata, Scot Martin, *University of British Columbia*

Until recently it was assumed that atmospheric secondary organic aerosol (SOA) is liquid and bulk diffusion is fast and the models used to describe the formation of SOA in the atmosphere were developed based on this assumption. However, recent evidence suggests SOA particles may form amorphous solid or semisolid states under some conditions. While these recent experiments have provided qualitative evidence that SOA may be solid or semi-solid under some conditions, quantitative measures of the rate of bulk diffusion or the dynamic viscosity are needed in order to understand the atmospheric implications and to accurately model SOA processes. The small sample volumes associated with SOA collection present a major obstacle in quantifying particle viscosities. Here we describe a straight-forward method for the quantification of particle viscosities at various relative humidities with implications for atmospheric models and atmospheric processes.

4AC.7

Comparison of Heterogeneous Oxidation Products of Branched and Normal Alkanes, as Characterized by Two-dimensional Gas Chromatography with Vacuum Ultraviolet High-Resolution Time-of-Flight Mass Spectrometry. CHRIS RUEHL, Theodora Nah, Gabriel Isaacman, David Worton, Arthur Chan, Katheryn Kolesar, Christopher Cappa, Allen H. Goldstein, Kevin Wilson, *Univeristy of California, Berkeley*

Previous research has shown that the molecular structure of alkanes (i.e., degree of branching and cyclization) influences the rate at which they are oxidized in the gas phase. The importance of molecular structure in heterogeneous oxidation is more complicated, however, because it may involve the distribution of phases within the particle (e.g., bulk-surface), particle viscosity, and/or distinct secondary (radical-propagating) reactions. We generated submicron particles composed of either squalane, n-octacosane, or n-triacontane, three saturated alkanes of similar volatility but different degrees of branching, and oxidized them in a NOx-free flow-tube photo-reactor. We characterized the molecular composition of the products using two-dimensional Gas Chromatography, with High-Resolution Time-Of Flight Mass Spectrometric detection utilizing Vacuum UltraViolet photoionization (GCxGC/VUV-HRTOFMS). This soft ionization technique permits detection of the parent ion; along with high resolution, which distinguishes between different compounds with the same nominal molecular mass, GCxGC/VUV-HRTOFMS allows for a more complete set of molecular product identifications than previously reported, including precursors with up to four oxidized carbons (up to two each of alcohols and carbonyls). In addition, we identify many of the smaller molecules that are products of fragmentation reactions. We report the relative yields of these compounds over a range of 0.25 to 6.6 hydroxyl radical lifetimes, to determine the influence of alkane branching on heterogeneous oxidation. We found that overall, the branched alkane (squalane) oxidized more rapidly than the normal alkanes. Oxidation of branched and normal alkanes led to comparable carbonyl functionalization. However, while hydroxyl functionalization was also important for the branched alkane, it was strongly suppressed for the normal alkanes. Furthermore, fragmentation reactions were much more prevalent for the branched alkane precursor. These results suggest that alkane branching allows for a wider range of heterogeneous photooxidation pathways, while alkanes containing only primary and secondary carbons (e.g., n octacosane) predominantly form ketones and aldehydes without fragmentation during heterogeneous photooxidation.

4AN.1

Computational Chemistry of Condensing and Clustering Vapors. THEO KURTEN, Neil Donahue, Ditte Linde Thomsen, Henrik Kjaergaard, Joseph Lane, Solvejg Jørgensen, Hanna Vehkamäki, *University of Helsinki*

According to current best knowledge, the formation and growth of atmospheric aerosols involves both oxidized sulfur compounds (mainly sulfuric acid), reduced nitrogen and nitrogen-carbon compounds (mainly ammonia and amines), and carbon compounds of varying oxidation states. Aerosol processes thus couple together the atmospheric parts of the biogeochemical sulfur, nitrogen and carbon cycles. Though much new information has been gained during the past years about the clustering processes responsible for the first steps of atmospheric new-particle formation, several important questions about the chemical sources and sinks of the participating condensing vapors still remain unanswered. Computational chemistry is a useful tool for answering these questions.

For example, our recent quantum chemical calculations, later verified by experiments, have shown that the reaction of Criegee Intermediates (carbonyl oxides) with sulfur dioxide is likely a major (and hitherto unaccounted for) source of gas-phase sulfuric acid. Carbonyl oxides may also play a role in the oxidation of central nitrogen compounds such as amines, though this reaction has not yet been studied much. Quantum chemical modeling is also improving our understanding of the alkene ozonolysis reactions responsible (among other things) for the formation of carbonyl oxides. However, many of the intermediates of the ozonolysis reaction chain have quite complicated electronic structures, and care must be taken in choosing computational methods appropriate to the task.

All these reactions may further be affected by clustering e.g. with water molecules, though our recent calculations indicate that water catalysis in the atmosphere may be less prevalent and important than suggested by some studies.

4AN.2

Equilibrium Size Distributions of Neutral and Negatively Charged Sulfuric Acid-Water Clusters from Self-Consistent Thermodynamic Tables. JAMISON A. SMITH, Karl D. Froyd, Owen B. Toon, *University of Colorado*

We are interested in creating a thermodynamic database of the association reactions for molecules involved in the nucleation of new atmospheric particles. We start with the simplest system of sulfuric acid and water, with the idea that once we have a framework for this simple system, the framework can be expanded to include other pertinent molecules.

Tables of reaction enthalpies and entropies are constructed from existing experimental measurements, quantum chemical calculations and classical thermodynamic models. Initially, this two-dimensional patchwork of Gibbs free energy is not self-consistent. For example, the Gibbs energy of formation of a cluster containing two water molecules and one sulfuric acid molecule depends on the path taken: associate two waters and then associate the acid or associate one water and one acid and then associate the second water. We enforce self-consistency on the Gibbs free energy surface by assuming a correction exists for every association reaction, and the corrections are minimized via the method of Lagrange multipliers. As such, self-consistent Gibbs free energy surfaces have been generated for the neutral clusters and the negative ion clusters.

Once the Gibbs free energy surfaces are self-consistent, the equilibrium size distributions for neutral and negative ion clusters are solved simultaneously for a variety of atmospheric conditions. In addition, energy barriers to nucleation are presented for the neutral and negative ion clusters for various atmospheric conditions.

4AN.3

Structure and Energetics of Uncharged Sulfuric Acid Clusters with Ammonia and Amines. JOSEPH DEPALMA, Douglas Doren, Murray Johnston, *University of Delaware*

Experimental and computational work has suggested amine substitution occurs favorably into charged ammonium bisulfate clusters of either polarity, implicating amines as a potential channel for new particle formation and growth. The energetics of amine substitution has been explained by a combination of cluster structural features, binding energies, and molecular gas phase basicity (DePalma et al., J. Phys. Chem., 2012). Yet in the atmosphere, the majority of clusters are uncharged. Uncharged clusters are more difficult to study experimentally, making computation an indispensible tool for characterization. The work to be presented here examines the structure, energetics, and reactivity of uncharged clusters of sulfuric acid with ammonia and dimethylamine using quantum mechanics. Clusters were studied with both classical numerical sampling and varying levels of quantum chemistry. Preliminary results suggest that uncharged clusters have structural features akin to both positively charged and negatively charged clusters of similar composition, and that these features are size dependent. Cluster binding energies are similar in magnitude to positively charged clusters of similar size. Amine substitution for ammonia appears to be favorable, with values comparable to positively charged clusters. While bisulfate anions are preferentially formed in small clusters, sulfate anions become more prevalent as the cluster size increases. The role of explicit hydration of uncharged clusters and its effect on structure, binding, and amine substitution is also being explored. Computational results will be discussed in the context of likely cluster growth pathways in the atmosphere.

4AN.4

Insights from Cluster Thermodynamics: Atmospheric Conditions that Promote Nucleation for a Variety of Neutral and Ionic Systems. KARL D. FROYD, *National Oceanic & Atmospheric Administration*

In this presentation we summarize the viability of several atmospheric chemical systems to generate atmospheric nanoparticles from molecular clusters. Positive ion, negative ion, and neutral cluster systems comprised of sulfuric acid and water, with and without ammonia, are considered. Step-wise association reaction energies are determined starting from bare monomers and continuing up through stable nanoparticles. For the smallest clusters, where thermodynamics most strongly influence the nucleation potential, association reaction energies are determined using experimental measurements and selected quantum chemical calculations from literature. Large, bulk-like nanoparticle energies are calculated using classical theory. Energies for the intermediate transitional clusters are determined by connecting the two approaches with globally consistent functions. The growth of molecular clusters into nanoparticles becomes thermodynamically favorable when the free energy surface contains a growth trajectory that has little or no uphill step, i.e., no energetic barrier to nucleation. Barrier heights, critical cluster compositions, and the overall potential for nucleation vary enormously between systems and as a function of precursor concentrations and temperature. Most of the binary and ternary mechanisms considered here achieve barrierless growth under conditions relevant to some region of the troposphere. The effect of amines and organic species are estimated based on the limited available cluster stabilities. Gaps and uncertainties in the thermodynamic database are addressed, and the need for future experimental and theoretical studies is discussed.

4AN.5

First-Principles Molecular Dynamics Simulation of Sulfuric Acid - Ammonia/Dimethylamine Clusters. VILLE LOUKONEN, I-Feng William Kuo, Matt J. McGrath, Hanna Vehkamäki, *University of Helsinki*

Today, the modern aerosol particle measurement devices are continuously reaching smaller and smaller diameter sizes: they routinely see small molecular clusters, and, some can even reach down to individual molecules. Regardless of this rapid development, currently the only direct way to probe the very first steps of aerosol particle formation are various computational techniques based on quantum mechanics. Here, we present results from first-principles molecular dynamics simulations investigating the stability of small (sulfuric acid)$_n$ (ammonia)$_{n-1}$ and (sulfuric acid)$_n$ (dimethylamine)$_n$ clusters (n=2,3,4). When these gases are present in the atmosphere, the studied pre-nucleation embryos are likely to form and the dynamics of these clusters will in part determine the dynamics of particle formation.

In these simulations the thermal motion of the molecules was taken explicitly into account. We found that the stability of the clusters is dependent on the hydrogen bonding patterns the molecules are able to form. Also, even after an equilibrium bonding pattern had emerged, the clusters showed pronounced bond rearrangement: the bonding patterns stayed the same, but the individual atoms forming the bonds changed, i.e. the thermal energy kept the molecules rotating. Regardless of this behaviour, the clusters remained bound together.

4AN.6

Nucleation Free Energy Landscapes: Sensitivity to Force Fields and Influence of Salt Nanoparticles.

SAMUEL KEASLER, Christopher Hogan Jr., Ilja Siepmann, *University of Minnesota*

Nucleation free energy (NFE) landscapes provide detailed information on the pathway of nucleation processes. Advanced Monte Carlo algorithms allow for the precise determination of the NFE landscape. Such computed NFE landscapes are known to be very sensitive to details in the force field used to described the intermolecular interactions. Using the unary nucleation of water as an example, it is shown that the sensitivity of the NFE profile to the force field can be dramatically reduced by comparing the simulation results at the same reduced temperature and supersaturation instead of the same absolute temperature and absolute pressure (or number density). That is, the phase diagram is much more sensitive to details of the force field than the nucleation process. The aggregation of water onto salt nanoparticles is an important process in atmospheric chemistry, yet efforts to better understand it have been hindered by the difficulty of isolating and characterizing the small transient clusters involved. Monte Carlo simulations are carried to probe the nucleation of water around Na_nCl_m nanoclusters. The effect of size and charge on the NFE landscape are discussed.

4AN.7

Molecular Dynamics Simulations of Aqueous-Organic Binary and Ternary Nanodroplets.

Fawaz Hrahsheh, GERALD WILEMSKI, *Missouri University of Science and Technology, Rolla MO*

The structure of nanodroplets plays an important role in many natural and technological processes including particle nucleation and growth and aerosol formation in the atmosphere. Among other factors, chemical miscibility and surface tension strongly affect the structure of multicomponent nanodroplets at low temperature. Here, we investigate the structure of water/butanol, water/nonane, and water/butanol/nonane nanodroplets using molecular dynamics (MD) simulations. Each binary system has a bulk miscibility gap that strongly influences nanodroplet structure. Our MD results confirm several of our previous theoretical predictions of structures for binary nanodroplets using density functional theory and lattice Monte Carlo techniques: Core-shell and well-mixed structures are found for water/butanol nanodroplets, while nonspherical, phase-separated Russian Doll (RD) structures occur for water/nonane nanodroplets at all temperatures studied, 220K – 300K. In the ternary nanodroplets, butanol plays the role of a surfactant that forms a thin interface surrounding the aqueous region of the droplet. Depending on the nonane concentration, two types of structures were found. At high nonane levels, an onion-like, spherically symmetric structure occurs with nonane completely wetting the butanol interface that covers the inner aqueous core. When the nonane content is reduced below a critical level, the droplet consists of a lens shaped nonane region that only partially wets the spherical water/butanol core-shell giving rise to an overall nonspherical RD structure. These different structures may have a strong effect on the contribution of water to the ternary droplet growth rate.

4CH.1

Aerosol Test Particles with DNA Barcodes. RUTH N. UDEY, Elizabeth K. Wheeler, Brian R. Baker, A. Daniel Jones, George R. Farquar, *Lawrence Livermore National Laboratory*

Novel test particles containing DNA barcodes for airborne particle transport studies have been created that are universal, safe, and biodegradable. Materials currently available for indoor transport monitoring are limited as they may only be used for one test, after which the environment is contaminated. These new test particles are easily customizable by adding different DNA molecules as unique identifiers. These particles are also safe as they are constructed from FDA-approved food additives. These customizable aerosol test particles will provide vital experimental feedback for evaluating atmospheric and particle transport models.

These novel particles are principally made of FDA-approved, Kosher certified saccharide food additives, including glucono-delta-lactone, mannitol, trehalose, and maltodextrin. Several non-coding DNA templates were incorporated into the particles and were detected using highly specific quantitative real-time polymerase chain reaction (qRT-PCR) assays. Two different technologies, a modified commercial inkjet printer and a commercial spray dryer, were evaluated for particle production. The inkjet printer offered low-cost, rapid production of small quantities for optimization studies, and the spray dryer generated grams of particles appropriate for atmospheric studies. The physical properties of the particles were evaluated using SEM and APS. The number of DNA copies/particle on average was determined by collecting particles on a glass coverslip, counting them using microscopic image analysis, and eluting them into solution for qRT-PCR quantitation.

The physical properties of the saccharide materials (e.g. glass transition temperature) were optimized by combining the sugars in varying ratios in order to produce a free-flowing powder. The resulting test particles had spherical morphology and were size-tunable between 1 and 10 micrometers by varying solution concentrations and particle production parameters. The saccharides did not interfere with the accurate qRT-PCR quantitation of the DNA. The mean number of DNA copies/particle was also tunable depending on the amount of DNA added.

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4CH.2

The Multiwavelength Aerosol Signature Testbed for BSL3 (MAST-3) Program. JONATHAN RICHARDSON, Robert Martinez, Joseph Lacirignola, Edward Froehlich, Andreas Gennis, Richard Vanderbeek, Mary Wade, Todd Sickler, Amber Prugh, Kevin Hung, *MIT*

Biological attack remains a clear and present threat to our military and homeland. Detection of bio-aerosol threats by optical means has the advantages of being rapid and low maintenance, require no reagents. Such methods rely on the optical properties of the bio-aerosols themselves, which depend primarily on the class (spore, virus, toxin, etc.) and comingled materials (residual growth media, etc.) present. In the case of wet-generated aerosols, the environmental conditions (e.g., relative humidity) are also important. This work will describe a new apparatus for measuring the optical properties of benign and malignant bio-aerosols under a wide range of growth and environmental conditions called the Multi-wavelength Aerosol Signature Testbed (MAST). The Phase 1 version of MAST has been involved in a signature measurements program for the past year at the Edgewood Chemical and Biological Center (ECBC), where it is located in a secure biosafety level 3 laboratory. This version of the MAST includes 355nm and 1550nm polarimetric scatter and 355nm spectroscopic fluorescence channels, all fiber-coupled. The apparatus fully contains the aerosol challenges and can be decontaminated in-place for periodic maintenance. In this presentation, we will describe the aerosol generation and optical system and discuss our ongoing program, in which we are developing our next generation apparatus.

4CH.3

High Temperature Short-Time Infrared Disinfection of Bioaerosols. BRIAN DAMIT, Chang-Yu Wu, *University of Florida*

With growing concerns about bioterrorism and flu pandemics, the control of pathogenic bioaerosols has been given increasing attention. Recently, researchers have investigated the use of high temperature short-time (HTST) treatment to control bioaerosols. Although HTST treatment was shown to be effective, previous studies had the limitations of insufficient detection, inadequate temperature exposure characterization, and impracticality. To address these issues, a bioaerosol disinfection technology which uses infrared (IR)-generated HTST treatment was developed in this study. With this technology, bioaerosols were uniformly subjected to ultra-high temperatures (> 450 C) for just milliseconds.

The system consisted of a porous activated carbon cloth which was positioned normal to bioaerosol-laden air flow. The low pressure drop cloth was absorptive to IR and was readily heated by IR irradiation. By using a 250-W IR bulb, cloth temperatures in excess of 450 C were achieved in a few seconds for a face velocity of 5.3 cm/s. With this face velocity, the bioaerosol residence time in the pores of the heated cloth was 2 ms. Escherichia coli and MS2 virus were tested to represent pathogenic bacteria and virus bioaerosols respectively. The test microbes were aerosolized and downstream concentrations were sampled with and without HTST treatment.

With HTST treatment, greater than 99.99% and 99.999% efficiency was achieved for virus and bacteria respectively. This proved that bioaerosols can be inactivated in milliseconds provided sufficient temperature. A lower face velocity resulted in greater inactivation due to higher cloth temperature and increased residence time in the cloth. Unlike other studies where large heating coils were used, the IR technology forced bioaerosols to pass through the cloth pores and thus very close to the super-heated cloth fibers. In this case, the bulk flow did not need to be heated. The results demonstrate the potential of the IR technology in reducing viable bioaerosol concentrations.

4CH.4

Collection of Aerosolized Bacterial Endospores from Post-Explosion/Combustion Air Environments. SERGEY A. GRINSHPUN, Michael Yermakov, Reshmi Indugula, Atin Adhikari, Tiina Reponen, *University of Cincinnati*

If a bio-weapon facility is accidentally or intentionally targeted, the bio-threat agent release to the atmosphere may lead to catastrophic consequences. Appropriate sampling methods need to be developed to assess bioaerosols in post-explosion/combustion air environments. In this laboratory-scale study, we tested five aerosol collection media, including four filter materials [Teflon, Polycarbonate, Mixed Cellulose Ester (MCE) and Gelatin] and a BioSampler. The objective was to investigate the effect of the collection media on bioaerosol samples exposed to different combustion products. A hydrocarbon fuel flame seeded with three fuel additives delivered to the burner from a powder disperser represented combustion environments. The air flow from the burner containing combustion products was directed to the exposure chamber, as well as a challenge bioaerosol (Bacillus endospores), generated by a Collison nebulizer, mixed with HEPA-filtered dry air, and charge-equilibrated. Endospores of two surrogates of Bacillus anthraces – B. subtilis var. niger (also referred to as B. atrophaeus or BG) and B. thuringiensis (Bt) – were tested. First, the endospores were collected on identical media to create “pre-loaded” samples. Some of them were exposed to combustion environments for a specific time period while others (controls) were exposed to an air flow with no combustion products in it. The spore viability was determined by analyzing the test and control samples. BG spores collected on the tested media were not significantly affected by the incoming combustion products if the sampling time was up to 1 min. A longer exposure could lead to a significant inactivation during collection. Testing Bt spores revealed a much more complex picture: the integrity of Teflon, Polycarbonate, and MCE filter samples was affected when combustion products contained aluminum. No similar effect was observed with either Gelatin filters or the BioSampler. The study findings will help distinguish the biological inactivation in aerosol from that on collection media.

4CH.5

Use of Atmospheric Pressure Non-thermal Plasma for Rapid Bioaerosol Inactivation. Yan Wu, Yongdong Liang, Ke Sun, Qi Chen, Fangxia Shen, Jue Zhang, MAOSHENG YAO, Tong Zhu, Jing Fang, *Peking University*

Here, non-thermal plasma generated by a dielectric barrier discharge(DBD) system was applied to inactivating aerosolized Bacillus subtilis cells and Pseudomonas fluorescens as well as indoor and outdoor bioaerosols. The culturability, viability, and diversity losses of the microorganisms in air samples treated by the plasma for 0.06-0.12 seconds were studied using culturing, DNA stain as well as polymerase chain reaction-denaturing gradient gel electrophoresis (PCR–DGGE) methods. In addition, the viable fraction of bacterial aerosols with and without the plasma treatment was also quantified using qPCR coupled with ethidium monoazide (EMA).

It was shown that less than 2% of B. subtilis aerosols survived the plasma treatment of 0.12 s, while none of P. fluorescens aerosols survived. Viability tests, EMA-qPCR results and Scanning Electron Microscopy (SEM) images demonstrated that both bacterial species suffered significant viability loss, membrane and DNA damages. Exposure of environmental bacterial and fungal aerosols to the plasma for 0.06 s also resulted in their significant inactivations, more than 95 % for bacteria and 85-98 % for fungal species. PCR-DGGE analysis showed that plasma exposure of 0.06 s resulted in culturable bacterial aerosol diversity loss for both environments, especially pronounced for indoor environment. The results here demonstrate that non-thermal plasma exposure could offer a highly efficient air decontamination technology.

4CH.6

Experimental Study of Agglomerate Particle Filtration Using Flat Filter Media. QISHENG OU, Da-Ren Chen, *Washington University in St. Louis*

In various industrial production processes, particulate contaminants are an important issue that must be resolved. Among all the means of removing and/or separating particles from a gas stream, filtration is known as the most economical one for achieving high removal efficiency of fine aerosol particles. Because particle collection in filters is a very complex problem, in most of the studies of particle filtration, the particle shape is generally assumed to be spherical to avoid further complication. However, in reality, many particles are branch-like agglomerates composed of primary (nearly monodisperse) particles having diameters d_p=10-100 nm. These agglomerates may contain from a few up to thousands of such particles and span sizes from a few tens of nanometers up to several micrometers. Theoretical and experimental investigations on agglomerate particle filtration, especially the loading behavior, are scarce.

In this study, a series of experiments was performed to study the loading behavior of flat filters loaded with agglomerate particles. The testing particles were generated from a diffusion flame burner, in which both branch-like agglomerates with fractal dimension of ~1.8, and chain-like agglomerates with almost linear structure (fractal dimension approaching to 1.0) were synthesized using different precursors. The loading behaviors in both depth and transition filtration regime, as well as surface filtration regime were investigated for a variety of filter media. The detailed experimental result will be presented in the talk.

4CH.7

A Thermal Precipitator for Fire Characterization Research. MARIT MEYER, Victoria Bryg, *NASA Glenn Research Center*

Characterization of the smoke from pyrolysis of common spacecraft materials provides insight for the design of future smoke detectors and post-fire clean-up equipment on the International Space Station. A thermal precipitator was designed to collect smoke aerosol particles for microscopic analysis in fire characterization research. Information on particle morphology, size and agglomerate structure obtained from these tests supplements additional aerosol data collected. Initial modeling for the thermal precipitator design was performed with the finite element software COMSOL Multiphysics, and includes the flow field and heat transfer in the device. The COMSOL Particle Tracing Module was used to determine particle deposition on SEM stubs which include TEM grids. Modeling provided optimized design parameters such as geometry, flow rate and temperatures. Microscopy results from fire characterization research using the thermal precipitator are presented.

4IA.1

Ultrafine Particle Removal by Central Heating and Air-Conditioning Filters in a Test House. BRENT STEPHENS, Jeffrey Siegel, *Illinois Institute of Technology*

Much of human exposure to ultrafine particles (UFPs: particles less than 100 nm in diameter) often occurs indoors, particularly in residences. Central heating and air-conditioning (HAC) filters can be a primary removal mechanism for particles in indoor environments, depending on particle size, HAC system runtime, and filtration efficiency. Unfortunately, most filter test standards do not incorporate the measurement of UFP removal efficiency. Additionally, laboratory tests involve particle concentrations, compositions, face velocities, pressure drops, and climate conditions that do not necessarily reflect real indoor environments. Therefore, there remains a need to improve knowledge of UFP removal by HAC filters, particularly in residential environments.

This work utilizes a whole-house filter test method to measure the UFP removal efficiency of a range of commercially-available HAC filters in a test house. Size-resolved UFP measurements were made using a scanning mobility particle sizer. UFP concentrations were elevated by burning sticks of incense in the well-mixed house and the subsequent first-order decay of UFP concentrations was measured during three experimental conditions: 1) with the HAC system off, 2) with the HAC system on without a filter installed, and 3) with the HAC system on with a filter installed. HAC system airflow rates were measured, the building volume was estimated, and filtration efficiency was calculated using differences in loss rates between system and filter conditions. Three 1-inch depth filters (MERV 4, 6, and 11) and three 5-inch depth filters (MERV 10, 13, and 16) were tested. UFP removal efficiency ranged from less than 20% for MERV 4, 6, 10 and 11 filters to 50-80% for MERV 16 filters for most particle sizes. These results can help standards organizations adopt adequate filtration requirements for UFP removal.

4IA.2

Experimental Comparison of Dust Resuspension Using a Consistent Test Mechanism. YILIN TIAN, Kyung Sul, Jing Qian, Andrea R. Ferro, *Clarkson University*

Human walking influences indoor air quality mainly by resuspending particles that are settled on the floor. For this study, walking-induced particle resuspension was characterized as a function of flooring type, surface dust loading, relative humidity and particle size. Distinct from previous studies, a consistent test mechanism was utilized instead of human participant to eliminate the impact of varied walking style and facilitate a systematic comparison of the influencing factors. Five types of flooring, including hardwood, vinyl, high density cut pile carpet, low density cut pile carpet and high density loop carpet, were tested with two levels of RH (30-40% and 70-80%) and surface dust loading (2 g/m^2 and 8 g/m^2). Resuspension rate coefficients for house dust were found to vary from 10^{-4} h^{-1} to 10^{-1} h^{-1}, which is within the range of previous studies with actual human walking. The statistical analysis results show that flooring type has a significant effect on resuspension rate coefficient for all particle size bins measured, while surface dust loading is influential for particles less than 3.0 micron in size. When the results for all floorings are combined, RH itself shows little effect on particle resuspension because the direction of effect of RH is opposite for carpet and hard flooring. The interactions between RH and flooring type as well as RH and surface dust loading verify that RH should be taking into account.

4IA.3

Ozone-initiated Oxidation of Indoor Organics and its Potential Health Impact. Guang Zeng, Hai Pham, Vu Luong Duc, YONG LIU, *University of Colorado Denver*

Indoor air pollution has emerged as major environmental risks and health concern. Many pervasive household chemicals such as detergents and pesticides can adhere to indoor surfaces for extended periods after application and undergo heterogeneous interaction with ozone, contributing to poor indoor air quality. Reaction mechanisms and products of interfacial ozone chemistry are often highly complex and not well understood. This could become even more complicated considering variations of temperature and relativity humidity indoors. In this work, we employed an environmental cell coupled to an ATR-IR spectrometer to investigate ozone interfacial chemistry with neem oil and squalene and roles of indoor temperature and relativity humidity. Neem oil is a major component for houseplant pesticide and squalene is a main composition of skin oil, both of which have been found indoors. In our study, reactive uptake of ozone and reaction products in both gas and condensed phases were determined using ATR-IR, GC-MS and LC-ToF-MS. In addition, changes in redox activity were evaluated by DTT chemical assay. Results show the heterogeneous oxidation reactions proceed via ozone addition to unsaturated C=C bond in the organics to form primary ozonides, followed by carbonyl oxide formation. This can further react with carboxylic group, if available, to yield highly oxygenated peroxide compounds. Overall ozone reactive uptake is nearly independent of indoor temperature and relativity humidity. In contrast, temperature and relativity humidity play more important roles in affecting reaction product formation. Results also reveal that redox activity of organics are significantly enhanced upon ozone exposure due to the formation of oxygenated species, and such enhancement is nearly linearly dependent on the exposure time.

4IA.4

Formation, Morphology and Hygroscopic Growth of Indoor Aerosols Formed by Oxidation of Household Products. Andrew Hritz, Dabrina Dutcher, TIMOTHY RAYMOND, *Bucknell University*

In this work, we have characterized the heterogeneous formation of particles from typical household materials and solvents. Gas phase VOCs are known to react with oxidants such as ozone to form new particles. Other household objects such as the foam mats and pressed wood furniture are known to emit formaldehyde and related products for the duration of the product's lifetime. Chemicals such as formaldehyde are known to be irritants but less is known about how they contribute to particulate phase pollutants in household environments. Scented candles and air fresheners may also contribute significantly to indoor air pollution.

A smog-chamber was used to characterize the contribution of different household objects to particle formation. Our smog chamber consists of a one cubic meter Teflon bag. The rate, number and size concentration and other features of the particle formation were monitored by a scanning mobility particle sizer (SMPS) and optical particle counter (OPC). Additionally, the particles were collected and subsequently viewed on the atomic force microscope (AFM) and scanning electron microscope (SEM), depending on the particles' size. We also used a Humidity Tandem Differential Mobility Analyzer (HTDMA), in which produced particles were subject to elevated humidities and temperatures, such as those found in human airways, and changes in physical size of the particles were monitored. The tendency of organic particles to grow in humid conditions depends on the chemical composition of the particles and thus needs to be measured directly. The final physical size of the particles determines where in the human airway the particles are likely to be collected and has significant implications in determining the associated health effects.

Results of this work, including particle growth, size distributions, morphology, and hygroscopic properties will be presented along with comparisons of pure-component VOCs that were constituents of the household products.

4IA.5

Particle Detachment, Resuspension and Dispersion Due to Human Induced Flow Field in Gate Cycle. IMAN GOLDASTEH, Yilin Tian, Kyung Sul, Goodarz Ahmadi, Andrea R. Ferro, *Clarkson University*

Particulate matter (PM) is an important component of air pollution in the indoor environment. Among the sources of PM, particle resuspension from flooring during human walking contributes substantially to the concentration of particles larger than 1 micrometer. Earlier studies showed that high speed airflows generated at the floor level between the shoe and flooring during the gate cycle is the main reason of for particle resuspension. The details of the resuspension mechanism and the subsequent particle dispersion, however, are not well understood.
In this study a combined experimental and computational studies were performed to shed light on the mechanisms of particle detachment from flooring during the gait cycle and the corresponding resuspesnion and dispersion in indoor environment. A mechanical foot experimental set up was developed and used to measure the rate of resuspension for a range of conditions. The mechanical foot device mimics human walking and may be used to generate reproducible data for particle resuspension. In addition, a three dimensional numerical model of a shoe during the walking cycle was developed using the FLUENT^{TM} software. The Reynolds Averaged Navier-Stokes (RANS) approach in conjunction with the k-ε turbulence model was used for simulating the unsteady airflow field around the shoe during the gait cycle. To account for the real motion of the shoe, a user defined function (UDF) was developed and the dynamic mesh method was used. Particulate phase resuspension and dispersion was modeled using the Lagrangian particle tracking approach. Particle detachment was analyzed using the recently developed Monte Carlo resuspension model that was incorporated in the FLUENT code with the use of the UDF. Physical characteristics of particle/flooring morphology and material properties were taken into account in the model simulation. The resuspension of particles due to human walking was estimated and the results were compared with the experimentally measured particle concentrations. It was shown that the computational model predictions are in good agreement with the experimental data.

4IA.6

Identifying the Indoor Particle Resuspension Mechanism for Human Walking. KYUNG SUL, Iman Goldasteh, Pooya Kabiri, Douglas Bohl, Goodarz Ahmadi, Andrea R. Ferro, *Clarkson University*

Resuspension of settled particles via human walking is known to be a significant source of indoor particulate matter (PM). Previous studies found that resuspension rates from carpet are higher than those from hard floorings. However, the reason is not fully understood. In this paper, airflows around a shoe for different types of floorings were studied in order to understand the differences in the associated aerodynamics. A mechanical foot experimental setup was used as a standardized resuspension device to study the resuspension mechanism during the gait cycle. The device replicates the motion of the shoe during the walking, and repeats identical cycles so that the data are reproducible. Particle image velocimetry (PIV) was used to evaluate the instantaneous airflow around the shoe during the gait cycle. Olive oil was used to seed airflow for PIV measurements. A plane of particle-laden airflow around the shoe was illuminated by a laser light sheet and consecutive images of the plane were captured while the mechanical foot device was operating. Synchronization and phase averaging approach were used for generating the instantaneous airflow velocity for different shoe configurations in the gait cycle. The PIV experiments were conducted for two types of floorings (hard flooring and carpet). The resulting airflow velocities were compiled and analyzed and the effects of different floorings were studied. In addition, a three dimensional computational model of the airflow around the shoe was developed using the FLUENT^{TM} computational fluid dynamics (CFD) package. A RANS approach with the RNG k-epsilon turbulence model was used for simulating the airflow field during the gait cycle. The induced airflow during the shoe motion was investigated numerically using the dynamic mesh approach. The PIV data for different case were compared with the CFD model results, and good agreement was found.

4IA.7

Effect of Store Type, Location and Season on the Microorganisms Captured in HVAC Filter Dust Recovered from Retail Facilities. ANDREW HOISINGTON, Juan Pedro Maestre, Sungwoo Bae, Jeffrey Siegel, Kerry Kinney, *The University of Texas at Austin*

Exposure to airborne microorganisms in U.S. retail stores has not been well characterized even though approximately 10% of the workforce is employed in the retail sector and approximately 40% of Americans visit a retail store on average each day. In this study, the airborne microorganisms captured on the dust in heating, ventilation and air conditioning (HVAC) filters recovered from 14 stores in Texas and Pennsylvania were delineated using a variety of culture-independent methods including 454-sequencing and quantitative polymerase chain reaction (qPCR). Four store types were investigated including home improvement, grocery, furniture and general merchandise. Two of the retail stores were visited in four seasons and four stores were sampled in alternate seasons. In each store, a clean filter was placed in an HVAC unit recirculating indoor air for a period of 30 days, after which the DNA in the HVAC dust was extracted for analysis.

The results to date indicate that the bacterial microbiome in the retail stores does not aggregate by store type; however, the diversity of microorganisms present is a function of store type with increased diversity present in grocery stores. The lowest diversity was found in a furniture store. Seasonal differences were observed for some stores but not for others. The most significant differences with respect to location were observed in the fungal microbiome with the dominant organisms present at the TX location not present in the microbial DNA recovered from the PA location. In addition, the bacterial and fungal communities have dissimilar beta-diversity indices across the same stores indicating that a priori knowledge of the one community is not sufficient to describe the other community. The results indicate that a robust bacterial and fungal community is captured in HVAC filters and these filters provide a time-integrated measure of the microorganisms present in the retail environment.

4IM.1

Characterization of Organic Aerosol Using Electrospray Ionization Coupled to Ion Mobility Spectrometry High-Resolution Time-of-Flight Mass Spectrometry (ESI-IMS-HR-TOFMS). JASON SURRATT, Ying-Hsuan Lin, Joel Kimmel, Manjula Canagaratna, Richard Knochenmuss, Douglas Worsnop, *University of North Carolina at Chapel Hill*

Organic aerosol (OA) has chemical properties comparable to that of the metabolome. Specifically, both have organic constituents with molecular weights below 1,000 Daltons containing numerous isomers and isobars with varying polarities and functional groups. As a result of this complexity, the full chemical characterization of both systems is a tremendous challenge when using existing analytical techniques such as reverse-phase liquid chromatography (LC) coupled to ESI-MS. Recent work in metabolomics has utilized ion mobility spectrometry (IMS) coupled to ESI-MS for the chemical characterization of small organic compounds similar to those constituting OA. These applications demonstrate the method’s rapid multidimensional separation capabilities and suggest its potential for increasing our knowledge on OA composition and formation mechanisms. IMS portion of this technique separates ions on the basis of their size/charge ratios and their interactions with buffer gases on millisecond time scales. This is analogous to LC or GC techniques; however, these traditional approaches require longer acquisition times. Importantly, during this presentation we will demonstrate the advantages of ESI-IMS-HR-TOFMS over existing off-line techniques for the chemical characterization of fine OA samples collected from both smog chamber and field studies. These advantages include: (1) separation of isobaric and isomeric OA constituents (2) improved chromatographic resolution relative to LC; (3) identification of water-soluble OA constituents not resolved by LC; (4) controlled fragmentation of all parent ions for structural analysis, with no prior knowledge of sample composition (5) improved molecular identification of aerosol constituents via accurate mass analysis of peaks in the high resolution two-dimensional spectra . These advantages demonstrate the possibility of developing ESI-IMS-HR-TOFMS as an online chemical characterization method for OA studies. Disadvantages of this technique will also be discussed when compared to existing techniques.

4IM.2

Atmospheric Amine Measurements with CI-APi-TOF. TUIJA JOKINEN, Mikko Sipilä, Heikki Junninen, Mikael Ehn, Gustaf Lönn, Jani Hakala, Roy Lee III Mauldin, Tuukka Petäjä, Markku Kulmala, Douglas Worsnop, *University of Helsinki*

Nucleation is one of the main sources of cloud condensation nuclei (CCN) contributing up to 50% to the global CCN budget. The initial steps of nucleation require the presence of sulphuric acid (SA) but additional vapours are needed because SA does not nucleate itself. Ammonia and dimethylamine (DMA) are found from charged clusters formed by ion induced nucleation and the conclusion is that amines are plausible candidates for stabilizing neutral clusters. Even ppt levels of amines can be enough to account for atmospheric nucleation rates.

We present the first ambient amine measurements using a Chemical Ionization APi-TOF (CI-APi-TOF). We used a special inlet for charging and acetone for the chemical ionization. In this experiment acetone was ionized using a bipolar charger to create positively charged acetone ions and clusters. In the proton transfer reaction only compounds that have higher proton affinity than the reagent ions will get charged and detected by the APi-TOF.

The data analysis is still ongoing and these results are preliminary. We identified amine clusters by their exact masses and isotope patterns. Two signals have been identified to correspond to common aliphatic amines. These signals are $C4H12N+$ (DMA) and $C6H16N+$ (triethyl amine). We can also demonstrate SA concentration anti-correlating with the amine signals. During a nucleation event, when SA concentration reaches its maximum, we only see a minimum amine signal. This may indicate that amines are reacting and/or clustering with freshly forming SA molecules.

This setup has a few disadvantages that need to be further developed. First, one of the most interesting amine signals, trimethyl amine, is overlapped with the acetone isotope signal. Second the inlet design needs to be improved to consume less chemicals and the reagent ion may have to be changed before quantitative analysis of atmospheric amines can be done using the CI-APi-TOF.

4IM.3

Direct Surface Analysis of Size- and Time- Resolved Organic Aerosol. STEPHEN FULLER, Markus Kalberer, Yongjing Zhao, Anthony Wexler, *University of Cambridge*

Ambient aerosol particles have been shown to have significant health and climate implications. Studies of the chemical composition of aerosol particles are important to establish the mechanisms of their reactivity. However the aerosol composition, especially the organic fraction is highly variable with both time and the particle size fraction concerned. Combining a rotating-drum impactor with Liquid Extraction Surface Analysis (LESA) - mass spectrometry allowed the study of separate size fractions collected over a 2-week period in May 2011 from a dairy farm in California to be analysed with a 40-minute time resolution using a high-resolution mass spectrometer for organic species identification.

LESA is a mode of operation of the electrospray NanoMate source (Advion) for mass spectrometers. A small amount of solvent is dispensed with a pipette tip on the surface of the sample; the micro liquid junction is maintained to allow analytes present on the surface of the sample to dissolve. The droplet is then aspirated and sprayed via an infusion method utilising the chip based electrospray ionsation. An ultra-high-resolution mass spectrometer was used determine the molecular formulae of the organic compounds found during the sampling period. The organic composition of particles in the two size fractions 2.5-1.1 and 0.3-0.09 micro-meters were investigated. The smaller size fraction was found to have higher nitrogen content, while the larger fraction higher oxygen content. The high time resolution achieved with the LESA technique allowed performing correlation analyses of the intensity variations for groups of compounds over the sampling period and groups of compounds with potentially the same source could be identified. This demonstrates that the combination of the RDI and LESA can be used for semi-quantitative analysis of organic components in ambient samples, with a high time resolution.

4IM.4

Introducing the Volatility and Polarity Separator (VAPS) for Total Organic Aerosol Characterization. RAUL MARTINEZ, Brent Williams, Yaping Zhang, Peter Mellott, Nathan Kreisberg, Susanne Hering, David Worton, Allen H. Goldstein, Thorsten Hohaus, Manjula Canagaratna, Donna Sueper, John Jayne, Douglas Worsnop, *Washington University in St. Louis*

Discrepancies between modeled and measured atmospheric organic aerosol (OA) have shown the need for real-time instrumentation that can characterize this material throughout its evolution in the atmosphere. Such an instrument must provide a high level of chemical separation with high time resolution, while maintaining near complete mass closure. Here, we propose and introduce the Volatility and Polarity Separator (VAPS) for such measurements. This novel instrument combines thermal desorption for volatility separation with short gas chromatography for polarity separation, and final detection using high-resolution time-of-flight mass spectrometry. The multi-dimensional space of volatility separation, polarity separation, and high resolution mass spectra will distinguish key chemical characteristics such as the oxygen-to-carbon (O:C) ratio and hydrogen-to-carbon (H:C) ratio of OA as a function of volatility and polarity, and allow identification of particle source markers. Laboratory and ambient measurements will be presented to explore this technique’s capability of reporting the atmospheric evolution of volatility- and polarity-resolved OA.

4IM.5

Advanced Analysis Procedures of Ambient Organic Aerosol from Thermal Desorption – Mass Spectrometry Measurement Techniques. YAPING ZHANG, Brent Williams, Raul Martinez, Manjula Canagaratna, Douglas Worsnop, Allen H. Goldstein, Ingrid Ulbrich, Donna Sueper, Jose-Luis Jimenez, *Washington University in St. Louis*

The feasibility of a simplified method to analyze thermal desorption aerosol gas chromatography (TAG) data was investigated. Chromatograms were divided into many "volatility" bins containing total eluting mass (both unresolved complex mixture (UCM) and resolved species). Positive Matrix Factorization (PMF), a factor analysis technique, was applied to compare the results between bin-based and peak-integrated methods using the TAG data in 2005 Study of Organic Aerosol at Riverside (SOAR). We found the procedure of bin-based method to take only a small fraction of the time to complete compared to peak-integrated method, significantly saving the operator time and effort. Many factors in the peak-integrated method had good correlations (R>0.5) with factors in the bin-based method. Here we explore the differences and similarities amongst our results. The bin-based method is a promising method of rapid analysis for chromatography data for the purpose of source apportionment and transformation mechanisms of atmospheric aerosols.

Additionally, automated preprocessing and analysis procedures for a new thermal desorption-mass spectrometery technique, volatility and polarity separator (VAPS), has been explored. IGOR software was used as the platform of the procedure. The automated preprocessing procedures contain auto retention time shifting, auto binning of volatility and polarity, auto internal standards mass calibration, and auto error matrix calculation and PMF export. Four datasets — simulated VAPS data, 15 mixture standards, biomass burning aerosol from custom combustion chamber, and ambient atmospheric data collected on the campus of Washington University in St. Louis — were tested through the automated preprocessing and analysis procedures. It has been proven to be an effective method for fully automated analysis and interpretation of VAPS data.

4IM.6

A Hybrid Impactor-Filter Collector Extends Semi- and Non-volatile Organic Aerosol Speciation by Thermal Desorption Aerosol Gas Chromatography (TAG). NATHAN KREISBERG, Yunliang Zhao, Chris Ruehl, Allen H. Goldstein, Susanne Hering,*Aerosol Dynamics Inc.*

Interest in intermediate volatility and semi-volatile (I/SVOC) organic compounds has increased because of their role in secondary aerosol formation. Traditionally, organic speciation is performed using a combination of filters and adsorbents to collect the particle and gas phases. The in-situ, semi-continuous thermal desorption aerosol gas chromatograph (TAG) targets particulates using inertial impaction inside a thermal desorption cell in conjunction with GC/MS analysis. By design, the TAG does not efficiently collect semi-volatiles, therefore, a thermally desorbable, all-metal-filter collector targeting low polarity I/SVOCs was developed (see Zhao et al. this conference). The thermal desorption and transfer efficiency of this new filter cell is excellent for I/SVOCs but performs less well in recovering non-volatile organic compounds as compared to the impactor cell. Although minimized by passivation techniques, irreversible sorption of non-volatile organics to a surface contributes to sample loss in thermal desorption systems. The inherently larger surface area of the filter cell relative to the original impactor cell is largely believed to explain the difference in sample recovery of the least volatile species. To extend the range of recoverable species by the filter cell, a pre-impactor stage was designed to be coupled directly to the inlet of the new cell to impact particles onto its throat, thereby closely matching the collector geometry of the original impactor cell. Size dependent particle measurements of the isolated pre-impactor stage show comparable collection efficiency to the original 9-jet impactor cell. Increased sample recovery of non-volatiles relative to the non-hybrid cell is tested using ambient measurements, and the effect of vapor collection at reduced pressure is considered. A pair of matched filter cells – one with the pre-impactor and one without – is used to measure sample recovery differences for simultaneous parallel sampling of Berkeley, CA aerosols followed by staggered GC/MS analysis.

4IM.7

Influence and Efficiency of a Catalytic Stripper in Organic Carbon Removal from Laboratory Generated Soot Aerosols.

JELICA PAVLOVIC, John Kinsey, *ORISE U.S.EPA*

A catalytic stripper (CS) is a device used to remove the semi-volatile, typically organic carbon, fraction by passing raw or diluted exhaust over an oxidation catalyst heated to 300 degrees C. The oxidation catalyst used in this study is a commercially available diesel oxidation catalyst (DOC), designed to remove volatile hydrocarbon from the diesel exhaust by oxidizing the volatile hydrocarbon species to CO2 and H2O (1).

The experimental system consisted of a soot generator, low speed flow tunnel, Scanning Mobility Particle Sizer (SMPS) instrument to monitor the number concentration as well as the size distribution, and a particulate matter (PM) mass measurement system. The PM mass concentration was measured by the filter sampling followed by the thermal/optical carbon analysis, multi-angle absorption photometry (MAAP), photoacoustic measurement, and laserinduced incandescence (LII). The responses of all instruments were evaluated with and without the CS to explore the efficiency of CS in removing the volatile particles. The specific emphasis was placed on the analysis of thermograms and OC and EC sub-fractions from the thermal/optical analysis, and the SMPS data, to gain deeper insights about the size and thermal characteristics of the OC removed by the CS as well as the OC and EC measured downstream of the CS. Influence of different inlet EC/OC ratios, different inlet soot concentrations, and position of the CS in the experimental system were also investigated.

1. Khalek, I. A. (2007). Sampling system for solid and volatile exhaust particle size, number, and mass emissions, SAE Paper 2007-01-0307, Society of Automotive Engineers, Warrendale, MI.

4UA.1

Aerosol Composition at a Rural Site Southeast of London Measured by High Resolution Mass Spectrometry.

NGA LEE NG, Lu Xu, Matthew Kollman, John Jayne, Scott Herndon, William Brooks, Leah Williams, Paola Massoli, Edward Fortner, Puneet Chhabra, Timothy Onasch, Douglas Worsnop, *Georgia Institute of Technology*

A High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and complementary instrumentations are deployed at a rural site in Detling (southeast of London) during the Clear Air for London (ClearfLo) campaign from January – February 2012. ClearfLo is a collaborative multidisciplinary project to study boundary layer pollution across London. The HR-ToF-AMS provides quantitative measurement of non-refractory submicron aerosol composition and size distribution with high time resolution. Total mass concentrations and diurnal trends of organics, nitrate, sulfate, ammonium, and chloride at the Detling sampling site are reported. It is found that air mass from the East (continental Europe) is characterized by high loadings, especially high nitrate. As increasing distance from an urban center is often correlated with increasing photochemical aging, the aerosol mass spectrometry data at the Detling site provide insights into composition of a more oxidized air mass and the evolution of organic aerosols (OA) in the atmosphere. Elemental analyses are performed to determine elemental composition of the bulk OA, including oxygen/carbon (O/C), hydrogen/carbon (H/C), and nitrogen/carbon (N/C) ratios. Positive matrix factorization (PMF) is used to deconvolve the OA into different components, reflecting OA of different sources and/or photochemical processing. Preliminary PMF analysis resolved three factors: hydrocarbon-like organic aerosols (HOA, surrogate for POA) and oxygenated organic aerosols (OOA, surrogate for SOA), and biomass burning OA (BBOA). Analysis of thermodenuder data revealed the presence of very non-volatile SOA components, with a thermodenuder temperature of 250 oC, the compounds remaining has an O/C of ~1.

4UA.2

Optical Characterization of Aerosols at a Rural Site in Southeast England During the Winter ClearfLo Campaign. Paola Massoli, Allison Aiken, Kyle Gorkowski, Scott Herndon, Edward Fortner, John Jayne, William Brooks, LEAH WILLIAMS, Puneet Chhabra, Nga Lee Ng, Timothy Onasch, Jonathan Franklin, Mavendra Dubey, Douglas Worsnop, Andrew Freedman, *Aerodyne Research, Inc*

We present results on the optical characterization of aerosols during the ClearfLo (Clean Air for London) Intensive Operating Period that took place from mid-January to mid-February, 2012 at a rural site southeast of London, England. The site, situated at the Kent Showground in Detling, is located approximately 50 km southeast of central London. Over the course of the campaign, the sampled air masses were of local (from a motorway proximate to the site), regional (Thames Estuary) or distant (continental European) origin. Data were collected from two separate inlets that were outfitted with 2.5 micron cutoff impactors. The first inlet was routed to a CAPS PMex (Aerodyne Research, ARI) particle optical extinction monitor and a Multi-Angle Absorption Photometer (MAAP) (ThermoFisher), both operated a nominal wavelength of 630 nm. The second inlet was routed to a CAPS PMex monitor operated at 450 nm and a Photo-Acoustic Soot Spectrometer (PASS-3) (Droplet Measurement Technologies) which provided particle absorption at three wavelengths (780 nm, 532 nm and 405 nm). The second inlet also contained a provision for alternately routing the air sample flow through a ARI particle denuder operated at temperatures up to 250 ºC. Optical extinction, absorption and the calculated single scattering albedo (SSA) were measured at multiple wavelengths over a period of approximately three weeks. Extinction levels varied from 7 to 230 Mm-1; the absorption varied between 1 and 32 Mm-1. The SSA averaged ~ 0.85 over the study. Periods of relatively low aerosol loadings and low SSA (0.6) corresponded to air masses dominated by emissions from local sources (e.g., traffic). Instead, high extinction and absorption levels corresponded to outflow from continental Europe. The optical data presented here are discussed in a broader context and combined with results from the chemical composition information obtained from co-located ARI SP-AMS and HR-ToF aerosol mass spectrometers (AMSs).

4UA.3

Seasonal Comparison of Comprehensive Aerosol Measurements in London During ClearfLo. DOMINIQUE YOUNG, James Allan, Paul Williams, Michael Flynn, Dantong Liu, James Whitehead, Niall Robinson, Andre Prévôt, Suzanne Visser, Markus Furger, Martin Gallagher, Hugh Coe, *University of Manchester*

A suite of state-of-the-art instrumentation, measuring aerosols, gases, radicals and meteorological parameters was deployed as part of the Clean Air for London (ClearfLo) campaign for two major intensive observation periods (IOPs) during 2012 at a number of sites in and near London. Here we report measurements from the main ClearfLo urban background supersite located in the grounds of a school in North Kensington, London for both IOPs. The winter IOP occurred took place between 11 January and 8 February and the summer IOP took place in July and August, covering the 2012 Olympic period. Measurements took place during clean westerly conditions and polluted conditions when transported European plumes influenced the site.

Comprehensive measurements of size segregated aerosol chemical composition, microphysical properties, and optical properties were taken to obtain high-resolution data sets on aerosol composition in conjunction with black carbon properties and hygroscopicity. Instrumentation included a 7-wavelength Aethalometer, Aerosol Particle Sizer, Aerosol Particle Spectrometer with Depolarization, Condensation Cloud Nucleus counter, Differential Mobility Particle Sizer, GRIMM dust monitor, Hygroscopicity Tandem Differential Mobility Analyser, Multi Angle Absorption Photometer, PhotoAcoustic Soot Photometer, Single Particle Soot Photometer, and a Soot Photometer Aerosol Mass Spectrometer. In addition, a GRIMM dust monitor, a Wide Issue UV Fluorescence Bioaerosol Spectrometer and a Rotating Drum Impactor (RDI) were located on the container's exterior. RDI samples were subjected to Synchrotron Radiation induced X-Ray Fluorescence Spectrometry analysis to determine trace elemental composition. A compact Time-of-Flight Aerosol Mass Spectrometer (cToF-AMS) was deployed between January and August providing long-term measurements of aerosol chemical composition.

Preliminary data from both ClearfLo IOPs along with data from the long-term cToF-AMS measurements will be presented highlighting diurnal and seasonal characteristics of London urban background pollution. These data will be used to quantify the contribution by different urban activities in London to both local and regional air pollution.

4UA.4

Fog Processing of Particulate Molecular Marker Species. Jershon Eagar, Franz Ehrenhauser, Youliang Wang, James Hutchings, Aurelie Marcotte, Olivier Delhomme, Raghava Kommalapati, Mary Wornat, Kalliat Valsaraj, PIERRE HERCKES, *Arizona State University*

Fog and cloud processing of carbonaceous aerosol material can impact atmospheric concentrations of molecular species through scavenging, aqueous phase reactivity and/and depositional processes. In 2 recent field studies in Fresno (CA) and Davis (CA) the processing of organic species in particular so called molecular marker species, used in source apportionment studies was investigated. Pre- and post fog as well as interstitial aerosol samples were analyzed as well as the aqueous phase (fog) composition. Laboratory studies were conducted to investigate the reactivity of select species in the aqueous phase and identify reaction products and rate under common fog conditions.

Observational results show a differential scavenging of molecular marker species, suggesting selective scavenging of aerosols of some sources over of aerosols from different sources. The results and implications on atmospheric lifetimes will be discussed in detail. A relationship between scavenging efficiency and fog liquid water content, as suggested by earlier studies, could not be confirmed.

Laboratory studies on chrysene reactivity in fog conditions show a surprising diversity of reaction products and the results will be discussed relative to the field observations of the oxygenated daughter species.

4UA.5

Air Quality Impacts of a Scheduled 36-hour Closure of a Major Highway. DAVID QUIROS, Qunfang Zhang, Suzanne Paulson, Rui Wang, Wonsik Choi, Arthur Winer, Yifang Zhu, *University of California Los Angeles*

On the July 16-17, 2011 weekend, a major Los Angeles highway, the I-405, was closed 36 hours for an overpass demolition. During this event we measured ultrafine particles (UFPs, < 0.1 micro-meters) and other air pollutants upwind, downwind, and at various distances of the I-405 pre-, during-, and post-closure using both fixed site and mobile platform monitors. We observed ~90% and ~40% traffic flow reductions on I-405 during closure on Saturday and Sunday, and ~20% reductions on the immediately adjacent Sepulveda Boulevard. During-closure downwind particle number concentration (PNC) decreased 73%, mass concentration (PM2.5) decreased 44%, and black carbon (BC) decreased 48%. We found traffic density (vehicles distance) correlated well with downwind BC (R-square=0.71). Daily average particle size distributions downwind were bimodal with pronounced nucleation and accumulation mode peaks during non-closure conditions and unimodal with an accumulation mode peak during closure conditions on Saturday July 16. We compared our current data to a similar dataset from 2001 and found that, over this 10-year period, the downwind-to-upwind PNC ratio decreased ~40%, but weekday traffic flow increased ~20%. This translates into an ~50% PNC reduction per-vehicle from the I-405 transit corridor. We speculate this decrease may have been from reduction of sulfur content in diesel fuels (from 500 to 15 ppm in 2006), the increased California Low-Emission Vehicle standards, and retirement of older vehicles.

4UA.6

MOUDI Size-Resolved Measurements of Elemental and Brown Carbon and Their Contributions to Light Absorption Based on Mie Theory Calculations.

JIUMENG LIU, Michael Bergin, Rodney Weber, *Georgia Institute of Technology*

Black carbon is traditionally regarded as the primary light absorber at visible wavelengths, while brown carbon, defined as light absorbing organic matter with a strong wavelength-dependent absorption in UV and UV-Visible ranges, is thought to mainly impact atmospheric photochemistry. Size-resolved atmospheric aerosol samples were collected using Micro-Orifice Uniform Deposition Impactors (MOUDI) at a number of sites in Georgia. The samples were analyzed for water-soluble organic carbon (WSOC), organic carbon (OC) and elemental carbon (EC), as well as bulk light absorption spectra of both water and methanol extracts. Concentrations of OC and WSOC both exhibited bimodal distributions, with a small coarse mode (3.2-5.6 micro-meter) peak and a large fine mode (0.56-1 micro-meter) peak, while EC was found to be enriched in particles of smaller size (0.18-0.56 micro-meter). Bulk light absorption of the methanol extract at 365nm wavelength had a similar size distribution to that of water-soluble brown carbon with peaks in the fine mode between 0.32 to 1 micro-meter, but the methanol extract was generally a factor of two more light absorbing. Methanol extracts had generally smaller absorption Angstrom exponents, with a value of 5.1±0.3, compared with 6.7±0.6 for water extracts averaged over all particle sizes, indicating more light absorption to higher wavelengths than the water extract. The bulk light absorption measurements at a number of wavelengths were used to determine the refractive index of OC, and simple Mie theory was applied to predict the light absorption of brown carbon. This method was validated by an EC light absorption closure between MOUDI and online absorption measurements that were made by MAAP and multi-wavelength Aethalometer. Comparisons of predicted light absorption by brown carbon to total light absorption show that water and methanol-soluble brown carbon can be a significant fraction at 365nm.

4UA.7

Investigation of Ultrafine Particle Deposition onto Vegetation Branches in a Wind Tunnel.

Ming-Yeng Lin, Gabriel Katul, ANDREY KHLYSTOV, *Research Triangle Institute*

The deposition of UFP onto vegetated surfaces remains a major challenge to be confronted because of the multiplicity of approaches that account for the presence of vegetation. On the one hand, some approaches represent the vegetation as fibrous filters with a preferential size, while other conventional approaches represent the vegetation as a random porous medium. Using wind tunnel studies, the collection efficiency of UFP by pine and juniper at five different wind speeds, two branch orientations, and two packing densities was measured and analyzed using these two representations for the canopy. The experiments agreed well with predictions from filtration theory when the derived effective fiber diameters for pine and juniper are 0.054 (±0.001) cm and 0.065 (±0.001) cm, respectively, with the values in parentheses representing 95% confidence intervals. Moreover, it was found that the near-linear pressure drop across the vegetation can provide a first order estimate of the UFP collection efficiency, in agreement with the filtration theory. The predictions from porous media representations of the vegetation-air system also agreed well with the wind-tunnel measurements here. Upon bridging these two approaches, estimates of the effective fiber diameter can now be derived from conventional canopy attributes, such as the leaf area index. These results provide an alternative way for atmospheric models to characterize the properties of vegetation for UFP deposition calculations.

5AN.1

An Acid-Base Chemical Reaction Model for Nucleation Rates in the Polluted Boundary Layer. MODI CHEN, Mari Titcombe, Jingkun Jiang, Jun Zhao, Chongai Kuang, Ilja Siepmann, David Hanson, Peter McMurry, *University of Minnesota*

Nucleation is observed throughout the boundary layer, and evidence suggests it may affect global climate. Previous studies indicate that, in most cases, atmospheric nucleation rates vary in proportional to the nth (n is between 1 and 2) order of the sulfuric acid concentration, and are several orders of magnitude smaller than the sulfuric acid collision rate. The fundamental mechanism of atmospheric nucleation, though, remains unknown. In this work, a new conceptual model for nucleation in the polluted atmospheric boundary layer, involving a sequence of reactions between sulfuric acid and gaseous basic compounds (ammonia and amines), is proposed. This model is based on data from both a field study and a laboratory chamber study. These data indicate that the formation of clusters that contain two or three sulfuric acid molecules ("dimer" and "trimer") is the primary bottleneck for nucleation. The sulfuric acid vapor uptake rate of the tetramer cluster is found to be close to the collision rate. Our measurements show that basic gaseous compounds stabilize clusters, thereby enhancing nucleation rates. A closed form expression for nucleation rates in terms of the sulfuric acid and basic gas concentration is proposed. In this expression, nucleation rates vary approximately in proportion to the square of sulfuric acid concentration as has often been observed, and evaporation from dimer and trimer and coagulation losses are responsible for the smaller-than-one pre-factor. Nucleation rates obtained from previous field measurements (Mexico City 2006 and Atlanta 2009) are in reasonable agreement with values predicted by this model.

5AN.2

Dimethylamine-Sulfuric Acid Clustering Can Explain Observed Atmospheric New Particle Formation. Ismael Kenneth Ortega Colomer, Oona Kupiainen, Tinja Olenius, Matt J. McGrath, Theo Kurten, VILLE LOUKONEN, Taina Yli-Juuti, Ilona Riipinen, Johannes Leppä, Markku Kulmala, Hanna Vehkamäki, *University of Helsinki*

Despite the importance of atmospheric particle formation for both climate and air quality, non-empirical models have so far been unable to reproduce atmospheric observations using realistic trace gas concentrations. We have used a kinetic cluster model, together with first principles evaporation rates, to simulate the formation rate of sulfuric acid – ammonia – dimethylamine clusters with mobility diameter 1.4-1.6 nm. We have compared the results with state-of-the-art experimental values, and have found a good agreement with the observed formation rates. The presence of trace (sub-ppt) concentrations of dimethylamine together with atmospherically realistic concentrations of sulfuric acid results in formation rates close to those observed in the atmosphere. Additionally, we have found that the effect of galactic cosmic rays on new particle formation is negligible when amines are present, though it may still play a significant role in conditions where the concentration of cluster-stabilizing trace gases such as amines is low.

5AN.3

Flux Induced Growth of Sub-Kelvin Nano-Particles by Organic Vapor. JIAN WANG, Robert McGraw, Chongai Kuang,*Brookhaven National Laboratory*

New particle formation (NPF) in the atmosphere strongly influences the concentration of atmospheric aerosol, and therefore its impact on climate. New particle formation is a two-stage process consisting of homogeneous nucleation of thermodynamically stable clusters followed by growth of these clusters to a detectable size (> 3 nm). Due to the large coagulation rate of clusters smaller than 3 nm with the pre-existing aerosol population, for new particle formation to take place, these clusters need to grow sufficiently fast before being removed by coagulation. While some previous modeling and field studies have indicated that condensation of low-volatility organic vapor may play an important role in the initial growth of the clusters, it is suggested that due to the small size of the clusters, the strong Kelvin effect may prevent typical ambient organics from condensing on these clusters. Here we show that the particle number flux induced by the heterogeneous nucleation of organics vapor can effectively grow clusters substantially smaller than the Kelvin diameter, traditionally considered as the minimum size of particles that can be grown through condensation. Including this flux can lead to a factor of up to 60 increase in the predicted rates of new particle formation and the subsequent production of cloud condensation nuclei.

5AN.4

Using Simulated Particle Formation Events for Testing and Improving Event Analysis Tools. KARI LEHTINEN, Hannele Korhonen, Johannes Leppä, Veli-Matti Kerminen, *Finnish Meteorological Institute, Kuopio, Finland*

The analysis of new particle formation events may involve issues such as estimation of particle formation rates, nucleation rates, growth rates and fractions of ion induced and neutral nucleation, and, through application of the first nucleation thorem, an estimation of the critical cluster composition. These are typically done by analysing the initial particle (and ion, if possible) size distribution evolution right after particle formation, plus some assumptions. For example, the particle growth rate may be estimated by following the peak location of the nucleation mode, the formation rate by looking at the change in number concentration of some size range, say 3-6nm, and the critical cluster composition from the slope of log(formation rate) vs. log(vapor concentration).

In this work, we analyze some of the most widely used event analysis methods by first generating the particle formation events through computer simulation of all relevant aerosol microphysics and then analyzing them. Since we know ’the correct answers’, we can find out how the methods perform. In addition, with some tuning based on the simulation results as well as aerosol microphysics theory, we can improve some of the methods significantly. One such improvement is modifying the estimation of nucleation rate from the observed particle formation rate to include the effect of size dependent growth rate.

5AN.5

Potential Factors Limiting Growth of Nucleated Particles into Cloud Condensation Nuclei. DANIEL WESTERVELT, Jeffrey Pierce, Peter Adams, *Carnegie Mellon University*

Aerosol nucleation is an important source of particle number in the atmosphere. However, in order to become cloud condensation nuclei (CCN), freshly nucleated particles must undergo significant condensational growth while avoiding coagulational scavenging. Previous work used observationally-based constraints to determine that, even when accounting for multi-day growth, boundary layer nucleation contributes just 2-14% of the total number of particles larger than 100 nm in a variety of locations. This work builds on that finding by quantifying the feedbacks associated with the small nucleation-CCN sensitivity. Using the GEOS-Chem-TOMAS global aerosol microphysics model, we simulate 15 different nucleation and growth scenarios and analyze individual nucleation events over one simulated year. Nucleation rate parameterizations include ternary nucleation (with multiple tuning factors), activation nucleation (with multiple pre-factors), binary nucleation, and ion-mediated nucleation. In previous work, GEOS-Chem-TOMAS was thoroughly evaluated against observed nucleation events at five locations: Pittsburgh, Hyytiälä, Atlanta, St. Louis, and San Pietro Capofiume. In the present work we calculate daily nucleation rates, growth rates, coagulation sinks, condensation sinks, sulfuric acid concentrations, particle survival probabilities, and CCN formation rates between the 15 different nucleation and growth sensitivity cases. We hypothesize that our small CCN sensitivity is explained by faster nucleation rates leading to a larger sink of condensable vapors which in turn limits survival and growth to CCN. Quantitatively, we find that a factor of 36 increase in the annual average nucleation rate between two particular nucleation simulations at Hyytiälä leads to only a factor of 1.6 increase in CCN formation from nucleation and a 13% increase in total CCN concentrations. The dampening in CCN changes appears to be caused by an increase in the condensation sink and an accompanying decrease in growth rates and condensable vapor concentrations. Work is ongoing to test more sites and parameterizations.

5AN.6

Nanoparticle Chemical Composition During New Particle Formation. BRYAN R. BZDEK, M. Ross Pennington, Murray Johnston,*University of Delaware*

The Nano Aerosol Mass Spectrometer (NAMS) permits quantitative measurement of the atomic composition of individual nanoparticles between 7 and 30 nm diameter. NAMS was deployed to urban, rural/coastal, and remote environments in order to determine the composition of 15-21 nm mobility diameter nanoparticles during new particle formation (NPF) events. In all three environments, only small changes in nanoparticle atomic composition were observed during NPF relative to composition before and after the events. These changes indicated a shift towards increased inorganic nanoparticle content during NPF (more nitrogen and sulfur, less carbon). Nonetheless, nanoparticles in this size range still contained a significant organic component, characterized by a high carbon content. For each environment, chemical composition changes did not correlate with changes in the event growth rate, suggesting (1) that a consistent source exists for all events at a given site and (2) that the driving forces affecting particle growth are physical (i.e. solar radiation, mixing, meteorology) rather than chemical and impact all chemical constituents of the particle in a roughly similar manner. Nonetheless, chemical composition is found to depend on parameters such as temperature or snow pack. NAMS-measured elemental sulfur content can be related quantitatively to ambient gas-phase sulfuric acid during NPF through the gamma parameter. Agreement between measured particulate sulfur and gas-phase sulfuric acid concentrations indicates that the assumption of collision-limited condensational growth of sulfuric acid is suitable for 10-20 nm diameter particles. Current work focuses on the contributions of organic matter and nitrogen-containing species such as base molecules (amines, ammonia) to particle growth.

5AN.7

The Role of Nitrate in New Particle Formation: Results from Ambient Measurements and Models. LEA HILDEBRANDT RUIZ, James N. Smith, Ilona Riipinen, Kelley C. Barsanti, Juliane L. Fry, Taina Yli-Juuti, Tuukka Petäjä, Markku Kulmala, Peter McMurry,*National Center for Atmospheric Research*

A crucial but poorly understood component of new particle formation (NPF) is the growth of nanoparticles from their smallest size (~ 1 nm in diameter) to tens of nanometers. Studies conducted by our group and others have shown that sulfuric acid condensation can often only explain a minor fraction of this early particle growth. We previously developed the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) to measure the chemical composition of 10-30 nm particles. We have recently upgraded the TDCIMS with a high-resolution time-of-flight mass spectrometer by Tofwerk AG, which allows us to collect data at higher time and mass resolution. We report the first measurements with this upgraded instrument during the Hyytiälä spring 2011 measurement campaign. TDCIMS measurements show that nitrate is the dominant species in 10-30 nm particles, suggesting its importance in nanoparticle growth. The abundance of nitrate in the particles is consistent with other measurements taken at the site.

We developed a box model to better understand the species and processes involved in NPF, building on a previous model developed to understand atmospheric nucleation. Using results from laboratory chamber experiments we developed parameterizations for the role of organic nitrate compounds in NPF. We compare model results of the relative contributions of sulfate and nitrate on nanoparticle growth to measurements in Hyytiälä and Atlanta, two very different environments.

5AN.8

The Effect of Coal-Fired Power Plant SO2, NOX Control Technologies and Background Particle Concentrations on Aerosol Nucleation and Growth in Source Plumes. CHANTELLE LONSDALE, Robin Stevens, Charles Brock, Paul Makar, Jeffrey Pierce,*Dalhousie University*

Nucleation and growth in coal-fired power-plant plumes can greatly contribute to particle number concentrations in plumes near source regions. The changing emissions rates of SO2 and NOx due to pollution-control technologies over recent decades may have a significant affect on aerosol formation and growth in the plumes, with ultimate implications for climate and human health. We use the System for Atmospheric Modelling (SAM) Large-Eddy simulation model with the TwO-Moment Aerosol Sectional (TOMAS) microphysics algorithm to model the nucleation and growth in the plume of coal-fired units. We test a range of cases with varying emissions to simulate the implementation of clean technologies between 1997 and 2010. For the W.A. Parish power plant (near Houston, TX) during this time period, NOx emissions were reduced by about a factor of 10 due to the addition of Selective Catalytic Reduction (SCR) technology, leading to a predicted increase in OH concentrations by about a factor of 10, while SO2 emissions have only decreased by ~30%. This increase in OH leads to faster production of H2SO4 in the plume, and nucleation and growth even though SO2 emissions were somewhat decreased. These results suggest that controlling NOx more strongly than SO2 may lead to increased nucleation and growth in power-plant plumes. We also compare our predictions for the W.A. Parish power plant to NOAA aircraft measurements through this plume taken during 2000 and 2006. Although variability in pre-existing aerosol concentrations between the measurement days dominates the difference between measurements, the measurements do suggest the influence of the emission-control changes on particle formation. Next, we use the case study results to understand more generally how NOx and SO2 emissions affect particle formation/growth and contribute to regional aerosol number concentrations through testing a wide range of NOx and SO2 emissions rates. Finally, we calculate statistics on how emissions controls added to all of the power plants in the US since 1997 may have effected particle formation in their plumes.

5CA.1

Organic Aerosols: What Happens Where and How Fast. NEIL DONAHUE, *Carnegie Mellon University*

Oxidation chemistry clearly can make organic molecules that stick to, or stay in organic aerosols. What phase that oxidation happens in, why molecules stick to particles, what chemistry occurs within the particles, and what physical process may impede the mass transfer between gas and particle phases remain unclear. Because organic aerosols consist of a very diverse mixture of different molecules, it is also perilous to extrapolate too freely from the behavior of one molecule to the overall behavior of the mixture. However, we do have a substantial collection of experimental and theoretical constraints to help identify the leading causes of organic aerosol properties, including mass concentration, oxidation state, hygroscopicity, etc. These include mass yield experiments, dilution experiments, thermodeuder measurements, and theoretical considerations of vapor pressure and oxidation mechanisms. Here we shall discuss how these constraints apply to the overall behavior of organic aerosols in the atmosphere.

5CA.2

Molecular Composition of Water-Soluble Organic Carbon in Nonurban Aerosols. LYNN MAZZOLENI, Parichehr Saranjampour, Megan Dalbec, Vera Samburova, Anna Gannet Hallar, Barbara Zielinska, Douglas Lowenthal, *Michigan Technological University*

Water-soluble organic carbon (WSOC) is a complex mixture of thousands of organic compounds which may have significant influence on the climate-relevant properties of atmospheric aerosols. An improved understanding of the molecular composition of WSOC is needed to evaluate the effect of aerosol composition upon aerosol physical properties. Products of gas phase, aqueous phase and particle phase reactions contribute to pre-existing aerosol organic mass or nucleate new aerosol particles. Thus, ambient aerosols carry a complex array of WSOC components with variable chemical signatures depending upon its origin and aerosol life-cycle processes. In this work, ultrahigh-resolution Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to characterize aerosol WSOC collected during the summer of 2010 at the Storm Peak Laboratory (3210 m asl) near Steamboat Springs, CO. Approximately 4000 molecular formulas were assigned in the mass range of 100–800 Da after negative-ion electrospray ionization. More than 50% of the assigned formulas contained nitrogen and/or sulfur. The double bond equivalents (DBE) of the molecular formulas were inversely proportional to the O:C ratio, despite a relatively constant H:C ratio of ~1.5. The observed trends indicate significant non-oxidative accretion reaction pathways for the formation of high molecular weight WSOC components. Several of the most prominent WSOC molecular formulas matched the most prominent β-caryophyllene/ozonolysis SOA molecular formulas, including $C_{14}H_{22}O_7$ (relative abundance (RA) = 95%), $C_{14}H_{22}O_6$ (RA = 84%) and $C_{15}H_{24}O_7$ (RA = 78%). Another compound, $C_{10}H_{17}NO_{10}S$ interpreted to be a nitrated analog of secondary organosulfates found in chamber studies of β-pinene oxidation, was assigned with very high RA. Based on molecular trends and a large number of common formulas, an overall SOA-like character was deduced, however a majority of the nitrogen and/or sulfur containing molecular formulas cannot be matched to experimental SOA. Their origin and transformation processes are yet highly uncertain.

5CA.3

Evaluating the Degree of Oxygenation of Organic Aerosols During Foggy Days and Hazy Days in Springtime in Hong Kong Using High-Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS). YONG J. LI, Berto Lee, Chak K. Chan,*Hong Kong University of Science and Technology*

The role of aqueous-phase chemistry in the formation of secondary organic aerosols is still poorly constrained. Here we present results on the effects of fine particle liquid water content (LWC_{fp}) on the degree of oxygenation of organic aerosols (OA) based on high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) measurements made at a coastal site in Hong Kong during springtime. Data from two foggy weeks and one hazy week were chosen for analysis. The degree of oxygenation of OA, as indicated by several parameters including f44 (Ng et al., 2010), O:C and H:C ratios (Heald et al., 2010), and the carbon oxidation state (Kroll et al., 2011) was evaluated against odd oxygen concentration, relative humidity, LWC_{fp}, ionic strength, ratios of measured to predicted NH_4, and in-situ pH. Results showed that for hazy week, the high concentration of OA and the high degree of oxygenation were mainly due to gas-phase oxidation. During the foggy days with low photochemical activities, the degree of oxygenation of OA was as high as that in hazy days, suggesting the important role of aqueous-phase chemistry in SOA formation. However, the evolution of OA behaved quite differently for the two foggy periods. The first foggy week in late April and early May had more LWC_{fp} and lower particle acidity, and the OA had more semi-volatile oxygenated organic aerosols (SV-OOA) as resolved by positive matrix factorization (PMF). The second foggy week in mid-May had lower $LWC_{fp}$and produced more low-volatility oxygenated organic aerosols (LV-OOA).

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5CA.4

Comparison of Biomass Burning Organic Aerosol Mixing Ratios and Their Evolution With Aging. MATTHEW JOLLEYS, Hugh Coe, Gordon McFiggans, Gerard Capes, James Allan, Jonathan Crosier, Paul Williams, Grant Allen, Keith Bower, Jose-Luis Jimenez, *University of Manchester*

No evidence for a regional net source of secondary organic aerosol (SOA) has been identified in measurements of biomass burning-influenced ambient air masses. Measurements included in this study were obtained from the deployment of an Aerodyne Quadrupole Aerosol Mass Spectrometer during four field campaigns, involving both research aircraft flights and ground-based measurements. OA concentrations, normalized to excess CO (OA/dCO), show strong regional and local scale variability, with a difference of more than a factor of five across fresh OA emissions between campaigns. Average OA/dCO is typically higher in the near-field than at a greater distance from source, indicating an absence of significant SOA formation, despite evidence to suggest OA becomes increasingly oxidized with age. This trend is in contrast with observations of anthropogenic OA in urban environments, where OA/dCO is consistently shown to increase with distance from source. There is no such agreement in the case of biomass burning OA (BBOA) amongst the literature base, with conflicting examples relating to the influence of SOA on aerosol loadings. A wide range of average initial emission ratios close to source are observed both within the datasets analysed here and within the literature, together with considerable variability in OA/dCO values throughout individual fresh biomass burning plumes. The extent of this variability far outweighs any change in average OA/dCO, suggesting that source conditions are of greater importance for the propagation of BBOA loadings within the ambient atmosphere. However, the exact effects of the fire conditions influencing emissions from biomass burning events remain poorly constrained, with results from chamber experiments showing inconsistencies in relationships with factors such as fuel type and combustion phase. These uncertainties regarding the evolution of biomass burning emissions emphasise the need for improved characterisation of BBOA to ensure accurate representation in global climate models.

5CA.5

Aging of Biomass Burning Aerosols: Comparison of Smog Chamber Experiments with Ambient Aerosols. JEFFREY L. COLLETT, Yury Desyaterik, Amy P. Sullivan, Christopher Hennigan, Allen Robinson, Amanda Holden, Sonia Kreidenweis, Bret Schichtel, *Colorado State University*

Knowledge of the chemical composition of atmospheric organic aerosols (OA) is essential for accurate representation of OA in air quality and climate models. On the global scale, biomass burning (BB) emissions could account for more than 50% of the total burden of organic aerosols (Reddy et al., 2004). Recent smog chamber studies have shown that the mass of the BB aerosol can increase more than two-fold, for some fuels, due to photooxidation (Hennigan et al., 2011). Through a series of laboratory experiments, we are working to quantify changes in the chemical composition of biomass smoke particles as a result of photochemical aging. One specific objective of this study is to identify markers for biomass burning SOA and test whether these markers can be used in atmospheric samples to quantify SOA formation from aging of biomass burning emissions.

In a series of experiments, biomass burning smoke was aged by photooxidation in a smog chamber. In order to initiate photochemistry, the chamber was irradiated with UV light. Filter collected aerosol samples were extracted with DI water, and analyzed with Time-of-Flight Electrospray Ionization Mass Spectrometry. Mass spectra of secondary organic aerosol formed in the aging experiments include important contributions from organic nitrates (nitrophenol, nitrocresol, nitrocatechol, and nitroguaiacol) and aromatic acids (benzoic acid, mono and di-hydroxybenzoic acid). Both the nitrates and acids are most likely formed due to the oxidation of the lignin decomposition products (guaiacol and syringol derivatives) by reaction with OH and NO2. The results of chamber experiments will be compared with ambient aerosol samples known to be affected by biomass burning.

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5CA.6

Probing Complex Hydrocarbon Mixtures in Atmospheric Organic Aerosols: Insights into Sources and Mechanisms. ARTHUR CHAN, Gabriel Isaacman, David Worton, Chris Ruehl, Katherine Schilling, John Seinfeld, Kevin Wilson, Allen H. Goldstein,*University of California, Berkeley*

Detailed speciation of organic compounds in ambient aerosol is often challenging owing to their complexity. In particular, a significant fraction of the hydrocarbons present in organic aerosol are not resolved by conventional gas chromatography (GC) techniques and show up in the so-called unresolved complex mixture (UCM). In this work, we combine the separation capabilities of comprehensive GCxGC with vacuum ultraviolet photoionization mass spectrometry (GCxGC/VUV-HRTOFMS) to analyze the composition of hydrocarbon mixtures in ambient aerosols. Using this technique, we are able to not only distinguish among compound classes (aliphatic, aromatic, oxygenated), but also resolve hydrocarbons in the UCM by their carbon number, branching and degree of unsaturation. Here we present analysis of aerosol filters collected from two different urban sites (Calnex LA and Bakersfield, 2010) and a rural site downwind of an urban area (BEARPEX 2009), and during a large biomass burning event (Station Fire 2009). The ratio of observed branched to straight-chain alkanes in the UCM was significantly higher in Bakersfield, CA than in Pasadena, CA (8.7-14.5 and 0.3-1.1, respectively) and can be explained by the difference in oxidation timescales between these two sites. The source of the UCM is shown to be related to motor vehicles based on isomer patterns. Since the UCM is a significant contributor to reduced organic aerosol (classified as HOA in aerosol mass spectrometry), these observations highlight the differences in the degree of processing of motor vehicle related emissions in these two sites. Also, semivolatile compounds observed during Station Fire contain many rings and double bonds owing to their terpenoid backbones. This results in good GCxGC separation from the alkanes found in the UCM and provides a unique signature of biomass burning aerosol in a 2-dimensional chromatogram.

5CA.7

Density and Elemental Ratios of Secondary Organic Aerosol: Application of a Density Prediction Method. SHUNSUKE NAKAO, Ping Tang, Xiaochen Tang, Christopher Clark, Li Qi, Eric Seo, Chia-Li Chen, Akua Asa-Awuku, David R. Cocker III,*University of California, Riverside*

This study investigates density and elemental ratios of secondary organic aerosol (SOA) formed by the oxidation of 23 different volatile organic compounds with a wide range of molecular size (C5~C15) in an environmental chamber. Differences in oxidation conditions (in terms of VOC:NOx, H_2O_2, and O_3) did not significantly effect SOA density. Reactants with a larger number of carbons (C14~15) yielded SOA with lower density (1.06~1.20 g/cm3) compared with smaller ones (e.g., phenol SOA: 1.42 g/cm3) consistent with different extents of oxidation of the parent molecule. A recent study proposed a semi-empirical relationship between elemental ratios (O/C and H/C) and organic material density (Kuwata et al., 2011). The prediction method therein is evaluated against the large experimental data set of this study acquired in the UC Riverside/CE-CERT environmental chamber. The predicted particle densities agree with experimental measurements within 20% for more than 90% of the experiments. The effects of nitrogen and sulfur on the density prediction remain unclear.

5CA.8

Investigation of Organic Aerosol Wet Removal during Fog Events. STEFANIA GILARDONI, Lara Giulianelli, Matteo Rinaldi, Vanes Poluzzi, Silvia Ferrari, Paola Massoli, M. Cristina Facchini, *ISAC-CNR*

Tropospheric aerosol was characterized during the ARPA Supersite Intensive Operational Period in the Po valley during fall 2011. The results presented here refer to observations performed in San Pietro Capofiume, a rural site located about 30 kilometers from Bologna (Italy). During the campaign, several techniques were deployed to characterize aerosol composition and trace-gas concentration, including off-line analysis of size segregated aerosol samples and on-line measurements with an Aerodyne high resolution aerosol mass spectrometer (HR-ToF-AMS). Submicron particles were composed mainly by organic aerosol (more than 40%), nitrate (about 30%), and ammonium (about 14%). The organic aerosol was mainly water-soluble and the AMS data show that oxidized organics were predominant. The campaign was characterized by frequent fog events, which lasted from one hour up to several hours. These events will be used to investigate the effect of aerosol wet removal, which is a significant source of uncertainty in global models especially for the organic aerosol component. During fog events the aerosol mass concentration decreased by a factor larger than two, and the accumulation mode particles (dry diameter between 100 nanometer and 1 micron) were those scavenged with the highest efficiency. The comparison of aerosol composition prior to and following fog formation indicates that scavenging removed ammonium and nitrate efficiently and left an interstitial aerosol enriched in organics, although the organics were dominated by water soluble oxidized components. The concentration of water soluble organic aerosol decreased by a factor of 1.6 – 1.8 during fog episodes, corresponding to 40-50% of scavenging efficiency. Therefore, these results point towards an overestimation in organic aerosol wet removal in the global models.

5FM.1

Flame Synthesis of Aerosol Gels. RAJAN CHAKRABARTY, Christopher Stipe, Hans Moosmuller, *Desert Research Institute*

Aerosol gels have properties similar to conventional aerogels. The name, aerosol gel, is derived from the fact that the material is made via the process of aerosol gelation in a flame, unlike the wet-chemical sol-gel process used for producing conventional aerogels. Flame synthesis is yet to be established as a viable method for production of aerosol gels, owing mainly to the aggregate fragmentation effects associated with buoyancy-driven flickering and shear stress of a diffusion flame's "tipping" front.

In this talk, we will present our recent findings on the production of carbonaceous aerosol gels using a reversed-gravity diffusion flame system, which is an upside-down burner arrangement. In such a flame system, a "stagnation plane" is formed at its non-tipping end, which eliminates buoyancy-driven flickering and enhances the aggregate residence time within the plane thereby facilitating the formation of gels. Material properties of the carbonaceous aerosol gels will be discussed. The talk will conclude with potential applications of this technique in the energy sector and future research directions of this project.

Reference:
Chakrabarty, R. K., H. Moosmüller, M. A. Garro, and C. B. Stipe (2012). Observation of Superaggregates from a Reversed Gravity Low-Sooting Flame. Aerosol Sci. Tech., 46, i-iii (published as Aerosol Research Letter).

5FM.2

Aerosol Growth and Potential Applications of Carbon Nanostructures. Ji Hoon Kim, Kook Joo Moon, Ji Young Ahn, SOO H. KIM, *Pusan National University*

We demonstrate a one-step method for selectively growing aerosol carbon nanostructures with different shapes, including straight wires, coils, and sea urchins. The growth of aerosol carbon nanostructures in this approach was made on the N-Al bimetallic nanoparticles by the combination of spray pyrolysis and thermal chemical vapor deposition. We propose that the diameter of seeded bimetallic particles and the growing temperature of carbon nanostructures played a key role in growing aerosol carbon nanostructures. Coiled carbon nanotubes (CNTs) were formed on the entire surface of a seeded bimetallic nanoparticle with the average size of smaller than ~100 nm at medium temperature ranges of 500~650degC. Straight CNTs can be easily obtained with relatively high temperature ranges of 650~800degC, which result in melting the Al matrix sites in the seeded bimetallic nanoparticles so that the liquid-like Al matrix was then consumed by subsequent CNT precipitation. However, sea urchin-like CNTs are mostly grown on the seeded bimetallic particles with average size of larger than ~100 nm, in which Ni sites sufficiently isolated by Al sites are seeded to radially grow multiple CNTs with the average diameter of approximately 60 ± 13 nm under the medium reaction temperature ranges of 500~650degC. If the processing takes place at relatively high temperature ranges of 650~800degC, this makes Al molten and results in significant size reduction of available Ni sites by thermal expansion of non-catalytic Al matrix sites so that one can obtain sea urchin-like CNTs with the average diameter of approximately 10 ± 4 nm. Finally we introduce that the as-grown aerosol CNTs in this approach can be used directly with potential applications as polymer composite reinforcements and charge-/heat-transfer mediums.

5FM.3

Combustion-Driven One Step Synthesis of Non-Oxide Nanoparticle Hybrid Films in a High Temperature Reducing Jet Reactor.

Munish Sharma, Raymond Buchner, William Scharmach, Vasilis Papavassiliou, MARK SWIHART, *University at Buffalo (SUNY)*

We present here the high temperature flame-based synthesis of non-oxide nanoparticle hybrid films using a high temperature reducing jet (HTRJ) reactor. We synthesized bimetallic copper-silver, palladium-copper, palladium-silver and ternary palladium-copper-silver nanoparticles and created nanostructured films by direct deposition of nanoparticles produced within the HTRJ reactor. The HTRJ process allows us to decouple the flame chemistry from the nanoparticle formation chemistry. The alloy and bi-component nanoparticles have potential applications in conductive ink formulations for printed electronics, in antibacterial coatings, and in heat-transfer fluids. The palladium-based alloy films have applications in hydrogen storage and purification. Alloying palladium with copper and/or silver prevents hydrogen embrittlement and results in higher hydrogen permeation fluxes. We synthesized these hybrid films in one step by thermal decomposition of low-cost, water-soluble, and environmentally-friendly precursors. The metal films were thermophoretically deposited on soda lime glass and on SS-316 porous discs. In this presentation, we will describe the HTRJ process briefly, and then focus on the synthesis and characterization of bimetallic copper-silver films on glass substrates. The hybrid copper-silver coating yielded in very high bulk electrical conductivity of 10^4 S/m at 40 wt% Ag. The effect of silver concentration in the mixed copper-silver films on the electrical conductivity of these coatings was studied systematically. We will also present synthesis and characterization of palladium-based alloy membranes on porous SS-316 discs for hydrogen storage and transport.

5FM.4

Effect of Shape of Au Nanoparticles on the Photoelectrochemical Water-Splitting Performance of Au-TiO2 Nanocomposite Thin Films.

TANDEEP CHADHA, Jinho Park, Woo-Jin An, Pratim Biswas, *Washington University in St. Louis*

Au-TiO2 composited thin films have received considerable attention due to the surface plasmonic nature of Au nanoparticles (Liu et al. 2011). Controlling the size of the nanoparticles simultaneously changes both the surface plasmon resonance (SPR) and the interfacial contact area between Au and TiO2. Hence independent contribution of these factors on the performance is not yet known. These two factors can be decoupled by changing the shape of the particles since it is known that Au particles of different shapes exhibit varied SPR behavior.

This study focuses on the effect of the shape of Au nanoparticles on the photoelectrochemical performance of Au-TiO2 composited thin films. Columnar TiO2 thin films were synthesized by the Aerosol-Chemical Vapor Deposition (ACVD) technique (An et al. 2009). Au nanoparticles of various shapes, including spheres, nanocages and nanorods, synthesized by liquid phase methods using a stabilizing agent were deposited onto these films by spin coating. The performance of these composited photoelectrodes was evaluated using a three electrode system in a quartz cell under illumination by an Arc Xe lamp. Preliminary results show that the saturated photocurrent density decreased from 4.3 mA cm-2 to 3.5 mA cm-2 when spherical Au particles of size 5 nm stabilized by citrate were deposited on the TiO2 thin films. The weak interaction between the citrate and the gold surface in a highly alkaline environment (Lana-Villarreal and Gómez 2005) caused the decreased performance. The performance of Au nanocages and Au nanorods stabilized by different stabilizing agents will be further explored. A description of the charge separation mechanism will be discussed.

References:

An, W.-J., Thimsen, E. and Biswas, P. (2009). Aerosol-Chemical Vapor Deposition Method For Synthesis of Nanostructured Metal Oxide Thin Films With Controlled Morphology. The Journal of Physical Chemistry Letters 1:249-253.

Lana-Villarreal, T. and Gómez, R. (2005). Interfacial electron transfer at TiO2 nanostructured electrodes modified with capped gold nanoparticles: The photoelectrochemistry of water oxidation. Electrochemistry Communications 7:1218-1224.

Liu, Z., Hou, W., Pavaskar, P., Aykol, M. and Cronin, S. B. (2011). Plasmon Resonant Enhancement of Photocatalytic Water Splitting Under Visible Illumination. Nano Letters 11:1111-1116.

5FM.5

Nanoparticle Synthesis and In-Situ In-Flight Functionalization in an Inductively Coupled Plasma Reactor. CHRISTOPHE DELVAL, Marc Leparoux, Christian Jaeggi, *Empa, Laboratory for Advanced Materials Processing, Feuerwer*

In the recent decades, nanoparticles have been widely synthesized using thermal plasma technology [1]. Flexibility regarding the precursors phase (gas, liquid, solid) and ability to generate plasmas with a controlled chemistry, allow the production of almost all materials including those with high melting point [2] at high production rates.

Among thermal plasmas, Inductively Coupled Plasma (ICP) processing is a powerful technique to produce all kinds of nanopowders , from oxides to metals and hard ceramics such as TiCN or SiC [3].

Longer residence time of the precursor and absence of contamination generated by electrodes make ICP a technique of choice to produce nanoparticles with well-defined properties.

At Empa, a RF-ICP, based on a Tekna PL-35 torch using a 13.56Mhz generator (Pmax=35 kW), has been setup to systematically investigate the plasma synthesis and in-flight functionalization of nanoparticles [4]. The reactor is equipped with many viewports enabling observations and characterizations of the overall process including plasma properties, gas phase characterization and plasma/particles interactions (FTIR and OES-spectroscopy, High-speed imaging).

Based on case studies such as in-situ carburization of silicon nanoparticles or in-flight coating of TiCN nanoparticles with surfactants, we will present the state of the art of plasma characterization, synthesis and functionalization of nanoparticles at Empa.

[1] Shigeta M. and Murphy A.B. 2010 Thermal Plasmas for nanofabrication J. Phys. D: Appl. Phys. 44 174025
[2] Ostrikov K., Cvelbar U. and Murphy A.B. 2011 Plasma nanoscience: setting directions, tackling grand challenges J. Phys. D: Appl. Phys. 44 174001
[3] Leparoux M., Schreuders C. and Fauchais P. 2008 Improved Plasma Synthesis of Si-nanopowders by Quenching Adv . Eng. Mat. 10 12 1147-50
[4] Leparoux M., Leconte Y., Wirth A. and Buehler Th.2010 In Situ Treatment of Thermal RF Plasma Processed Nanopowders to Control their Agglomeration and Dispersability Plasm. Chem. Plasm. Proc. 30 779-793

5FM.6

Numerical Study of Growth Process of Binary Alloy Nanopowders in Thermal Plasma Synthesis. MASAYA SHIGETA, Takayuki Watanabe, Toyonobu Yoshida, *Tohoku University*

The growth processes of binary alloy nanopowders in thermal plasma synthesis are investigated numerically using our unique model. The model makes it possible to compute the collective and simultaneous combined process of binary nucleation, binary co-condensation of high temperature metallic vapors, and coagulation among nanoparticles even with different compositions successfully. The freezing point depression due to nanoscale particle diameters is also taken into account. This study analyzes two representative systems. One is the Nb-Si system which has a large difference of the saturation pressures between the two materials, and the other is the V-Si system which presents a small difference. In the Nb-Si system, at the early stage, Nb-rich nuclei are generated by nucleation followed by condensation of Nb vapor on the nuclei, which produces a number of Nb-rich nanoparticles. Subsequently, Si vapor condenses on the Nb-rich nanoparticles. The finally obtained nanopowder consists of larger Nb-rich nanoparticles and smaller Si-rich nanoparticles. Furthermore, the present model predicts that several kinds of intermetallic compounds (Nb_3Si, Nb_5Si_3, and $NbSi_2$) are produced, which agrees with our previous experiment. On the other hand, in the V-Si system, a large number of V-Si-mixed nuclei are generated by the binary nucleation and immediately V vapor and Si vapor co-condense on those nuclei simultaneously. Almost the same saturation pressures of V and Si cause such a co-condensation process. This type of systems tends to produce a single phase alloy nanopowder, which also agrees with the experiment results. Moreover, the effect of the cooling rate on the final profile of a nanopowder is examined. In both systems, at the higher cooling rate, the mean sizes and the standard deviations of sizes become smaller. The standard deviation of Si content in the nanopowder becomes larger in the Nb-Si system, while that in the V-Si system is less affected.

5FM.7

Plasma-Produced Silicon Nanocrystals for Light-Emitting Devices. REBECCA J. ANTHONY, Kai-Yuan Cheng, Zachary C. Holman, Russell J. Holmes, Uwe R. Kortshagen, *University of Minnesota*

Silicon nanocrystals (SiNCs) produced in a nonthermal plasma can exhibit efficient and tunable luminescence, making them attractive for use in opto-electronic devices such as light-emitting devices (LEDs). By adjusting the gases used, gas flowrates, and power supplied to the plasma reactor, we can exert control over the size, structure, and surface coverage of the SiNCs, which are also linked to luminescence characteristics. Here we demonstrate two routes to making LEDs using plasma-produced SiNCs.

First, we present a hybrid organic / SiNC LED structure, fabricated using solution-phase techniques. The SiNCs are surface-functionalized in a liquid-phase thermal reaction and then spin-cast onto device substrates incorporating polymer and small-molecule charge-transport layers. These devices exhibit exceptional performance (>8% external quantum efficiency) for a nanocrystal-based LED.

Second, we introduce a gas-phase-only method for fabricating devices. Using exclusively aerosol techniques, SiNCs can be synthesized, surface-passivated, and deposited as dense films suitable for LED construction. We demonstrate the viability of this method by depositing the SiNCs directly from the reactor onto device substrates and completing the device structure with a thermally-evaporated top electrode. These LEDs demonstrate >0.02% external quantum efficiency, which is a promising performance for this as-yet unoptimized device. This streamlined and versatile process opens the door to using nanomaterials in a manner that is compatible with traditional cleanroom techniques.

5FM.8

Aerosol Synthesis of Superparamagnetic Silica-Coated Iron Oxide Nanoparticles. PINGYAN LEI, Steven Girshick, *University of Minnesota*

Superparamagnetic iron oxide nanoparticles (SPIONs) are currently of interest for biomedical applications, including as contrast agents for magnetic resonance imaging and as targeted agents that can be heated by applying an alternating magnetic field, killing cancer cells by hyperthermia. We here report the synthesis of SPIONs that are coated with thin layers of silica. Silica coatings improve the nanoparticles' stability, suppress agglomeration, and can serve as an excellent substrate for additional surface layers or biofunctionalization. The SPIONs were synthesized by injecting ferrocene vapor and oxygen into an argon/helium DC thermal plasma. Size distributions of particles in the reactor exhaust were measured online using an aerosol extraction probe interfaced to a scanning mobility particle sizer, and particles were collected on transmission electron microscopy (TEM) grids and glass fiber filters for off-line characterization. The morphology, chemical and phase composition of the nanoparticles were characterized using TEM and X-ray diffraction, and the magnetic properties of the particles were analyzed with a vibrating sample magnetometer and a magnetic property measurement system. Aerosol at the reactor exhaust consisted of both single nanocrystals and small agglomerates, with a modal mobility diameter of 8-9 nm. Powder synthesized with optimum oxygen flow rate consisted primarily of magnetite (Fe_3O_4), and had a room-temperature saturation magnetization of approximately 40 emu/g, with a coercivity and remanence of 26 Oe and 1.5 emu/g, respectively. After exiting the plasma reactor the SPIONs are coated with very thin layers of silica, using photochemical vapor deposition, driven by a xenon excimer lamp that emits at 172 nm. Tetraethylorthosilicate (TEOS) vapor was used as the coating precursor. Results are presented for the effect of operating parameters on coating thickness, surface chemical composition, magnetic properties, and stability of the nanoparticles in aqueous dispersion.

5IM.1

A Sizer for Neutral Weakly-Bound Ultrafine Aerosol Particles. Bruce Yoder, Jessica Litman, RUTH SIGNORELL, *University of British Columbia*

The determination of accurate size distributions and chemical composition of volatile and semi-volatile ultrafine aerosol particles with sizes in the subnanometer to several tens of nanometers range is a problem that plagues many studies in aerosol research. We propose to employ sodium-doping of the aerosol particles with subsequent photoionization in the ultraviolet combined with mass spectrometric detection to solve this problem. Comparison with "soft" EUV ionization demonstrates that the sodium technique can determine size distributions and to some extent the chemical composition of weakly-bound ultrafine aerosol particles largely destruction free. We also discuss how sodium-doping can be turned into a viable quantitative technique for the sizing of ultrafine aerosol particles.

5IM.2

A New Instrument to Classify Particles by Their Aerodynamic Size. FARZAN TAVAKOLI, Jonathan Symonds, Jason Olfert,*University of Alberta*

A new aerosol particle classifier, the Aerodynamic Aerosol Classifier (AAC), is presented. Aerosol classifiers are used to produce a monodisperse aerosol, that is, they select a narrow range of particles from a larger distribution of particles. The instrument uses centrifugal force and a sheath flow between two concentric rotating cylinders to produce a monodisperse aerosol classified by aerodynamic diameter. The instrument does not rely on particle charging so it produces a true monodisperse aerosol without classifying multiply-charged particles like other classifiers. This work reports the theoretical and experimental results of the new instrument.

A diffusion model and a non-diffusion model have been used to predict the performance of the AAC. From the analytical model the normalized transfer function was obtained as a function of the particle relaxation time and the particle aerodynamic diameter. The transfer function has been studied for different flow rates. The analytical model of the AAC does not include particle diffusion. Thus, the diffusion model has been developed by solving the convective-diffusion equation for the AAC which has been solved using the Crank-Nicolson method. The diffusion effect has been studied for different particle density and particle size. Also, the experimental results will be compared to the theoretical models.

5IM.3

Polar Nephelometer for the Measurement of the Particle Asymmetry Parameter. Paul Kebabian, Timothy Onasch, Joda Wormhoudt, ANDREW FREEDMAN, *Aerodyne Research, Inc.*

Radiative transfer models use the particle asymmetry parameter, g, as a measure of scattering angle because it is far more computationally efficient than including the entire scattering phase function. We present a proof-of-principle demonstration of an apparatus capable of directly measuring the aerosol scattering phase function and aerosol asymmetry parameter without the need for calibration or adjustment of data. The measurement technique utilizes a technique which allows for the collection of scattered light at all angles simultaneously and thus offers the potential for more rapid acquisition of scattering data from ambient polydisperse aerosols compared to polar nephelometers which measure scattered light from one angle at a time. Measurements of monodisperse polystyrene latex and polydisperse ammonium sulfate particles indicate that the measured value of the asymmetry parameter is within ±0.03 of that calculated using Mie theory.

5IM.4

Particle Size Distributions Following Condensational Growth in Continuous Flow Aerosol Reactors as Derived from Residence Time Distributions: Theoretical Development and Application to Secondary Organic Aerosol. MIKINORI KUWATA, Scot Martin, *Harvard University*

Condensational growth in continuous flow reactors, such as continuously mixed flow reactors (CMFRs) and flow tube reactors, is widely employed in the field of aerosol science and technology to produce particles for industrial use and scientific research. The development of analytical equations for the number-diameter distribution n(d) of the particles in the outflow from these reactors is advantageous both for the inversion of data sets to obtain thermodynamic and kinetic parameters as well as for the rational design of experiments. In this study, equations are derived that relate the number-diameter distribution n(d) to the probability density function p(t) of particle residence time. Specifically, the condensational growth rate is used to derive n(d) based on p(t). Analytical equations are developed for CMFRs, laminar-flow reactors, and dispersive plug-flow reactors, with a focus on CMFRs. The CMFR equation accurately describes data sets collected for α-pinene and β-caryophyllene ozonolysis in the Harvard Environmental Chamber. The interpretation is that condensational growth can be considered as the principal mechanism for change in particle diameter in these experiments.

5IM.5

Water-Based Fast Integrated Mobility Spectrometer. STEVEN SPIELMAN, Chongai Kuang, Jian Wang, Susanne Hering,*Aerosol Dynamics Inc.*

The Fast Integrated Mobility Spectrometer (FIMS), developed by Kulkarni and Wang (2006), can capture an aerosol mobility distribution with 1-second time resolution. As with a conventional scanning mobility particle spectrometer, FIMS uses an electric field to separate particles by electrical mobility. However, rather than counting only those particles within a scanned mobility window, FIMS uses a camera to detect every particle, deducing the mobility by its position in the channel. The separator sheath flow is saturated with butanol vapor which condenses on the positioned particles in a cold condenser. The droplets are illuminated by a laser.

We have modified FIMS to use water as the growth condensate. Elimination of butanol will allow operation of FIMS in environments that cannot tolerate the solvent or its vapor. Also, butanol in the sheath flow can potentially affect the sizes of some particles before they are size-separated, whereas with the water method, the separator sheath air composition could match that of the sampled air.

We constructed a parallel-plate water condensation growth cell and incorporated it into the existing FIMS system. To prevent condensation on the optics, the dew point of the outflow was controlled by a new two-stage condenser design. The wicks forming the walls were wetted by a new water-feed system that eliminates the need for overflow barriers in the air channel, which would disrupt the laminar flow.

Stand-alone tests of the growth cell, operating at flow rate of 13 L/min with a 31 C temperature jump, showed ambient particles growing to become 5 to 6 micron droplets. Operating under similar conditions, the assembled water-FIMS system was tested with monodisperse and ambient aerosols. It measured concentration spectra with a size range of 30-100 nm.

P. Kulkarni, J. Wang, J. Aerosol Science 37 (2006) 1303-1325

5IM.6

The Impact of Efficient Trapping Millions of Atmosphere-Sampled Singly-Charged Nanoparticles up to 200 nm. PETER T. A. REILLY, Xinyu Wang, Huijuan Chen, Katherine G. E. Donahoe, *Washington State University*

Recently our group has demonstrated trapping of atmosphere-sampled singly-charged nanoparticle by the millions at a point just before the exit end cap electrode of linear quadrupole ion trap. These ions were collected and held there until they were ejected on-demand in a well collimated plug into the entrance of an orthogonal acceleration time-of-flight mass analyzer. Normally, the ions are pulsed into the flight tube for high resolution mass analysis. The mass range for high resolution mass analysis of this instrument is defined by the detector and currently limited to approximately 10^6 amu thereby permitting high resolution mass analysis below 10 nm. The expressed limit is set by the analyzer—not the inlet and trapping system. To define the mass/size limit of the inlet and trapping system, polydisperse aerosols of urea were generated by nebulization and dried. The dried aerosols were sampled through a commercial differential mobility analyzer (DMA) to size select the charged aerosol. The DMA effluent was split with approximately 100 ml/min sampled through the 100 micrometer diameter flow limiting inlet orifice. The rest of the effluent was sampled into a Faraday detector to define the number density of the monodisperse charged aerosol. The particles admitted into the mass spectrometer were sampled and trapped for varying periods to be subsequently ejected on demand to pass through the TOF acceleration region and into a Faraday plate detector. The gain of the detector was 10^9 V/A. The baseline widths of the ions detected at the Faraday plate routinely measured between 125 and 150 microseconds across the entire range between 10 and 200 nm with amplitudes of 2-5 V. The results of these experiments will be presented and discussed to define the future of high resolution mass analysis to characterize aerosols

5IM.7

Field Testing of Genetically Tagged Spores for Specific Detection and Tracking of Biological Simulants in the Environment. TIFFANY SUTTON, *US Army Edgewood Chemical Biological Center*

The development of spores simulant of Bacillus thuringiensis var. kurstaki (Btk) with a stable single copy of uniquely amplifiable DNA integrated into the genome provides a powerful tool for tracking the fate of biological agents that are intentionally released into the environment. The use of tailored PCR assays specific for detecting barcoded regions overcomes the ambiguity of discerning the test release material from pre-existing environmental flora or background clutter from prior releases. Here we report the testing of this new simulant in a 200 meter ambient breeze tunnel followed by a 100 gram aerosol release of a dried powder of barcoded Btk spores (BtkB) in an outdoor field in Aberdeen Proving Grounds, Edgewood, Maryland. The release of spores was imaged from a distance by a Light Detection and Ranging (LIDAR) laser system that tracked the cloud by first detecting a large biological particulate intake followed by automated immunological detection transmitted to a command post. Multiple sampling units were arrayed on the proving grounds and tested immediately following the release followed by additional testing over a two week period. An unambiguous genetic identification of the BtkB spores at Day 1 correlated with the cloud track predicted by prevailing winds, and was supported by data tracks provided by the LIDAR system. The number of collection devices with positive response diminished significantly by Day 4 to a single response down from the five collection systems that had previously responded on Day 1. The field was then agitated by a leaf blower in a fifty foot swath in an attempt to instigate re-aerosolization of the settled spores. Re-aerosolization was observed with four collections systems registering detection events. This data is in agreement with controlled studies conducted on seeded tiles set in an ambient breeze tunnel which clearly demonstrated a gradual spread of biological contamination.

5IM.8

Multiple Charging Correction for SMPS Algorithm. Meilu He, SURESH DHANIYALA, *Clarkson University*

Critical to accurate calculation of aerosol size distributions from scanning mobility particle spectrometer (SMPS) measurements is the knowledge of particle charge characteristics. If the investigating particles are mostly smaller than 50nm, i.e., nanoparticles, the SMPS data can be accurately inverted considering just the singly-charged fraction. However, when a significant fraction of particles are larger than 100 nm, the role of multiple-charged particles in data inversion cannot be ignored. The SMPS is typically operated with an impactor at the inlet to eliminate the contribution of multiply-charged large sized particles to the mobility distribution. Coupled with an impactor, if the SMPS can be scanned to particle sizes larger than the impactor cutoff size, accurate particle size distributions can be calculated with a multiple-charge corrected inversion algorithm. Sometimes, an impactor cannot be used or the SMPS cannot be scanned to sizes beyond the impactor cut-size, e.g., for particles with low density and hence small aerodynamic diameters or under high altitude operation when the DMA upper voltage limit is reduced. Under such situations, the current multiple-charge correction inversion algorithm may produce incorrect size distribution, often with an artificial large particle mode. To overcome this problem, a new multiple-charge correction data inversion algorithm will be presented. Modeling results show that the new algorithm can produce accurate size distribution from SMPS data even under conditions of partial scanning and without an impactor in place.

5MB.1

Fungal Concentrations in Air Samples Correlated with Environmental Relative Moldiness Index Values in French Homes.DELPHINE MÉHEUST, Pierre Le Cann, Tiina Reponen, Larry Wymer, Stephen Vesper, Jean-Pierre Gangneux, *Ecole des Hautes Etudes en Santé Publique, IRSET, France*

Exposure to homes with high (fourth quartile) Environmental Relative Moldiness Index (ERMI) values have been shown to be associated with the development of childhood asthma. The ERMI is derived from the analysis of a dust sample obtained from the living room and bedroom. We determined if aerosol-based measures of fungal contamination were correlated with dust-based ERMI values in Brittany, France dwellings. Dust and air samples were obtained from 40 dwellings and analyzed by quantitative PCR (QPCR) and/or by culturing on malt extract agar (MEA). Dust samples were collected by vacuuming two m^2 in the living room and two m^2 in a bedroom for five min each with a Mitest™ sampler-fitted vacuum. The Coriolis cyclone collector (Bertin Technologies, Saint-Quentin-en-Yvelines, France) was used at a flow rate of 300 L/min for 10 minutes to sample air in the living room and bedroom. Airborne microorganisms were sampled in collection liquid with an initial volume of 15 mL. The 36 fungi that make-up the ERMI were analyzed by QPCR in the dust and aliquots of the air samples. Air samples were also analyzed by culturing. ERMI values were correlated with QPCR-based fungal concentrations in air samples in the living room ($p<0.001$; Kendall’s tau =0.438, p concordance 0.719) and bedroom ($p=0.028$; Kendall’s tau =0.212, p concordance 0.606). In addition, the culture data from the Coriolis samples were significantly correlated with the ERMI values in the living room ($p=0.002$; Kendall’s tau =0.313, p concordance 0.656) and bedroom ($p=0.001$; Kendall’s tau =0.344, p concordance 0.672). Some fungal species, such as Penicillium brevicompactum, Cladosporium cladosporioïdes and Wallemia sebi, were commonly found in both French air and dust samples. Aerosol samples obtained with the Coriolis cyclone collector and analyzed by QPCR or culturing may provide a useful addition to the QPCR analysis of dust in understanding indoor fungal contamination.

5MB.2

Phylogenetic-based Fungal Population Comparisons of Dust Collected from Water-damaged and Nonwater-Damaged Homes. KAREN DANNEMILLER, Jordan Peccia, *Yale University*

The presence of dampness or visible mold in homes is a consistent risk factor for respiratory infection in children, and is associated with the development of asthma, asthma exacerbation, and allergic rhinitis. The quantity and diversity of fungi in house dust has commonly been measured using culture-based techniques, which are known to introduce biases due to the unknown viability and limited culturability of allergenic fungal fragments. This work seeks to improve current fungal allergen quantity and diversity assessment in homes by using DNA-based, phylogenetic techniques. The main objective of this work is to produce quantitative, molecular-based microbial diversity descriptions of indoor dust samples collected from 200 homes in the Northeastern US. Many of these homes have documented water damage or mold growth, thus allowing for a comparative assessment. Phylogenetic libraries were created using 454 pyrosequencing of extracted DNA from all samples and by targeting both the internal transcribed spacer (ITS) genetic region for accurate species-level identification, and the rRNA large subunit (LSU) gene region to allow for alignment and comparison of populations based on phylogenetic distances. In addition, six selected species, human DNA, and universal fungal genomes were quantified by qPCR. Results will be presented that reveal associations between water and non-water-damaged homes both in terms of overall population differences, as well as statistical determination of species that are uniquely associated with water damage. Beyond these tangible outcomes, this work will provide information towards the establishment of safe mold level guidelines that reduce the risks of allergenic, infectious, and asthmatic disease.

5MB.3

Spatiotemporal Analysis of Microbial Diversity Patterns from the 454 Pyrosequencing of Bioaerosols Recovered from Flooded Commercial Office Environments. Kevin McCabe, Alina M. Handorean, Bharath Prithiviraj, Alison L. Ling, Keeley Hernandez, Norman R. Pace, MARK T. HERNANDEZ, *University of Colorado at Boulder*

Indoor microbiome studies seek to understand the ecological signatures of airborne microbial communities, and the associated potential to affect human and animal health. A recent study using high-throughput sequencing has determined that the diversity and composition of microbes within commercial office buildings qualify to be compared to complex ecosystems. Indoor bacterial diversity can be comprised of a multitudes of microbial taxa that may interact with each other, with humans and the indoor infrastructure (Green et al. 2012). Culture-independent methods, such as high-throughput molecular sequencing that leverages robust data analysis tools (e.g., QIIME & MGRAST) have transformed research on the human microbiome and the microbial ecology of aquatic and terrestrial ecosystems (Turnbaugh et al., 2007; Caporaso et al. 2010; Nemergut et al., 2011). Until recently, there have been few attempts to comprehensively survey the microbiome associated with the built environment (Rintala et al., 2008; Tringe et al., 2008; Amend et al., 2010). We present a study in which DNA-free liquid impingers collected composite air samples within flooded and non-flooded areas of the Engineering Center at the University of Colorado Boulder, which suffered extensive water damage following a catastrophic water pipe failure on its upper floors. Aerosol sampling was initiated within 48 hours of the breach, and continued for at least 60 days. 454 pyrosequencing of bacterial 16S rRNA genes was performed from DNA extracts of aerosol samples. Sequence data processing, based on custom barcode sequences, was performed using the QIIME pipeline at a 97% homology level using UCLUST. Sequence alignment using the PyNAST algorithm was performed, and taxa assignment at the Genus level followed using the RDP classifier retrained with the Green genes dataset.

Phylogenetic analyses of bioaerosols that were recovered from flooded indoor sites undergoing renovations, suggested an increased representation of Acinetobacter sp., Staphylococcus sp. and Streptococcus sp, over those aerosols recovered from proximal non-flooded areas, and the immediate outdoor environment (where these species were completely absent). These genera continue to be associated with respiratory diseases and nosocomial infections in many health care settings. Alpha diversity analysis revealed increased presence of these taxa in the days immediately following the flood, as well as several weeks (53 days) post-flooding. The results suggest that airborne microbial loads can be significantly influenced by water damage in both short- and long-time frames, regardless of conventional renovation activities to the indoor environment.

5MB.4

Stenotrophomonas Maltophilia Exposure in Homes. ERIC KETTLESON, Sudhir Kumar, Delphine Méheust, Sergey A. Grinshpun, Tiina Reponen, Stephen Vesper, Atin Adhikari, *University of Cincinnati*

Respiratory health outcomes including asthma and allergy can be influenced by indoor microbiome, which is ultimately shaped by home characteristics. The objective of this study was to investigate the concentration of Stenotrophomonas maltophilia, an emerging global pathogen, in air and dust samples. Forty-two homes were selected from the birth cohort of Cincinnati Childhood Allergy and Air Pollution Study (CCAAPS) based on home moldiness as measured using Environmental Relative Moldiness Index (ERMI). House dust was collected by floor vacuuming and sieved with a 355 µm mesh screen. Air samples were taken over a 24-hr period using a NIOSH 2-stage cyclone sampler, which collected airborne particles in three size fractions: <1.0 micro-meter, 1.0 – 1.8 micro-meter, and > 1.8 micro-meter. Bacterial DNA was extracted and S. maltophilia was quantified using a quantitative PCR assay with bacteria-specific primers and TaqMan probe. The S. maltophilia concentrations in indoor dust were greater in homes with high ERMI ($p = 0.017$). Highest concentrations of airborne S. maltophilia were measured in the size range of >1.8 micro-meter, indicating likely aggregation of the bacterial cells with typical physical size of 0.5 to 1.5 micro-meter in length. S. maltophilia dust concentrations were correlated with concentrations measured in air samples in the 1.0 – 1.8 micro-meter size fraction ($r = 0.480$, $p =0.003$) as well as with the total airborne concentration (all three size fractions combined) ($r = 0.374$, $p = 0.025$). Associations between indoor molds (as well as ERMI) and bacteria are relatively unknown. S. maltophilia is the first bacterial species associated with higher ERMI values in homes. The association of S. maltophilia with high concentrations of indoor fungi may be related to its chitinase production. These enzymes allow the bacterium to utilize chitin, a structural component of the cell wall of fungi, algae, and the exoskeleton of insects.

5MB.5

Microbial Content of Vacuum Cleaner Dust and Emitted Bioaerosols. CAROLINE DUCHAINE, Luke Knibbs, Congrong He, Marc Veillette, Ariane Pelletier, Remi Charlebois, Lidia Morawska, *Université Laval, Canada*

Indoor cleaning using high quality vacuum cleaners and bags is often recommended as a way of reducing allergen exposure in the home of asthmatic and allergic individuals. However, it has been shown that vacuuming can also promote the release of large concentrations of antigens by mechanical disturbance and release from the cleaner. In addition to releasing allergens and antigens from the surfaces, there is some evidence to suggest that vacuum bags may be a source of bioaerosol exposure through the release of their content during vacuuming. This is also potentially a source of dissemination of infectious bacteria. In the current study, we aimed to characterize the emission of bioaerosols from 21 in-use vacuum cleaners spanning a wide range of ages (6 months to 22 years) and prices (AUD $75 to $800). This report presents the findings of the second part of a larger study looking at biological and non-biological particles released from various vacuum cleaners (Knibbs et al., 2012). The emission of bacteria, Penicillium/Aspergillus genera as well as Clostridium cluster 1 and the presence of antibiotic resistance genes, Clostridium botulinum toxin gene in dust and air was measured. The bacterial biodiversity of vacuum dust and air samples taken during the assays was also assessed. The overall emission rates of bacteria ranged from 0 to to 7.4 × 10E5 bacteria min-1. Dust from vacuum bags contained up to 1 × 10E8 bacteria, Penicillium and Aspergillus per gram, and up to 6 × 10E5 Clostridium per gram. Antibiotic resistance genes were detected in 4 out of 18 dust samples and in 5 out of 18 air samples from operating vacuum cleaners. The DGGE biodiversity revealed several ribotypes from human and environmental origin. No samples were positive for the C. botulinum toxin gene and Archeae. Our study demonstrates that vacuum cleaner dust bags can contain significant quantities of bacteria and molds, and that extent to which these are emitted into the air varies greatly depending on the individual vacuum cleaner. Vacuum cleaner emissions are a source of indoor bioaerosol exposure. Frequent users, such as professional cleaners, may incur elevated exposures compared to other groups.

5MB.6

Detection of Tetracycline Resistance and Class 1 Integrase Genes in Indoor and Outdoor Air. ALISON L. LING, Mark T. Hernandez, Norman R. Pace, Timothy M. LaPara, *University of Colorado*

Antibiotic resistance genes are considered an emerging environmental contaminant. Of the possible transfer routes, airborne transmission of antibiotic resistance is the least understood, but may be a major pathway in indoor environments. Most studies of airborne microbes and their antibiotic resistance potential have been culture-based, which likely underestimates the abundance of airborne resistance genes.

This study verifies the presence of tetracycline resistance genes in both indoor and outdoor air using quantitative PCR to target two tetracycline resistance genes (tet(X) and tet(W)) and a class 1 integrase (intI1) gene, in conjunction with the bacterial 16S rRNA gene (a marker for total bacteria abundance). Aerosol samples were collected from potentially high exposure indoor environments (two livestock farms, two clinics, and a homeless shelter), as well as outdoor sites on Colorado’s Front Range (urban, agricultural and pristine). Gene copy abundance was normalized to volume of air sampled. Abundance of all genes observed were 10-100 times higher in confined animal feeding operations than in other environments, and tet(W) gene counts were typically 10-100 times higher than either tet(X) or intI1. The ratio of resistance genes to bacterial 16S genes was higher in the clinics and the homeless shelter than in the farms, indicating that a higher percent of airborne bacteria carry resistance potential in these environments. Genes encoding tet(W) were detected in outdoor air near livestock operations, and tet(X) and intI1 gene sequences were detected in air collected from a high alpine forest. Sequencing revealed a higher amount of variation in the gene sequences obtained for tet(W) and tet(X) genes (65% for both) than for intI1 genes (50%). These results indicate that antibiotic resistance and class 1 integrase genes can persist in both indoor and outdoor air, and suggest the possibility of both short-range and long-range atmospheric transport of antibiotic resistance potential.

5MB.7

Comparing the Indoor Microbiome from Seven Different Bioaerosol Samplers. ANDREW HOISINGTON, Juan Pedro Maestre, Sungwoo Bae, Kerry Kinney, Jeffrey Siegel, Maria D. King, *The University of Texas at Austin*

Microorganisms are ubiquitous in the indoor environment and are of concern for a variety of reasons including infectious diseases transmission, and the potential to aggravate asthma or allergy symptoms. Several microbial indoor air samplers have been developed for characterizing the microbiome but limited studies have been conducted to provide a side-by-side comparison. The objective of this study is to compare the bacterial and fungal sequencing results obtained from simultaneously sampling the indoor environment with seven different microbial samplers. The sampling was repeated in two consecutive weeks at the same location, only altering the air exchange rate between events.

In this study, we operated five bioaerosol samplers (SKC biosampler, button sampler, PEM 2.5 sampler, Andersen 6-stage viable impactor and the wetted-wall cyclone collector system) simultaneously in the same occupied, indoor environment at different flow rates for three consecutive 15 min sampling periods. In addition, airborne dust samples were collected from the building HVAC filters and settled dust samples from two adjacent indoor surfaces. Microbial DNA was extracted and analyzed from all samples by pyrosequencing, targeting the bacterial 16S region and the fungal ITS and 28S regions. Sequences were processed with identical criteria for denoising, chimera removal, trimming, and BLASTn search. Operational taxonomic units, phylogenetic trees, alpha-diversity and beta-diversity indices were calculated to compare the molecular results.

Results to date indicate that the samplers identify different microbial species. The differences could be attributed to sampler design (e.g. aerodynamics, air-inflow rate, destruction of cells/DNA, capture efficiency, volume of sample) or limitations in taxonomic identification. Similarly, the alpha-diversity estimates were different in the samplers across both bacterial and fungal communities. All seven samplers identified different microbial communities compared to the outdoor microbiome. The data set generated represents the first side-by-side assessment of these techniques and may enhance comparisons between studies that utilize different samplers.

5MB.8

Indoor Bioaerosol Dynamics: Fluorescent Particles in a College Classroom. SEEMA BHANGAR, Elizabeth Heredia, J. Alex Huffman, William Nazaroff, *University of California, Berkeley, CA*

Our research aims to characterize bioaerosol emissions, behavior, and fate in common, occupied indoor environments, using particle fluorescence as an indicator of biological origin. In a weeklong monitoring study conducted in a mechanically ventilated university classroom in March 2012, we observed strong transient increases associated with janitorial activities in the number concentration of fluorescent particles (N_F) and in the indoor/outdoor concentration ratio of all particles (I/O). We also observed increases in N_F, I/O and in the ratio of fluorescent to total particles (N_F/N_T) at the beginning and end of class sessions when human movements in the room were most vigorous.

Focusing on the aggregate behavior of 1-20 micro-meter particles, preliminary analyses show that during weekdays, when classes were in session and the air-handling system was on, mean levels of N_F, N_F/N_T, and I/O were 1.6 cm^{-3}, 23%, and 0.82, respectively. In the evenings, when the room was used less intensively but before the air handling system was turned off, mean levels of N_F, N_F/N_T, and I/O were reduced to 0.77 cm^{-3}, 15%, and 0.49. Overnight and on weekends, when occupancy was zero and the air handling system was off, fluorescent particle levels decreased by an order of magnitude. The mean N_F, N_F/N_T, and I/O during these times were 0.15 cm^{-3}, 3.8%, and 0.40. All three indicators varied strongly with particle size. Mean weekday values of N_F/N_T varied from 2% for 1 micro-meter particles to 68% for 10 micro-meter particles.

The data are being further interpreted to assess total and fluorescent particle emission and decay rates as functions of key influencing variables: human occupancy, building design and operational parameters, and particle size. Repeated sampling in this classroom and in other common indoor environments is planned.

5UA.1

Characterization of Exhaust Emissions from In-Use Motor Vehicles. TIMOTHY DALLMANN, Steven DeMartini, Thomas Kirchstetter, David Worton, Edward Fortner, Scott Herndon, Timothy Onasch, Ezra Wood, Robert Harley, *University of California, Berkeley*

Detailed measurements of particle emissions from motor vehicles driving in a highway tunnel in the San Francisco Bay area in July 2010 are reported. This study features highly time-resolved measurements of pollutant concentrations in the exhaust plumes of individual diesel trucks. Emission factors for individual trucks were calculated using a carbon balance method, in which emissions of pollutants in each exhaust plume were normalized to emissions of carbon dioxide. Pollutants considered include $PM_{2.5}$ and BC mass, particle optical properties (b_{abs}, b_{scat}, b_{ext}), and gaseous species including CO, NO, and NO_2. Fleet-average emission factors and emissions distributions were characterized for each species. Results indicate the average BC emission factor decreased 35 ± 11% relative to levels measured at the same location in 2006. Emissions distributions for all species were skewed with a small fraction of trucks contributing disproportionately to total emissions. For example, the dirtiest 10% of trucks emitted half of total $PM_{2.5}$ and BC emissions. Emission rates for NO_2 were found to be anti-correlated with all other species considered here, likely due to the use of catalyzed diesel particle filters to help control exhaust emissions. Absorption and scattering cross-section emission factors were used to calculate the aerosol single scattering albedo (SSA, at 532 nm) for individual truck exhaust plumes, which averaged 0.14 ± 0.04.

A soot particle mass spectrometer (SP-AMS) was used to characterize the emitted fine particles from gasoline and diesel vehicles. This instrument provides a unique and selective method for measuring the mass, chemical composition, and size distribution of fine particles including refractory components such as black carbon. SP-AMS measurements will be used to develop emission profiles that describe the organic aerosol and black carbon emitted by gasoline vehicles, and separately, diesel trucks, and to investigate variations in emission signatures for individual diesel exhaust plumes.

5UA.2

On-road Emission Factors of PM Pollutants for Light-duty Vehicles (LDVs) Based on Real-world Urban Street Driving Conditions. WINNIE KAM, James Liacos, James Schauer, Ralph Delfino, Constantinos Sioutas, *University of Southern California*

An on-road sampling campaign was conducted on two major surface streets (Wilshire and Sunset Boulevards) in Los Angeles, CA, to characterize particulate matter (PM) components including metals, trace elements, and organic species for three size fractions ($PM_{10-2.5}$, $PM_{2.5-0.25}$, and $PM_{0.25}$). Fuel-based emission factors (EFs) (mass of pollutant per kg of fuel) were calculated to assess the emissions profile of a light-duty vehicle (LDV) fleet that is reflective of real-world urban driving. EFs for metals and trace elements were highest in $PM_{10-2.5}$ while EFs for polycyclic aromatic hydrocarbons (PAHs) and hopanes and steranes were highest in $PM_{0.25}$. $PM_{2.5}$ EFs were also compared to previous freeway, tunnel, and dynamometer studies based on an LDV fleet to determine how various environments and driving conditions may influence concentrations of PM components. The on-road sampling methodology deployed in the current study captured substantially higher levels of metals and trace elements associated with vehicular abrasion (Fe, Ca, Cu, and Ba) and crustal origins (Mg and Al) than previous LDV studies. The semi-volatile nature of PAHs resulted in higher levels of PAHs in the particulate phase for LDV tunnel studies and lower levels of PAHs in the particulate phase for freeway studies. With the exception of a few high molecular weight PAHs, the current study's EFs laid in between the LDV tunnel and LDV freeway studies. In contrast, hopane and sterane EFs were generally comparable between the current study, the LDV tunnel, and LDV freeway, as expected given the greater atmospheric stability of these organic compounds. Overall, EFs from the dynamometer studies for metals, trace elements, and organic species are lower than the current study. Lastly, n-alkanes (C19-C40) were quantified and alkane carbon preference indices (CPIs) were determined to be in the range of 1-2, indicating substantial anthropogenic source contribution for surface streets in Los Angeles.

5UA.3

Gas-Particle Partitioning of Primary Organic Aerosol Emissions from Gasoline and Diesel Vehicles. ANDREW A. MAY, Albert A. Presto, Ngoc T. Nguyen, Christopher Hennigan, Timothy Gordon, Allen Robinson, *Carnegie Mellon University*

Gas-particle partitioning of primary organic aerosol (POA) emissions from motor vehicles has important implications toward understanding atmospheric organic aerosol concentrations. Source testing from a fleet of 45 in-use light-duty gasoline (LDGV) and two in-use light-duty diesel vehicles (LDDV) was performed at the California Air Resources Board Haagen-Smit Laboratory. Three in-use heavy-duty diesel vehicles (HDDV) were tested at the California Air Resources Board Heavy-Duty Engine Testing Laboratory. Four different methods were used to characterize the semi-volatile nature of the POA emissions: 1) artifact-corrected POA emission factors from a constant volume sampler (CVS); 2) isothermal dilution from the CVS into an environmental chamber; 3) evaporation induced by heating in a thermodenuder; and 4) inference of volatility distributions from thermal desorption/gas chromatography/mass spectrometry (TD-GC-MS) analysis. All four methods indicate that the POA emissions are semi-volatile. Measurements from the CVS showed that 30-80 % of POA emissions collected on bare-quartz filters reside in the particle phase; the remainder is semi-volatile vapors. Dilution into the chamber reduced the fraction of organic material in the particle phase by a factor of two or more. Nearly all LDGV POA emissions evaporated when heated to 100 ^{o}C in a thermodenuder. However, only a portion (~40%) of the LDDV and HDDV POA emissions evaporated when heated to 100 ^{o}C; this may be caused by a different gas-particle partitioning mechanism, such as adsorption instead of absorption. The median volatility distribution for the light-duty gasoline and diesel vehicles determined from the TD-GC-MS method was used to model experimental data with partitioning theory with excellent performance, especially for dilution and thermodenuder data. It is recommended that future studies apply this volatility distribution in order to estimate POA concentrations atmospherically-relevant conditions.

5UA.4

Evolution of Traffic-Related Atmospheric Pollutants Near Roadways. CHEOL-HEON JEONG, Greg J. Evans, John Liggio, Jeremy Wentzell, Ralf Staebler, Jeff Brook, *SOCAAR, University of Toronto*

Traffic-related atmospheric pollutants (TRAP) are believed to adversely impact the health of populations living and working near roadways. Estimation of the exposure of these populations to TRAP is a challenging task as concentrations of TRAP varies both spatially and temporally.

To characterize the spatial and temporal variations of TRAP in near-road environments, the evolution of ambient pollutants near a highway was investigated in Toronto in the summer of 2010 through the Fast Evolution of Vehicle Emissions near Roadways (FEVER) campaign. For this study, the U of T mobile laboratory (MAPLE) was deployed to measure the decay gradients of TRAP as a function of the distance from the highway. The study included mobile measurements of particle size distributions and chemical composition using a Fast Mobility Particle Spectrometer (FMPS), an Aerodynamic Particle Sizer (APS), an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), an Aethalometer, a particle-bound PAH (p-PAH) monitor including trace gases and meteorology. The ATOFMS was equipped with an automated thermo-denuder (TD) allowing rapid alternation between TD-treated and untreated sampling, to characterize variation of non-volatile particle composition. In addition, the micro-scale gradient of ultrafine particles (UFP) within 20 m from the highway was evaluated using two FMPSs with the TD system. Preliminary results indicate that downwind UFP, p-PAH, and black carbon concentrations at 30 m distance from the highway was 3-6 times higher than average concentrations measured downwind at 270 m. For near-roadside (< 20 m) particles, volatility measurements showed a loss of ~60% by number and ~80% by volume with a heating of 250 ^{o}C. High-time resolution mobile measurements of TRAP spatial patterns upwind and downwind of a highway will be discussed.

5UA.5

Comparing Primary and Secondary Particulate Matter from On-Road Sources: Gasoline vs. Diesel Vehicles. TIMOTHY GORDON, Albert A. Presto, Ngoc T. Nguyen, Allen Robinson, Hector Maldonado, Sulekha Chattopadhyay, Alvaro Gutierrez, William Robertson, Mang Zhang, Matti Maricq, Eric Lipsky, *Carnegie Mellon University*

Bahreini et al. (2012) recently reported that gasoline vehicle emissions are responsible for a much greater fraction of the secondary organic aerosol (SOA) in Los Angeles than diesel emissions. This conclusion was based on airborne and ground-based ambient measurements, and while the data are suggestive, it is difficult to link ambient conditions to specific sources without direct measurements of the emissions from those sources. Synthesizing the results from a large, multi-year study, our report compares the measured primary and secondary particulate matter (PM) from heavy-duty and light duty diesel vehicles (HDDV and LDDV) with that from light duty gasoline vehicles (LDGV).

Three different HDDV with and without aftertreatment were operated on a chassis dynamometer at the California Air Resources Board over a range of driving cycles and fuels. LDDV and LDGV were driven on a chassis dynamometer following the California Unified Cycle. The two LDDV were fueled with ULSD and biodiesel. Fifteen LDGV were tested, spanning a range of model years and emissions control standards (pre-LEV, LEV I and LEV II).

The gas- and particulate-phase emissions were characterized by collecting samples from a constant volume sampling system. Tenax sorbent samples were collected to characterize the emissions of semivolatile and intermediate volatility organic compounds. The dilute emissions were injected into a smog chamber and then photochemically aged, and the SOA production was quantified. Although BC and POA emissions varied significantly for HDDV, LDGV and LDDV, the amount of SOA per mass of fuel burned was comparable. Since fuel consumption is dominated by gasoline vehicles, the data suggest that gasoline vehicles are the greater on-road source of SOA. When the dramatic reduction in primary PM observed with aftertreatment-equipped HDDV is factored into the analysis of the net (primary + secondary) PM emissions, newer HDDV stand out as remarkably clean vehicles.

5UA.6

Mobile Monitoring: a Better Tool to Measure Vehicle Emission Factors. SCOTT FRUIN, Neelakshi Hudda, Ralph Delfino, Constantinos Sioutas, *University of Southern California*

Tunnel studies and remote sensing can track trends in fleet emissions, important in judging the effectiveness of emissions standards, but these methods are expensive and often do not capture the full range of vehicle operating conditions. A novel, mobile approach was developed that is more cost effective and appears to capture the spread in vehicular emissions during real-world operating conditions, important in capturing the contributions from high emitting vehicles, some of which are only high emitting during certain driving modes. Emissions were directly measured on-road using a mobile monitoring platform. When combined with real time traffic data, distributions of emission factors (EFs) for gasoline powered light-duty (LDV) and diesel powered heavy-duty vehicles (HDV) can be accurately calculated. Fleet average LDV EFs were generally in agreement with most recent studies and an order of magnitude lower than HDV EFs. However, HDV EFs appeared to reflect the continuing decreasing trend in diesel emissions, due to tighter new truck emission standards (e.g., 2007) and recent regulations focused on goods movement in Los Angeles. In particular, the HDV EFs on I-710, the primary route used for goods movement in LA were frequently lower than on other freeways. Therefore, it appears the contributions from higher LDV vehicle miles traveled (VMT) on freeways with lower truck volumes are now beginning to erode the traditional dominance of higher truck volumes in producing the highest total freeway emissions. This finding provides further evidence of the importance in reducing the rates of LDV VMT growth for urban air quality, despite the relatively low emissions per mile now achieved by LDVs.

5UA.7

Effects of Truck Retrofit/Replacement Program on Diesel Engine Emissions at the Port of Oakland. CHELSEA PREBLE, Timothy Dallmann, Steven DeMartini, Nathan Kreisberg, Susanne Hering, Robert Harley, Thomas Kirchstetter, *University of California, Berkeley*

To reduce pollutant emissions from trucks around ports and rail yards, the California Air Resources Board’s Drayage Truck Regulation required replacement of trucks with pre-1994 engines and retrofit with diesel particulate filters (DPFs) of trucks with newer engines. We measured pollutants in the exhaust plumes of individual heavy-duty trucks at high time resolution (1-2 Hz) as they drove by a mobile lab that was parked on a bridge above the traffic en route to the Port of Oakland. This study adds to prior fieldwork at the Port that demonstrated 50 and 40% reductions in fleet-average emissions of black carbon and nitrogen oxides (NOx), respectively, resulting from the first phase of the emission control rule. Emissions of ultrafine particles (number and size distribution), black carbon, and nitrogen dioxide (NO2), in addition to the NO2/NOx emission ratio, were measured in this study and linked on a truck-by-truck basis to detailed information about each engine and installed emission control equipment. This analysis examines the distribution of pollutant emissions across all Port trucks, and among various subpopulations (e.g., specific engine years, types of emission controls). The current age distribution indicates that the majority of trucks are now equipped with DPFs. A fraction of trucks have DPFs that are several years old, and a significant portion of the Port truck fleet is now also equipped with selective catalytic reduction systems. The results of this study are significant as a similar regulation targeting emissions from all on-road trucks and buses in California is being implemented, and other states are likely to follow California’s lead.

5UA.8

Ultrafine Particle Exposure of Street Users Walking, Cycling, and Driving Along an Urban Residential Roadway. DAVID QUIROS, Eon Lee, Yifang Zhu, Rui Wang, *University of California, Los Angeles*

Elevated concentrations of ultrafine particles (UFPs, < 0.1 micro-meters), which have been linked to adverse health effects, are commonly found near roadways. We measured particle number concentration (PNC) across three transportation modes on an urban residential street in Santa Monica, CA: walking, cycling, and driving with windows open and windows closed. We repeated measurements concurrently for nine days during the morning (7:30-9:00), afternoon (12:30-14:00), and evening (17:00-18:00). We observed ~60% PNC reductions when driving with closed with recirculation, relative to modes with direct contact to the outside air (cycling, walking, and driving with windows open). Afternoon and evening period PNC was ~75% lower than morning period PNC. We found nearly four times higher exposure to commuters cycling and walking due to higher ventilation rates and longer durations per round trip. We found positive associations between PNC and road grade and proximity to intersections. We classified on-roadway fleet by vehicle type from video recorded footage, and found our measured PNC originated ~30% from older (before 1980) gasoline vehicles, ~40% from newer gasoline vehicles, and ~30% from diesel trucks (school buses, garbage trucks, and heavy-duty diesel trucks). This is one of the first transportation mode comparison studies in the United States for assessment of commuter exposure to UFPs and other air pollutants. The study site is currently under redesign construction and when completed will meet the California Complete Streets Act standards. Our study serves as a baseline condition for UFP exposure across all street users.

6AC.1

A Comparison of the Chemical Sinks of Atmospheric Organics in the Gas and Aqueous Phase. SCOTT A. EPSTEIN, Sergey Nizkorodov, *University of California, Irvine*

It is now recognized that aqueous-phase reactions in the atmosphere can contribute to the production and/or aging of organic aerosols. However, the role of direct vs. indirect aqueous photochemical processes is currently uncertain. To better understand the significance of different gas-phase and aqueous-phase photochemical processes in transforming atmospheric volatile organic compounds (VOCs), we estimate the relative rates for oxidation by hydroxyl radical (OH) and of direct photolysis by actinic radiation in the gas phase and of VOCs dissolved in cloud droplets. We constrain these rates with published rate constants that are well established in the literature. However, the atmospheric significance of direct aqueous photolysis is uncertain due to the lack of absorption cross sections and photolysis quantum yields measured in the aqueous phase. Our relative rate approach allows us to examine the importance of aqueous photolysis for the compounds investigated in spite of the limited published data. We determine the relative magnitudes of these four photochemical sinks for 27 atmospherically relevant species inside air parcels containing cloud and fog droplets. Results of this analysis will help guide researchers by identifying compounds that are likely to be destroyed by photolysis inside cloud or fog droplets, and lead to the generation or aging of organic aerosols.

6AC.2

Secondary Organic Aerosol Formation on Wet Aerosols: Model Simulation and Implications. SIYUAN WANG, Jian Zhen Yu,*Hong Kong University of Science & Technology*

In recently years, a growing number of studies suggest that SOA formation via aqueous-particle processes may account for a significant fraction of the currently missing SOA [1]. Water-soluble organics, such as glyoxal, may undergo a series of aqueous-phase processes in aerosol liquid water that eventually lead to the formation of highly oxidized, high-molecular-weight compounds [2].

In the present study, an observation-based modeling work is conducted, incorporating state-of-the-art gas-/aqueous-phase mechanisms to evaluate SOA formation potential on wet aerosols. The model is driven by real-time ambient measurements (e.g. NMHCs, NOx, CO, Ozone, AMS) obtained in summer Hong Kong, located in sub-tropical Asia with high relative humidity. The modeling results indicate that the SOA formed via aqueous-particle processes could account for 1/5 of total SOA in summer. Major aqueous-phase products include C2-C4 di-carboxylic acids, oligomers and organosulfates. The simulated effective Henry's law constant of glyoxal, effective SOA formation rate relative to glyoxal and reactive uptake coefficient of glyoxal all fall in the respective ranges reported in the literatures. Furthermore, we herein demonstrate that aqueous-particle processes may explain the formation of some di-carboxylic acids and organosulfate (glycolic acid sulfate and IEPOX-sulfate) observed in ambient aerosols.

This modeling work suggests the potential importance of aqueous-particle processes on SOA formation under humid conditions, which is currently not incorporated in air quality models yet. More detailed chemical speciation techniques for aerosol-phase components (e.g. di-carboxylic acids, organosulfates, oligomers) are in crucial need, in order to further evaluate these processes.

References

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6AC.3

SOA Formation from Glyoxal in the Aerosol Aqueous Phase: A Case Study From Mexico City Using an Explicit Laboratory-based Model. ELEANOR WAXMAN, Barbara Ervens, Katja Dzepina, Julia Lee-Taylor, Rainer Volkamer, *University of Colorado*

Glyoxal is an important contributor to secondary organic aerosol (SOA) formation via aerosol aqueous phase processing. This work takes a glyoxal-SOA model parameterization based on laboratory data and combines it with ambient measurements in a box model. This is applied to the Mexico City Metropolitan Area case study on April 9, 2003 to determine if aerosol uptake and processing of glyoxal in aerosol water can explain the previously observed gas phase glyoxal imbalance. We find that we can explain the imbalance and that the time series of the glyoxal-SOA formation from our model suggests that a surface uptake process is occurring in Mexico City. We compare the AMS-measured OOA to SOA predictions using our glyoxal model combined with background aerosol, traditional aerosol, and either Robinson, Grieshop, or GECKO-A S/IVOC aerosol parameterization mass. Additionally, we compare the AMS-measured O/C ratios with O/C calculated from our glyoxal model combined with background aerosol, traditional aerosol, and either Robinson, Grieshop, or GECKO-A S/IVOC parameterization. We find that our glyoxal model is necessary to bring the O/C ratios in line with those measured in Mexico City. Finally, we explore the effect O/C has on likely particle growth for the Mexico City aerosol.

6AC.4

SOA Formation through Aqueous Chemistry: Volatility and Yields. BARBARA TURPIN, Yong Bin Lim, Diana Ortiz-Montalvo, Allison Schwier, V. Faye McNeill, *Rutgers University*

Oxidation of organic emissions leads to the abundant formation of small, polar compounds that readily partition into cloud, fog and aerosol waters. Subsequent reactions in the aqueous phase can form low volatility products that remain in the particle phase even after water evaporation. Liquid water is the most abundant condensed phase species in the atmosphere. Thus, gas followed by aqueous chemistry could be a substantial source of secondary organic aerosol (SOAaq). If gas phase production of a water-soluble compound is slow, the compound will be rapidly depleted from the gas phase when it encounters a cloud, and the subsequent aqueous chemistry will proceed as in a batch reactor. If gas-phase production is rapid, that compound will be taken up and present continuously in the aqueous phase with its aqueous products, as in a continuously stirred tank reactor (CSTR).

We used chemical modeling and droplet evaporation experiments to develop insights regarding yields, composition and volatility of SOAaq from aromatic and alkene emissions for these bounding scenarios. Droplet evaporation experiments were conducted using organic mixtures that mimic the aqueous chemical composition predicted by chemical modeling for CSTR and batch reactor scenarios. Monodisperse droplets were generated, evaporated and the resulting particle size was measured. The volatility behavior of mimics was compared with standards with known vapor pressure. Gas-particle partitioning of SOAaq species was also studied using Aerosol Chemical Ionization Mass Spectrometry. Effective heats of vaporization were lower for the complex mixture of organic products than the theoretical values for pure components. Effective vapor pressure was substantially lower when ammonia was added. Modeling results suggest that glyoxal/methylglyoxal SOAaq yields from CSTR scenarios are greater because of oligomerization of unreacted aldehyde; yields of organic acids were virtually identical for batch and CSTR scenarios. Implications to SOAaq formation in clouds and wet aerosols will be discussed.

6AC.5

Analysis of Atmospheric Water-Soluble Organic Compounds Using H-NMR and Liquid Chromatography High Resolution Mass Spectrometry. VERA SAMBUROVA, Lynn Mazzoleni, Alexander Laskin, Julia Laskin, Parichehr Saranjampour, Anna Gannet Hallar, Douglas Lowenthal, Barbara Zielinska, *Desert Research Institute*

It is well known that atmospheric aerosols play an important role in many atmospheric processes, such as cloud formation, light absorption-reflection, droplets formation, etc. Many studies have shown that organic compounds are a major fraction of the total aerosol mass. Inorganic components are well studied at the present time, while the fraction of organic compounds requires more investigation and analysis. The chemical characterization of the organic fraction is a challenging task, because this fraction is a complex mixture of different individual organic species, with a various functional groups (e.g. carboxylic, aliphatic, aromatic, phenolic, sulfate, nitrate, etc.).

In the present study, H-NMR and liquid chromatography (LC) high resolution mass spectrometry (MS) were used to characterize atmospheric water-soluble organic compounds and analyze their functional groups. Aerosol samples were collected during the summer of 2010 at the Storm Peak Laboratory on Mt. Werner, Steamboat, CO (3210 m AMSL). High-volume samplers equipped with size-selective PM2.5 inlets were used to collected particles on pre-cleaned 8”×10” Teflon-impregnated glass fiber filters. 38 aerosol samples were extracted with high purity water and combined into six composites. The aqueous composites were pre-concentrated using freeze-drying technique which prevents losses of light organic compounds. XAD-8 / XAD-4 resin columns were applied for separation of water-soluble organic matter from inorganic constituents. A high resolution LTQ-Orbitrap mass spectrometer (Thermo Electron, Inc.) equipped with an electrospray ionization (ESI) source was used to acquire mass spectra after LC separation with C18 LC column. Molecular formulas of organic species were assigned using accurate mass measurements (m/z) of detected ions. In addition, the aliphatic, arylic, phenolic, and carboxylic functional groups were quantified using H-NMR. All the results were evaluated and compared with ultra-high resolution Fourier Transform-Ion Cyclotron Resonance MS analysis (see abstract Mazzoleni et al.).

6AC.6

Organic-nitrogen Compound Formation via Aqueous Photo-oxidative Processing of Glyoxal in the Presence of Different Inorganic Salts. ALEX K. Y. LEE, John Liggio, Shao-Meng Li, Jonathan Abbatt, *University of Toronto*

Formation of particle-phase organic-nitrogen compounds has been proposed via aqueous chemistry of glyoxal and $(NH_4)_2SO_4$ in dark and illuminated conditions. In the atmosphere, glyoxal likely co-exists with many other inorganic components in aqueous droplets but their molecular interactions are still not well understood. The primary goal of this study is to investigate the formation of organic-nitrogen species through aqueous photo-oxidative processing of glyoxal in the presence of different inorganic salts (e.g., $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3, Na_2SO_4 and $NaNO_3$). Aqueous-phase OH oxidation of glyoxal was performed using a photochemical reactor that allows simultaneous atomization of the reacting solution. The elemental composition of aqueous droplets were analyzed by the Aerodyne High Resolution Aerosol Mass Spectrometer (HR-AMS).

According to our preliminary results, organic-nitrogen fragments at m/z 68 ($C_3H_4N_2^+$) and 69 ($C_3H_3NO^+$) immediately formed when glyoxal was mixed with $(NH_4)_2SO_4$, NH_4HSO_4 or NH_4NO_3 in dark conditions. Note that these organic-nitrogen fragments were not observed in pure glyoxal or pure inorganic solutions. The above observations are possibly due to the formation of 1H-imidazole-2-carboxaldehyde in the mixed solution. By contrast, mixing of glyoxal with Na&_(2)SO&_(4) or $NaNO_3$ did not produce these fragments, further suggesting that the NH_4^+ is an essential component to produce organic-nitrogen compounds in these systems. From the photo-oxidation experiments of glyoxal, we observed that the organic fragment $C_3H_4N_2^+$ at m/z 68 increased in abundance with OH exposure in the case of $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3. In particular, aqueous-phase OH oxidation of glyoxal-NH_4NO_3 solutions can produce much higher m/z 68 signal than all other solutions. Because $NaNO_3$ and $(NH_4)_2SO_4$ did not lead to the same effect as NH_4NO_3 during photo-oxidation, we believe that the organic-nitrogen peaks are predominantly arising through ammonium chemistry but photo-chemistry involving nitrate may play a role in enhancing this formation processes. Furthermore, our results suggest that the presence of Na^+ may suppress the organic-nitrogen species formation.

6AP.1

Kinetics of Heterogeneous Nucleation in Supersaturated Vapor: Fundamental Limits to Neutral Particle Detection Revisited. ROBERT MCGRAW, Jian Wang, Chongai Kuang, *Brookhaven National Laboratory*

We examine the nucleated (with barrier) activation of perfectly wetting (zero contact angle) particles ranging from essentially bulk size down to approximately one nanometer mass diameter. While similar studies trace back to the pioneering work of Fletcher [1958], we present here a novel approach to the analysis based on general area constructions that enable key thermodynamic properties including surface and bulk contributions to nucleation work to be interpreted geometrically with reference to the Kelvin curve. The kinetics of activation is described in more detail in terms of the mean first passage time (MFPT) for barrier crossing. MFPT theory and benchmark calculations are used to develop and test a new approximate but simpler to use analytic expression for barrier crossing rate. The present study is motivated by recent condensation particle counter (CPC) studies that appear to finally establish the long-predicted detection of "sub-Kelvin" particles in the nano-size regime. Corresponding states thermodynamic and kinetic scaling approaches are used to facilitate the correlation and selection of optimal CPC working fluids and operating conditions based on a new metric for heterogeneous nucleation, the signal to noise ratio, and on physical and chemical properties.

6AP.2

The Effects of Heat Release During Nanoparticle Nucleation. JUN LIU, Sean Garrick, *University of Minnesota*

In this work we study the effects of heat release during the homogeneous nucleation of metal nanoparticles. We perform direct numerical simulation of zinc nucleation in laminar and turbulent jets. The flows consist of hot metal vapor issuing into cooler inert gas. As the hot metal vapor is transported and mixes with the cooler background gas, particles nucleate. Nucleation is an exothermic process and the energy released has the effect of increasing the local temperature. As nucleation rate and critical diameter are highly sensitive to temperature, the nucleation—heat-release interaction is coupled one. As energy is released, the temperature increases and the rate of particle nucleation decreases. However, the energy release also has effects on fluid, mass, and thermal transport. We examine this complex dynamic in both laminar and turbulent flows using a high-order accurate numerical scheme to obtain the fully resolved, unsteady evolution of the fluid, thermal, scalar, and particle fields.

6AP.3

Scattering Calculations to Predict Mobilities from Molecular Models. CARLOS LARRIBA, Christopher Hogan Jr., *University of Minnesota*

A common method for the characterization of small charged particles and molecular clusters in the gas-phase is mobility analysis. The ability to predict the mobility of a charged cluster from a molecular model of that structure is therefore of particular interest, as high resolution mobility measurements in conjunction with correct mobility prediction could be used to directly infer molecular cluster structure. Although methods to make such calculations are used commonly in conjunction with mobility analysis of electrosprayed ions, they are used sparingly in the combination with mobility analysis of aerosol particles and clusters. In this presentation, we review previously developed and introduce new methods of mobility calculation from structural models. These new methods of calculation account for non-specular gas-molecule scattering upon collision with a particle/cluster, and it is shown that these methods are suitable for aerosol particle mobility prediction. In total, we discuss the following three calculation methods, the projected area (PA) method, the vibration-diffuse hard sphere scattering method (VDHSS), and the vibration-diffuse trajectory method (VDTM), with the PA method with the lowest computational demands and the VDTM with the highest computational demands, but the fewest assumptions made in the calculation.

6AP.4

The Structure of Nanoparticle Nucleation in Three-Dimensional Planar Jets. NATHAN MURFIELD, Sean Garrick, *University of Minnesota*

The effects of large-scale mixing and vapor concentration on homogeneous nucleation rates are investigated via direct numerical simulation (DNS) of dibutyl-phthalate (DBP) nucleation during cooling and mixing in three-dimensional planar jets. DNS is used as it contains no inherent assumptions about the cooling or mixing processes. In the simulated cases, a heated jet doped with DBP issues into a co-flow of room-temperature air. As the two streams mix, the DBP vapor becomes highly supersaturated and particles are formed by homogeneous nucleation. The simulation results provide a demonstration of how nucleation takes place in narrow regions where molecular mixing of the two streams occurs. Two distinct nucleation events are observed: initial shear layer nucleation, and later nucleation in coherent structures or eddies generated by the velocity difference between the jet and the co-flow. These observations agree with the trends seen in the experimental studies of DBP nucleation carried out by Lesniewski and Friedlander (Proc. R. Soc. Lond. A 454, 1998). A scatter plot diagram of observed dilution paths in temperature versus condensable vapor concentration space where nucleation rates are superimposed is shown to be a convenient tool for analyzing nucleation events. Convection by large-scale eddies gradually spreads the range of mixing paths in this space towards higher nucleation rates. The results also show that boundary conditions, including inlet concentration and velocity ratio, have both significant effects on particle nucleation. Both increased large-scale convective mixing and increased inlet DBP concentration are shown to increase nucleation rates. Additionally, heat release during nucleation is shown to affect the flow field in cases where the nucleation rate is very high.

6AP.5

D2O and Nonane Non-equilibrium Droplet Growth in the Free Molecular Regime. HARSHAD PATHAK, Kelley Mullick, Barbara Wyslouzil, Shinobu Tanimura, *The Ohio State University*

Nanodroplet growth of water and n-alkanes is observed in industrial processes including, for example, the removal of condensibles from natural gas or during the expansion of steam in low pressure turbines. The process commences with homogenous nucleation of the supersaturated vapor to form droplets. Droplet growth then quenches nucleation by depleting the vapor and releasing heat to the flow. The competition between nucleation and the initial stages of droplet growth determines the number of droplets formed and, thus, strongly influences the aerosol size distribution. We study the growth of D_2O or nonane droplets in the free molecular regime under the highly non-equilibrium conditions found in supersonic nozzles and compare the measured growth rates to the predictions of the isothermal Hertz-Knudsen (HK) and non-isothermal Hertz-Knudsen-Smolders (HKS) growth laws. Pressure trace measurements (PTM) combined with small angle X-ray scattering (SAXS) characterize the droplet size and number densities as a function of the flow time in a supersonic nozzles with 5-10 microsecond time resolution. For the D_2O aerosols coagulation clearly plays a role, while for the nonane aerosols number densities are low enough that coagulation is not important. Fourier transform infrared spectroscopy experiments also detect freezing in the coldest D_2O droplets. For the nonane droplets, there is essentially no difference between the predictions of the isothermal and non-isothermal growth laws since the equilibrium vapor pressures are so low that the ratio of the evaporation to condensation rates is effectively zero. The experimental D_2O growth rates are more closely predicted by the non-isothermal growth law rather than isothermal growth law, but there are still significant differences that cannot be explained by coagulation.

6AP.6

Molecular Dynamics of Evaporation and Mass Accommodation of Water for Various Droplet Sizes. JAN JULIN, Manabu Shiraiwa, Ulrich Pöschl, Ilona Riipinen, *Stockholm University*

We have studied the mass accommodation coefficient of water molecules on water surfaces using molecular dynamics (MD) simulations. The mass accommodation coefficient describes the ability of a surface to uptake gas phase molecules, and is an important quantity in understanding the condensational growth of atmospheric aerosol particles. Unfortunately, even for water-on-water a discrepancy exists between reported coefficients, with values ranging from 0.1 to 1. In MD simulations for water the coefficient has been consistently found to be one. However, to our knowledge, the studies have so far considered only planar surfaces. In order to study possible aerosol size-dependent factors affecting mass accommodation we have performed mass accommodation simulations for different droplet surfaces at T=273.15 K, as well as the planar surface. Additionally, we have also performed simulations for the planar surface in various temperatures to elucidate any temperature dependence. The simulations were performed using the TIP4P-ew water potential.

The simulation setup is the familiar one: incident molecules are generated at set time intervals at a distance from the surface, and shot towards the surface. A total of 1000 impact events are simulated per target surface. We also simulated evaporation from a surface without any incident molecules present, and found the evaporative flux to be consistent with the theoretical prediction calculated using equilibrium vapor pressure. Comparing to the evaporation events observed in the mass accommodation simulations, we can identify the evaporation induced by the incoming molecules. Thus we can identify the magnitudes of the two options for non-accommodation: the direct reflection of incoming molecules and the exchange of an incident molecule with a surface molecule. In any case, the mass accommodation coefficient is close to unity, even for droplets with 2 nm radius. The results from MD simulations are further used to assess and improve assumptions used in kinetic mass-transport models.

6CC.1

Impact of Biomass Burning Aerosols on Regional Climate Over Southeast USA. PENG LIU, Yongtao Hu, Alexandra Tsimpidi, Athanasios Nenes, Armistead Russell, *Georgia Institute of Technology*

Aerosol from biomass burning, which is rich in black carbon and organic compounds, is a major contributor to the particulate matters over Southeast USA, and may have significant feedbacks to regional climate through the direct and indirect effects.

In this study, the cloud droplet activation parameterization of Kumar et al.(2009), which considers the competition between soluble and in soluble aerosols for water vapor during cloud droplet formation in ascending air parcels, is implemented in WRF-Chem. The water uptake properties of the biomass burning aerosol (required for predicting optical depth for direct radiative forcing, and CCN activity for indirect effects) are constrained using observations of fresh and aged biomass burning aerosol sampled during the 2008 ARctas campaign (Jacob et al., 2010). We first couple the aerosol module only with radiation module to estimate direct effect, and then with microphysics module for the indirect effect.

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6CC.2

Particle-Resolved Simulations on the Effects of Black Carbon Mixing State on Cloud Droplet Number Concentration and Radiative Forcing. JOSEPH CHING, Nicole Riemer, Matthew West, *University of Illinois at Urbana-Champaign*

The climate impacts of black-carbon-containing particles are complex. On the one hand particles of this type absorb solar radiation (the direct effect), on the other hand they may act as cloud condensation nuclei (CCN), which in turn form cloud droplets and hence reflect solar radiation (the first indirect effect). The latter impact is further complicated since the potential of black-carbon-containing particles to form cloud droplets does not only depend on the physico-chemical properties of the black carbon particles. It also depends on the other particles present in the population, which all compete for water vapor, and on environmental parameters such as the updraft speed.

In this study we investigate how the aerosol mixing state impacts the cloud-forming ability of black-carbon-containing particles. We employ a two-step approach by using the particle-resolved aerosol model PartMC-MOSAIC in conjunction with a particle-resolved cloud parcel model. First, we use PartMC-MOSAIC to simulate a suite of 2-day evolutions of the aerosol population in an urban plume, varying the emission rates of black-carbon-containing particles and the concentration of background particles to cover a wide range of atmospherically relevant conditions. We then use the hourly output of these particle-resolved simulations as input to a particle-resolved cloud parcel model to study the activation and the condensational growth of the CCN. With this method we explicitly resolve the composition of individual particles and cloud droplets in a given population of different types of aerosol particles, and accurately track their evolution due to emission, dilution, condensation and coagulation. We investigate the impact of black carbon mixing state on cloud droplet number concentration (CDNC) by comparing the CDNC obtained from a particle-resolved population to that obtained from its derived counterpart in which particles are completely internally mixed. We discuss the relevance of accounting for aerosol mixing state when estimating the radiative forcing.

6CC.3

Internal or External? The Mixing State of Biomass Burning Aerosol, Its Photochemical Evolution, and Climate Impacts.MICHAEL GIORDANO, Lelia Hawkins, Akua Asa-Awuku, *University of California, Riverside*

Biomass burning is a global, yet poorly constrained, emitter of both primary and secondary organic and inorganic aerosols. The emission and downwind photochemical oxidation of these aerosols can both directly and indirectly modify climate. As these aerosols transform (age) in the atmosphere, their composition, cloud condensation nuclei (CCN) activity, soluble organic content, surface tension, and optical properties are all subject to change. To explore this process, controlled burns of common Southwestern shrubs, Manzanita and Chamise, were conducted at UC-Riverside's CE-CERT facility. The biomass was burned in a wood stove, diluted, and injected into a 12m3 Teflon chamber. UV lights were turned on to promote photochemistry and a suite of instruments measured the gas and aerosol phases. This presentation continues the series of biomass burning studies at UCR and will focus on new information that highlights the significant changes in the organic and inorganic makeup of the aerosol as it ages as well as its CCN ability and optical properties. The organic content of the aerosol is analyzed with an Aerosol Mass Spectrometer and the inorganic content deduced from an online water soluble organic carbon analyzer and an SMPS. Additionally, changes in CCN ability with the use of different oxidizing agents (NO, NO2,O3), which can depress kappa below .1 and promote chemistry that raises kappa by 300% under photooxidative conditions, will be discussed.

6CC.4

The Impact of Decreasing Black Carbon Emissions on California's Climate. ODELLE HADLEY, Lukas Valin, Surabi Menon, Thomas Kirchstetter, *Lawrence Berkeley National Laboratory*

Ground measurements show that black carbon (BC) aerosol concentrations in California have decreased by approximately a factor of two between 1985 and 2005. In this study, we use the WRF-Chem model to estimate the seasonal scale changes in radiative forcing, surface temperature, and precipitation resulting from the reduced BC concentrations over this period. To do this, two simulations of WRF-Chem were run for the year 2005. In the first simulation, we used a chemical emissions inventory developed by Streets and Bond (2006) for the ARCTAS campaign. For the second simulation, the BC emissions were doubled to mimic the higher concentrations observed in 1985. The results are seasonally averaged to reduce the statistically insignificant noise that dominates on shorter time scales. We find significant BC radiative forcing over CA (+ 5 W m-2 at the surface and + 4 W m-2 at TOA) and differences in precipitation (+ 80 mm) and surface temperatures (+ 0.25 ºC) as a result of the decrease in BC emissions and surface concentrations. The patterns of radiative forcing, as well as temperature and precipitation changes are regionally dependent and, depending on the region, can be either positive or negative. The 2005 simulations are validated against available measurements of BC, total PM2.5, surface solar flux, cloud cover, temperature, and precipitation.

6CC.5

The Impact of Source-Oriented Aerosols on Fog Formation and Energy Budget in the California Central Valley.

HSIANG-HE LEE, Shu-Hua Chen, Michael Kleeman, Steven DeNero, *UC Davis*

Tule fog events are common in California's heavily polluted San Joaquin Valley (SJV) during the winter season, where they provide an aqueous volume for secondary reactions. The aerosol number concentration, size, and composition can alter fog formation and the radiation budget. Direct emissions of anthropogenic particles serve as the majority of the cloud condensation nuclei (CCN) during fog events in the SJV, but most current models that predict interactions between aerosols and fogs/clouds make simplified assumptions about the mixing state of anthropogenic particles.

The primary goal of this research is to implement a source-oriented CCN module in the Weather Research and Forecasting model (WRF-Chem) to investigate the effects of aerosols from various sources on fog formations and their optical properties. This work builds on a recent project to implement a source-oriented framework for particulate matter operations within WRF-Chem (SO-WRF-CHEM6D) at UC Davis. Particle radius, number concentration, and chemical composition are calculated explicitly for each particle source and size bin. The new source-oriented CCN module in SO-WRF-CHEM6D is combined with the two-moment Purdue Lin microphysics scheme including cloud feedbacks on aerosol distribution and number concentration.

Four numerical experiments will be conducted for two fog events (February 21, 2007 and January 17, 2011) to understand the influence of aerosol particles serving as CCN in clean and polluted environments on the fog formation and radiation budget. Aerosol direct and indirect effects will be studied in these numerical experiments. Comparison among these experiments will help us understand the impact of source-oriented aerosol-cloud-radiation effects on the energy and moisture budget, boundary layer instability, fog lifetime, fog thickness, etc.

6CC.6

Investigating Effects of Ambient Temperature on Hygroscopic Properties of Atmospheric Aerosol using ATR-IR.

YONG LIU, Dong Fu, *University of Colorado Denver*

Phase and hygroscopic properties of atmospheric particles affect global radiation budget and atmospheric composition by changing light scattering and absorption abilities and reactivity of aerosol. Temperature in the troposphere spans over a wide range from 217K in the tropopause to close to room temperature at sea level. At present, our knowledge about the role of ambient temperature in hygroscopic properties such as deliquescence, efflorescence, and hygroscopic growth of aerosol, especially water soluble organic salts, is still fairly limited. In the present work, we demonstrated feasibility of using an environmental cell coupled to an ATR-IR spectrometer to probe hygroscopic behavior of atmospheric aerosol and the temperature dependence. We selected several model aerosol samples of atmospheric importance (NaCl, $NaNO_3$, and $(NH_4)_2SO_4$) first to validate the approach. We determined values of deliquescence relative humidity (DRH) and efflorescence relative humidity (ERH) by integrating absorbance of H_2O bands from infrared spectra as a function of RH. We also calculated water to solute ratios (WSR) and growth factors (GF) with the integrated absorbance values of H_2O band and corresponding infrared active bands. We compared the results with our bulk water activity measurement and literature data and obtained an excellent agreement. This indicates that our approach is capable of acquiring reliable temperature dependent hygroscopic data. In this study, we also investigated temperature dependent hygroscopic property of CH_3SO_3Na, an important composition of chemically processed aerosol samples in marine boundary layer. In addition, our results showed that the ambient temperature in the troposphere could play an important role in hygroscopic properties of atmospheric aerosol, but it is largely dependent on the compositions.

6IA.1

The Concentration of Reactive Oxygen Species in a Sample of Houses in Austin, Texas. SHAHANA KHURSHID, Jeffrey Siegel, Kerry Kinney, *The University of Texas at Austin*

Reactive oxygen species (ROS) are an important class of secondary air pollutants which include hydroperoxides, organic peroxides, hypochlorite ions, and alkyl peroxyl radicals. High levels of ROS in the body can induce cell injury and cause a variety of deleterious health effects. In outdoor air, ROS is mainly generated from photochemical reactions in polluted air containing VOCs and NO_x. In indoor environments, reactions between ozone and unsaturated organic compounds may be an important additional source of ROS. While ROS can exist in both gas and particulate phases, particulate ROS (especially particles smaller than 2.5 micrometers) can penetrate deep into the lungs. In this research, $PM_{2.5}$ particles were collected on Teflon filters inside and outside single-family residences in Austin, Texas and ROS was assessed with a fluorescent reagent. The background fluorescence produced by nine different kinds of filters (by Pall, SKC, and Whatman) was assessed and Pall PTFE filters on a polypropylene support were selected for use in the assay because of their low background fluorescence and structural integrity. The average concentration of ROS inside the sample of houses was found to be 1.7 times higher than the average outdoor ROS concentration (3.03 nanomoles H_2O_2/m^3 as compared to 1.78 nanomoles H_2O_2/m^3). The indoor concentration of ROS was a weak function of the outdoor ROS concentration, building age and building size. Additionally, the outdoor concentration of ROS was found to be higher near roadways. The outdoor concentrations agree with other studies which have reported outdoor ROS levels in the range 0.54-5.71 nanomoles/m^3. This study provides insight into the indoor to outdoor ratio of particulate ROS and is one of the first studies to assess ROS in indoor environments, especially houses. A better understanding of accurate levels of ROS in the places we occupy is essential to establish healthy living environments.

6IA.2

The Impact of Energy Efficiency Retrofits on Indoor PM Levels. SARAH FREY, Matthew Fraser, Pierre Herckes, *Arizona State University*

Retrofitting building for energy efficiency often entails improved sealing of the building envelope to decrease demand for air conditioning. As indoor sources of pollution often have a greater impact on exposure of residents than outdoor pollutant levels, this sealing of the building envelope could impact the indoor air quality. To investigate this, we conducted indoor air quality sampling before and after an energy efficiency retrofit of a senior living facility in Phoenix, AZ. At the same time, we also interviewed the residents about their health and any other behaviors (i.e. smoking) that would impact indoor air quality.

We report the indoor PM levels for SunnySlope Manor, an apartment complex for low income seniors run by the City of Phoenix. Initial sampling, before the energy efficiency retrofit, was conducted during the summer of 2010. Follow-up sampling, after the energy efficiency retrofit, was conducted from June – August, 2011. A total of 72 apartments were studied in Panel 1, while only 53 units were studied in Panel 2. Panel 3 is scheduled for June 2012.

Analysis of the data shows the important parameters that determine if particle concentrations increase as a result of the retrofit, the impact of indoor sources on PM levels, as well as relationships between apartment ventilation rates (measured by blower door tests) and indoor PM levels. We will also present preliminary analysis of data from Panel 3, showing long term impacts on PM levels.

6IA.3

Evaluation of Environmental Tobacco Smoke Concentrations within Detroit Residential Households. QUENTIN MALLOY, Jonathan Thornburg, Cortina Johnson, Allan Vette, Gary Norris, Janet Burke, Stuart Batterman, *RTI International*

Environmental Tobacco Smoke (ETS) is associated with asthma and airway irritation in children and has also been associated with increased risk of Sudden Infant Death Syndrome, respiratory infections, and otitis media (Lanphear et al, 2001; US DHHS, 2008). Optical analysis of filters for ETS was performed during two four-week intensive campaigns within the greater Detroit area during the fall of 2011 (n=24) and spring of 2012 (n=18). Samples were taken for 5 consecutive 24-hour periods inside and outside households in which children with diagnosed asthma resided. ETS concentration distributions were found to follow similar patterns during both sampling seasons with average concentrations of 9.3 microgram/m^3 and 12.1 microgram/m^3 respectively. Daily variations were found to be minimal with weekend averages of 10.2 microgram/m^3 and weekday averages of 10.6 microgram/m^3, while coefficient of variations for weekend and weekday ETS concentrations were 1.5 and 1.8 respectively. Cohort variations were significant, ranging from 8.4 for households within designated as low traffic high diesel locations up to 21.8 for households within low traffic low diesel areas.

6IA.4

Investigation of Personal and Environmental Factors Affecting Indoor Air Quality in a Green Residential Building.GEDIMINAS MAINELIS, Zuocheng Wang, Leonardo Calderon, Clinton J. Andrews, Richard Wener, Jennifer Senick, MaryAnn Sorensen-Allacci, Jin Young Shin, *Rutgers, The State University of New Jersey*

Green buildings are designed to reduce energy consumption, while providing occupants with a high quality residential environment. Presently, indoor air quality (IAQ) of green buildings has been sparsely studied, with the conventional wisdom being that building design determines IAQ outcomes. We investigated IAQ of a green residential high rise building and analyzed personal, building and environmental factors affecting the IAQ. The investigated factors included smoking frequency, presence of pets and pests, cleaning products and habits, flooring type, ventilation and seasons.

IAQ baseline was determined in 17 apartments, and then the participating residents were given cleaning materials and tips and provided with natural alternatives to chemical cleaners. The IAQ measurements were then repeated twice. In each apartment, we measured the following: culturable bacterial and fungal aerosols, total fungal spores, CO_2, CO, various fractions of airborne particulate matter (PM), volatile organic compounds (VOCs), including formaldehyde, temperature and humidity. Outdoor measurements were performed for comparison. Personal information regarding health and cleaning habits was also collected.

The data show that IAQ parameters can vary greatly in the same building depending on occupants' habits and personal environment. Concentrations of culturable bacteria and mold varied from 20 CFU/m^3 to approximately 3000 CFU/m^3. Most of the CO_2 and CO levels were below 1000 ppm and 2 ppm, respectively. PM2.5 concentrations ranged from 3 to 80 micrograms/m^3 and were usually higher indoors than outdoors. PM concentrations were seen to increase due to smoking and dust resuspension. The primary detected VOC compounds were chloroform, benzene, toluene, dichlorobenzene, and formaldehyde - compounds commonly found in household chemicals and products, tobacco smoke and gasoline vapors. In general, indoor/outdoor ratios of most of the pollutants increased in the wintertime due to reduced ventilation. The study is among the first to provide a large set of IAQ data in green buildings.

6IA.5

Ultrafine Particles Emitted from Microwave Popcorn. Qunfang Zhang, Jessica Avalos, YIFANG ZHU, *University of California, Los Angeles*

Microwave popcorn could release significant amounts of volatile organic compounds, particulate matter, and air toxics when popping and opening bags. This study was designed to characterize ultrafine particles (UFPs, diameter < 100 nm) emitted from microwave popcorn. A microwave oven was enclosed in a chamber with ports for air sampling and a fan to control air exchange rate inside the chamber. Pre-packed popcorn was cooked in the microwave oven while UFP size distribution and number concentration were measured. The popcorn tested in this study covered six different flavors. The UFP emission rates of microwave popcorn ranged from $1.2\times10^{1}1$ to $2.4\times10^{1}3$ particles/hour. The UFP size distributions were unimodal, with the mode around 40 nm for two flavors and around 80 nm for the others. The bag-to-bag variation of UFPs emitted by microwave popcorn was greater than the flavor-to-flavor variation, indicating limited influence of flavor on UFP emission rate. Foil-lined popcorn bags increased UFP emissions during popping by a factor of 2~13 compared with brown paper lunch bags, suggesting innovative package might reduce exposure to UFPs from microwave popcorn. UFP emission rates were slightly lower when cooking with a new microwave oven than a used oven, although not statistically significant. A positive relationship between UFP emission rate and power setting of microwave oven was observed.

6IA.6

HVAC Filters as Samplers of Particle-Bound Contaminants. JEFFREY SIEGEL, Kerry Kinney, *The University of Texas at Austin*

Heating, ventilation, and air conditioning (HVAC) filters are left in place for long periods of time and are subjected to large airflows. Filters in recirculating conditioning systems thus provide a temporally and spatially integrated sample of indoor particles. When combined with an in-situ filter efficiency measurement and an assessment of the total volume of air that flows through the filter, a compositional analysis of the dust can reveal a time-integrated estimate of particle-size and contaminant resolved particle concentrations. We have used this technique to assess DNA-based microbial contaminant levels as well as heavy metal concentrations. The results from these assessments suggest considerable variation amongst similar buildings and point to the limitations of both short-term air samples and settled-dust analysis. The purpose of this presentation is to explore both the value and the limitations of this HVAC filter-based technique as well as to extend the technique to other contaminants including allergens, SVOCs, viruses, and radionuclides. Issues of sensitivity, particle size associations, compositional changes in the dust while the filter is installed, and inhibition of DNA extraction are all explored. The results of this analysis suggest promise of the technique for many common indoor particles and further that it is most suited to contaminants that are stable and associated with super-micron particles. Systems with a long run-time and high filter efficiency are particularly suitable for this approach.

6IM.1

A New Laminar-Flow Water Condensation Method. SUSANNE HERING, Steven Spielman, Gregory Lewis, *Aerosol Dynamics Inc.*

Our original, laminar flow water condensation technology uses a “pre-conditioner” followed by a single-stage “condenser”. As applied to the water-condensation particle counters (TSI WCPCs), flow passes through a single, wet-walled tube, the second portion of which is warmer than the first. The heating of the second section creates a large partial pressure of water vapor at the walls. As the water is a smaller molecule than either nitrogen or oxygen, it diffuses into the cooler entering flow more quickly than the flow warms, creating a region of water vapor supersaturation. This approach provides activation of particles as small as 3-5 nm, depending on operating temperatures. However, it has the disadvantage that the dew point of the air exiting the growth region is quite high. Typically WCPCs operate with the first section at 20°C, and the second portion around 60°C. The dew point at the end of the growth tube is close to the 60°C temperature of the heated wall.

To eliminate the high dew point at the exit of our water condensation cell, we developed a two-stage condenser system consisting of a warm-wet walled “initiator” followed by a cool-walled section. The initiator is 25-30% of the length of the original condenser, and the combined length of both sections is the same as for the single stage condenser. The initiator is hot and provides the water vapor that activates the condensational growth. The second, cooler walled section maintains the supersaturation and provides the time for droplet growth while lowering the exit dew point. Modeling shows the activation sizes are unchanged, and the resulting droplet size is only slightly smaller, yet the exiting dew point brings the flow to below saturation at room temperature.

6IM.2

Inter- and Intra-model Comparisons of Water-based Condensation Particle Counters near a Major Freeway with Significant Heavy-duty Diesel Traffic. EON LEE, Yifang Zhu, Andrea Polidori, Michael Koch, Philip Fine, Ahmed Mehadi, Donald Hammond, Jeffery Wright, Antonio H. Miguel, Alberto Ayala, *University of California, Los Angeles*

Accurate and precise measurement of ultrafine particle (UFP) number concentration is challenging because of uncertain variability among the currently available condensation particle counters (CPCs). This study investigated the performance of three TSI water-based CPC models by measuring atmospheric UFP levels in close proximity (15 m) to the I-710, a major Southern California freeway with significant heavy-duty diesel traffic. The three TSI models (3781, 3783, and 3785) were operated in triplicate (nine units in total) in parallel with two sets of Scanning Mobility Particle Sizer (SMPS) spectrometers for the concurrent measurement of particle size distributions for one month. Inter-model comparisons using one-minute data showed that all three CPC models agreed well during upwind conditions (UFP concentration range between 10^3 and 10^4 particles cm^{-3}). However, significant differences were observed under downwind conditions (particle count above 10^4 particles cm^{-3}). We also evaluated the effect of using longer averaging time intervals in an effort to increase inter-model linear correlations. An averaging time of at least 15-minutes achieved R^2 values of 0.95 or higher when comparing all three models. Similar results were also observed for intra-model comparisons. Sensitivity analysis on concentration ranges found that TSI 3783 recorded the highest average particle count which was 6% higher than that measured by TSI 3785 under high concentration conditions (above 10^4 particles cm^{-3}). TSI 3781 measured an average UFP level that was 18% lower than that observed by TSI 3783 during the same time period. Our analysis showed that all three TSI 3781 units underestimated particles with a count median diameter less than 45 nm. The same problem was also observed for one TSI 3783 and one TSI 3785 units. Subsequently, we quantified inter-model bias using exponential regression analysis and proposed correction equations to adjust the data from TSI 3781 and 3785 to the most recently developed TSI 3783 model.

6IM.3

High Temperature Condensation Particle Counter. KANCHIT RONGCHAI, Nick Collings, *University of Cambridge*

Condensation Particle Counters (CPCs) are commonly used to measure the number concentration of airborne nanoparticles in various applications. A typical CPC consists of three major stages. They are: a saturation stage, a condensational growth stage and an optical particle counter (OPC). The working temperature of a typical CPC is around ambient or slightly higher.

This work is concerned with the development of a CPC that operates at such a high temperature that volatile material is not measured, due to it being evaporated. The obvious application is measurement from internal combustion engines, where the European legislated particle number method (PMP) requires a complex system for the removal of volatile material, prior to measurement by a conventional CPC.

The study involves theoretical modelling, design, construction and testing of a high temperature CPC. Di-Ethyl-Hexyl-Sebacat (DEHS) has initially been chosen as the “working” fluid, because it is non-toxic, is a liquid at room temperature and has a high boiling point. The saturator and condenser would be held at approximately 210˚ C and 190˚ C respectively.

The supersaturated region in the condenser where particles are grown, is modelled by numerically solving heat and mass transfer equations based on the finite difference method. The model was found to be in good agreement with an alternative model due to Stolzenburg and McMurry (1991). Particle growth was modelled by the heat and mass balance at the droplet surface. The simulations suggest that the high-temperature CPC will be able to grow and detect fine particles.

When a step decrease in particle concentration was introduced at the aerosol inlet, the high-temperature CPC has been shown to successfully grow and detect NaCl particles and ambient particles.

Stolzenburg, M. R., and McMurry, P. H. (1991) An Ultrafine Aerosol Condensation Nucleus Counter, Aerosol Science and Technology, 14:1, 48–65.

6IM.4

Advances in Concentrated Particle Collection with the Laminar Flow Growth Tube. GREGORY LEWIS, Steven Spielman, Susanne Hering, *Aerosol Dynamics Inc.*

Aerosol Dynamics Inc, has developed a series of instruments which collect airborne particle into very concentrated samples. Impaction on a warm dry surface results in a spot size of approximately 0.3mm diameter. Because the particles are coated in water, and dry after impaction, there is no bounce. Impaction is also done into liquid volumes of between 100 and 500 microliters. We have made instruments with maximum flow rates of 1.0, 1.5 and 5 Liter per minute and capable of an approximately 5:1 flow rate range. Collection efficiency above 90% is easily achieved.

The instruments use a water-based laminar flow growth tube technology, which is similar to the basis of TSI's Water-based Condensation Particle Counters (WCPC). The WCPCs use a two stage system--a cold section followed by a hot wet wall section. The fist stage cools and saturates the incoming air. Because water vapor diffuses faster then heat, the flow becomes super saturated in the second stage. In the new instrument we radically shorten the second stage and add a cold third stage. Numerical models and experiment show that the relative humidity profiles and the final particle size are minimally dependent on the third stage temperature, showing no practical disadvantage. However the addition of the third stage, has three advantages. 1) It greatly reduces the water consumption of the instrument. 2) It allows control of the exiting flow dew point, which minimizes excess water when collecting using liquid impaction. 3) The sample collection temperature can be reduced to room temperature or preserving the integrity of biological or volatile components of the particles. 4) The maximum temperature the majority of the flow sees is greatly reduced.

6IM.5
Determination of Particle Counting Pressure Correction for Turbine Engine Exhaust Sampling. MATTHEW DEWITT, Edwin Corporan, Christopher Klingshirn, *Air Force Research Laboratory/Propulsion Directorate*

Characterization and quantitation of particulate matter (PM) emissions from turbine engines are of continued interest due to potential environmental and health implications. Since the majority of PM from turbine engines is emitted as sub-micrometer sized particles, there is interest in quantifying the Total Number Concentration (TNC) of particles (total number of particles per volume of exhaust gas) in the engine exhaust stream. Condensation Particle Counters (CPC) are used to quantify the TNC, but these require sampling, conditioning and transport of the exhaust sample from the engine to the instrument, which can result in a varying absolute pressure at the CPC (typically ~10-15 psia) depending on these factors. Two prevalent units currently in use are the TSI Models 3022A and 3025A CPCs, which quantify the TNC via optical measurement of particles in the sample stream while controlling the sample flow rate. Experimental measurements and analyses were performed to determine if the measured TNC with these CPCs is affected by instrument pressure and if normalization to a standard condition is required for data comparison. It was found that the sample inlet pressure affected the measured TNC by influencing both the sample gas density and volumetric control flow rate, of which the latter effect has not been previously reported in the literature. Therefore, correction of the indicated TNC for both of these factors is necessary to quantitatively compare measurements obtained under different conditions. The experimental methodology employed, analyses performed and resulting correction factor relationship are presented. Implications to next-generation CPCs is also discussed.

6IM.6
Traceable CPC Calibration in a Wide Particle Size Range: From 10 Nanometer up to 10 Micrometer. JAAKKO YLI-OJANPERÄ, Hiromu Sakurai, Kenjiro Iida, Jyrki M. Mäkelä, Kensei Ehara, Jorma Keskinen, *Tampere University of Technology*

Aerosol particle measurement is widely applied for example in clean rooms of production facilities and in studying the particulate emissions from traffic and industry. In these applications, the particle number concentration is of particular interest because it is limited by standards and/or legislation. However, the calibration of the applied instruments (e.g. OPCs/CPCs) is very challenging for at least two reasons. Firstly, traceable calibration services are offered only by few institutes (e.g. Fletcher et al., 2009; Schlatter, 2009; Sakurai and Ehara, 2011). Secondly, no single standard can cover the measuring particle size range of these instruments, which can be several orders of magnitude.

In our recent study, a comparison between three number concentration standards was conducted by calibrating the same CPC unit (Model 3772, TSI Inc.) with each standard (Yli-Ojanperä et al., 2012). All together, the calibration results cover the particle size range between 10 nanometer and 10 micro-meters without gaps in the size axis. The standards were: the primary NCS of the National Institute of Advanced Industrial Science and Technology (AIST, Japan), the Single Charged Aerosol Reference (SCAR, Finland) and the Inkjet Aerosol Generator (IAG) of AIST. All of the measurements were carried out at AIST in the same laboratory.

The results obtained with the three standards were found to agree within the uncertainty limits at all overlapping particle sizes. As a result of this study, a traceable calibration that covers the whole operating particle size range of the CPC was carried out for the first time (Yli-Ojanperä et al., 2012). Interesting calibration results will be presented.

Fletcher et al. (2009), Aerosol Sci. Technol., 43, 425-441.
Sakurai, H. and Ehara, K. (2011) Meas. Sci. Technol,. 22 024009
Schlatter, J. (2009) Final Report of EURAMET Project 1027 (www.euramet.org)
Yli-Ojanperä et al. (2012), Submitted to Aerosol Sci. Technol.

6SA.1

Source Apportionment of PM10 in Mumbai by the Chemical Mass Balance Receptor Model. INDRANI GUPTA, Abba Elizabeth, Rakesh Kumar, *NEERI, CSIR*

Mumbai with its large population and mixed land use characteristics poses a major challenge to understand its sources of air pollution. Each residential area or industrial area has its own specific feature with regard to type of sources, local meteorology and activity profile. A comprehensive sampling of PM10 was undertaken for four representative sites during December 2007- February 2008. Samples were analyzed for 19 elements, 7 ions besides organic and elemental carbon. Samples were analyzed for elemental concentrations by ICP-AES; EC/OC using DRI's Thermal/Reflectance Optical Carbon Analyzer and ions using Ion Chromatograph. Factor analysis (FA) has been carried out prior to Chemical Mass Balance (CMB) modeling with a view to understand a priori major components. The CMB model is one of several receptor models that have been applied by several researchers to air quality management. Using major source profiles developed first time in India under Central Pollution Control Board's, Six cities air quality studies, receptor model CMB 8.2 was applied to sampled data for all four sites to understand the sources and their contribution locally. Results of industrial site indicate that major sources are soil dust (30%), solid waste burning (21.3%), secondary aerosol (12.3%) and Heavy duty diesel vehicles (10.4%). At Khar, an upper class residential area, the major sources are vehicles (41.8%), soil dust (37.7%), secondary aerosol (10.1%) and wood combustion (9.1%). At Dharavi, a lower class residential site the major sources are soil dust (47.9%), vehicles (25.6%), marine aerosol (9.6%) and secondary aerosols (10.5%). Vehicular, soil dust and marine aerosol have been found to occur at all four sites as more ubiquitous sources by both CMB and FA. Another source is the indirect source secondary aerosol observed at all four sites by CMB model.

Keywords: Source apportionment; Particulate matter, CMB 8.2, Mumbai

6SA.2

Source Apportionment of PM2.5 Nitrite and Sulfate in China using a Source-Oriented Chemical Transport Model.HONGLIANG ZHANG, Jingyi Li, Qi Ying, Jian Zhen Yu, Dui Wu, Cheng Yuan, Kebin He, Jingkun Jiang, *Texas A&M University*

Nitrate and sulfate account for a significant fraction of PM2.5 mass. In this work, a source-oriented version of the Community Multiscale Air Quality (CMAQ) model that directly tracks the contributions from multiple emission sources to secondary PM2.5 is developed to determine the regional contributions of power, industry, transportation and residential sectors as well as biogenic sources to nitrate and sulfate concentrations in China in January and August 2009.

The source-oriented CMAQ model is capable of reproducing most of the available PM10 and PM2.5 mass, and PM2.5 nitrate and sulfate observations. Model prediction suggests that monthly average PM2.5 inorganic components (nitrate+sulfate+ammonium ion) can be as high as 60 µg m-3 in January and 45 µg m-3 in August, accounting for 20-40% and 50-60% of total PM2.5 mass. The model simulations also indicate significant spatial and temporal variation of the nitrate and sulfate concentrations as well as source contributions in the country. In January, nitrate is high over Central and East China with a maximum of 30 µg m-3 in the Sichuan Basin. In August, nitrate is lower and the maximum concentration of 16 µg m-3 occurs in North China. In January, highest sulfate occurs in the Sichuan Basin with a maximum concentration of 18 µg m-3 while in August high sulfate concentration occurs in North and East China with a similar maximum concentration. Power sector is the dominating source of nitrate and sulfate in both January and August. Transportation sector is an important source of nitrate (20-30%) in both months. Industry sector contributes to both nitrate and sulfate concentrations by approximately 20-30%. Residential sector contributes to approximately 10-20% of nitrate and sulfate in January but its contribution is low in August.

6SA.3

Source Apportionment of Ambient PM2.5 in Santiago, Chile: 1999 and 2004 Results. HECTOR JORQUERA, Francisco Barraza, *Pontificia Universidad Catolica de Chile*

In this work we have applied a receptor model analysis to ambient $PM_{2.5}$ measurements taken at Santiago, Chile in 2004 (117 samples) on a receptor site on the eastern side of the city. In addition we have reanalyzed data from a similar campaign conducted in 1999 (95 samples) at the very same site. For both campaigns, six sources have been identified at Santiago and their relative contributions (std.err.) in 1999/2004 are: motor vehicles: 28(2.5)/31.2(3.4)%, wood burning: 24.8(2.3)/28.9(3.3)%, sulfates: 18.8(1.7)/16.2(2.5)%, marine aerosol: 13(2.1)/9.9(1.5)%, copper smelters: 11.5(1.4)/9.7(3.3)% and soil dust: 3.9(1.5)/4.0(2.4)%. Similarity of results for both data sets — analyzed with different techniques at different laboratory facilities — shows that the analysis performed here is robust.

Source identification was carried out by inspection of key species in source profiles, seasonality of source contributions and also by looking at wind trajectories computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) from USA's National Oceanic and Atmospheric Administration (NOOA); for the wood burning sources the MODIS burned area daily product was used to confirm their identification along the year. Using this combined methodology we have shown conclusively that: a) marine air masses do reach Santiago's basin in significant amounts but combined with anthropogenic sources; b) all copper smelters surrounding Santiago — and perhaps coal-fired power plants as well — contribute to ambient PM2.5; c) wood burning is the second source in relevance, being a local source in fall and winter but a regional one in spring and summer.

Since ambient PM2.5 at Santiago has been reduced in the last 20 years both local and regional sources must have decreased their emissions; nonetheless there are still spring and summertime daily concentrations that exceed 35 [µg/m3] across the city. Results of the present analysis can be used to improve emission inventories, air quality forecasting systems and cost-benefit analyses at local and regional scales.

6SA.4

A Bayesian – Based Ensemble Technique for Source Apportionment of PM2.5. SIVARAMAN BALACHANDRAN, Howard Chang, James Mulholland, Armistead Russell, *Georgia Institute of Technology*

A Bayesian-based ensemble average of source apportionment results is used to develop new source profiles for use in a chemical mass balance (CMB) source apportionment (SA) of fine particulate matter (PM2.5). The approach estimates source impact uncertainties from a short-term application of four individual SA methods: four receptor-based models and one chemical transport model, the community multiscale air quality (CMAQ) model. The uncertainties for each method are used as weights in the ensemble-averaged source impacts.

The Bayesian based posterior distribution has a weakly informative prior distribution and treats the root mean square errors (RMSEs) between each method source impact and the ensemble average as the updated data. For each day of the short term application of the four SA methods, source impact uncertainties are sampled from the Bayesian-based posterior distribution. These uncertainties are used as weights to determine an ensemble average. Since the Bayesian analysis uses the RMSE, which requires knowledge of the ensemble average, iteration is required. All methods are treated equally to determine the initial ensemble average. The RMSEs from this first estimate of the average is used to determine a posterior distribution of SA method uncertainties, which are subsequently used to determine a new ensemble average. This process is repeated until the ensemble average converges. A Monte Carlo technique is used to estimate a distribution of Bayesian ensemble –based source impacts for each day in the ensemble.

These distributions of source impacts are then used to determine distributions of two seasonally-based source profiles. For each day in a long term PM2.5 data set, 10 source profiles are sampled from these distributions and used in a CMB application resulting in 10 SA results(for each day). This formulation results in a distribution of daily source impacts rather than a single value with an estimated uncertainty.

6SA.5

Assessing Top of Atmosphere Polarization Sensitivity to Aerosol Emissions Using the GEOS-Chem Chemical Transport Model Adjoint.

BRIAN MELAND, Xiaoguang Xu, Daven Henze, Jun Wang, *Univesity of Colorado, Boulder*

Atmospheric aerosols play important roles in determining the radiative balance of the earth's atmosphere and in heterogeneous chemical reactions with trace atmospheric gases. However, there is still a great deal of uncertainty in the temporal and spatial distribution of atmospheric aerosols. This can lead to errors in radiative transfer calculations as well as in chemical transport models which both rely on accurate estimates of aerosol concentrations or emissions as inputs.

Recent studies have found that measurements of the full Stokes vector, rather than just the intensity component, of light scattered from atmospheric aerosols can provide additional information on aerosol physical and chemical properties. Since atmospheric aerosols can have lifetimes on the orders of days or weeks, they can be transported over intercontinental scales and impact radiative forcings far from their source regions. Using a vectorized radiative transfer model (VLIDORT) in conjunction with the adjoint of the GEOS-Chem chemical transport model, we seek to quantify the sensitivity of top of atmosphere (TOA) polarization to aerosol emissions, chemical composition, and assumed microphysical properties.

The GEOS-Chem forward model is used to calculate aerosol concentrations of 13 aerosol species on a 47 layer grid over North America. These concentrations are used as inputs for the VLIDORT radiative transfer model which calculates the full Stokes vector and its Jacobian matrix of scattered light at the TOA. The Jacobian matrix then serves as the adjoint forcing terms in the GEOS-Chem Adjoint model which steps backwards in time to determine the contributions of previous (non-local) emissions on polarization. These results help to show the utility of development and application of polarimetric measurements from remote sensing platforms.

6SA.6

Top-Down Estimate of Dust Emissions through Integration of MODIS and MISR Aerosol Retrievals with the GEOS-Chem Adjoint Model.

JUN WANG, Xiaoguang Xu, Daven Henze, Jing Zeng, *University of Nebraska - Lincoln*

Predicting the influences of dust on atmospheric composition, climate, and human health requires accurate knowledge of dust emissions, but large uncertainties persist in quantifying mineral sources. This study presents a new method for combined use of satellite-measured radiances and inverse modeling to spatially constrain the amount and location of dust emissions. The technique is illustrated with a case study in May 2008; the dust emissions in Taklimakan and Gobi deserts are spatially optimized using the GEOS-Chem chemical transport model and its adjoint constrained by aerosol optical depth (AOD) that are derived over the downwind dark-surface region in China from MODIS reflectance with the aerosol single scattering properties consistent with GEOS-chem. The adjoint inverse modeling yields an overall 51% decrease in prior dust emissions estimated by GEOS-Chem over the Taklimakan-Gobi area, with more significant reductions south of the Gobi Desert. The model simulation with optimized dust emissions shows much better agreement with independent observations from MISR AOD and MODIS deep blue AOD over the dust source region and surface PM10 concentrations. The technique of this study can be applied to global multi-sensor remote sensing data for constraining dust emissions at various temporal and spatial scales, and hence improving the quantification of dust effects on climate, air quality, and human health.

7AC.1

Yields of Alkyl Nitrates and Hydroxynitrates Formed from the Reactions of C8–C14 n-Alkanes with OH Radicals in the Presence of NOx. GEOFFREY YEH, Paul Ziemann, *UC Riverside*

Alkanes account for nearly one half of total anthropogenic non-methane hydrocarbon emissions and are precursors of secondary organic aerosol (SOA). In the atmosphere, alkanes react with OH radicals to produce a variety of oxygenated products including alkyl nitrates and hydroxynitrates. In the experiments described, C8–C14 n-alkanes were reacted with OH radicals in the presence of NOx in an environmental chamber, and yields of alkyl nitrates and hydroxynitrates were measured. Particle-phase hydroxynitrates were sampled on filters, extracted, and analyzed by liquid chromatography with ultraviolet absorbance detection (LC/UV). Particle- and gas-phase alkyl nitrates were sampled on Tenax adsorbent and analyzed by gas chromatography with flame ionization detection (GC/FID). Gaseous alkyl nitrates in the size range studied can also be lost to chamber walls, so gas-wall partitioning was investigated by adding synthesized alkyl nitrates to the chamber and monitoring their losses over time. Whereas C8 alkyl nitrate remained entirely in the gas phase, C10–C14 alkyl nitrates partitioned increasingly with carbon number and proximity of nitrate substitution to the terminal carbon, and exhibited losses up to 85%. Using these data, an isomer-specific group contribution approach to estimate gas-wall partitioning was developed and used to correct the measured alkyl nitrate yields for wall losses. These results can be used to develop more accurate models of SOA formation from the atmospheric oxidation of alkanes.

7AC.2

Secondary Organic Aerosol Formation from Aromatic Compounds: Relationship between SOA Yield and Chemical Structure. PING TANG, Shunsuke Nakao, Chia-Li Chen, David R. Cocker III, *University of California, Riverside*

Formation of secondary Organic Aerosol (SOA) from benzene, toluene, ethylbenzene, xylene isomers, ethyltoluene isomers, thrimethylbenzene isomers, propylbenzene, isopropylbenzene, tetramethylbenzene, pentamethylbenzene and hexamethylbenzene was investigated in a series of smog chamber experiments. Experiments were performed in dry air under no NO_x and low NO_x conditions. It is observed that under low-NO_x conditions aerosol formed from aromatic hydrocarbon with more carbon atoms has a lower yield, which is consistent with Odum's definition of high-yield and low-yield aromatics (Odum, 1996). While under no-NO_x conditions no such trend was observed. This might relate to the hydroxyl radical (OH radical) level available in these systems. Under no-NOx conditions, H_2O_2 photolysis can provide a stable OH source. Mz43($C_2H_3O^+$)/mz44 (CO^{2+}) ratio determined by ToF-HR-AMS increased with increasing number of alkyl substituent on aromatic ring, which indicates more ketone/ aldehyde was formed. Ketones are harder to oxidize than aldehydes and therefore go through lesser oxidation thus result in a lower aerosol yield. In addition, aerosol volatility measured by VTDMA was compared. It is found that aerosol formed from aromatic with more carbon number has a higher volatility.

7AC.3

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

The gas-liquid partitioning of oxidized volatile organic carbon (VOC) is strongly dependent on the composition of the oxidation products and can be correlated to the distribution of oxygenated moieties present in these products. A liquid chromatography/tandem mass spectrometry (LC/MS-MS) methodology is described to probe this distribution in organic aerosol particles. In this study, we present the distribution of carbonyls (aldehydes and ketones), hydroxyls, and carboxylic acids present in particles derived from the oxidation of octyl radicals that are formed from iodooctane photolysis. A flow cell apparatus utilizing uncoated fluorescent lights (254 nm mercury line sources) for photolysis is used as a reactor with concentrations that yield rapid oxidation in a NO_x-free environment. A series of chemical derivatization steps on samples extracted from filtration of the flow cell output provides significant information about the presence of oxygenated functionalities on the observed products. Additionally, the iodooctane photolysis yields a broad range of recombination products with relatively low oxygen content relative to their masses, consistent with waxy, hydrophobic oligomers. The measured distributions are then used to constrain a permutation model of the oxidation that can effectively predict the major condensed-phase products and yields by assuming different contributions to the predicted vapor pressures from the observed oxygenated functionalities.

7AC.4

Transitions from Functionalization to Fragmentation Reactions of Laboratory Secondary Organic Aerosol (SOA) Generated from the OH Oxidation of Alkane Precursors. ANDREW LAMBE, Timothy Onasch, David Croasdale, Justin Wright, Alex Martin, Jonathan Franklin, Paola Massoli, Jesse Kroll, Manjula Canagaratna, William Brune, Douglas Worsnop, Paul Davidovits, *Aerodyne Research, Inc.*

Functionalization (addition of oxygen) and fragmentation (loss of carbon) reactions governing secondary organic aerosol (SOA) formation from the OH oxidation of alkane precursors were studied in a flow reactor in the absence of NOx. SOA precursors were n-decane (n-C_{10}), n-pentadecane (n-C_{15}), n-heptadecane (n-$_{C17}$), tricyclo[5.2.1.$0^{2,6}$]decane (JP-10), and vapors of diesel fuel and Southern Louisiana crude oil. Aerosol mass spectra were measured with an Aerodyne high-resolution time-of-flight aerosol mass spectrometer, from which normalized SOA yields, hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios, and $C_xH_y^+$, $C_xH_yO^+$, and $C_xH_yO_{>1}^+$ ion abundances were extracted as a function of OH exposure. Normalized SOA yield curves exhibited an increase followed by a decrease as a function of O/C (OH exposure), with maximum yields at O/C ratios ranging from 0.29 to 0.74. The decrease in SOA yield correlates with an increase in oxygen content and decrease in carbon content, consistent with transitions from functionalization to fragmentation. For a subset of alkane precursors (n-C_{10}, n-C_{15}, and JP-10), maximum SOA yields were estimated to be 0.39, 0.69, and 1.1. In addition, maximum SOA yields correspond with a maximum in the $C_xH_yO^+$ relative abundance. Measured correlations between OH exposure, O/C ratio, and H/C ratio may enable identification of alkane precursor contributions to ambient SOA.

7AC.5

Heterogeneous Ozonation and Nitration Products of Polycyclic Aromatic Hydrocarbons. RICHARD COCHRAN, Haewoo Jeong, Shokouh H. Haddadi, Alexandra C. Smith, Rebeka F. Derseh, Nagaraju Dongari, Josef Beranek, Alena Kubatova,*University of North Dakota*

Polycyclic aromatic hydrocarbons (PAHs) have long been known to be mutagenic. Recent toxicological studies have attributed the genotoxicity of particulate matter (PM) to higher polarity species as well, notably nitro-, dinitro, oxy-, and hydroxy-PAH oxidation products. While the gaseous reaction of PAHs in atmospheric processes have been extensively explored, the knowledge regarding the formation of PAH oxidation products through heterogeneous reactions is limited. Typically the most abundant PAHs in PM are semi-volatile species with 3–4 aromatic rings. Therefore, in this work we have studied the heterogenoues nitration and oxygenation of phenanthrene, anthracene, fluoranthene, and pyrene using nitrogen dioxide and ozone. While the reactions have previously been explored the focus of this study was on the detailed identification of reaction products. Several oxidation products with multiple functional groups, including carboxaldehyde, carboxylic acid, and/or hydroxylated species, were identified, especially for reactions of anthracene and pyrene with ozone. These species were also found to form 1-nitropyrene and 9-nitroanthracene upon reaction with nitrogen dioxide. In reactions with both nitrogen dioxide and ozone a broader distribution of oxidation products were observed, most likely due to the in-situ formation of the more powerful oxidant NO3. Detailed identification was confirmed using standards and sequential derivatization of carbonyl and hydroxyl functional groups with pentafluorobenzyl hydroxylamine (PFBHA) and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), respectively, followed by gas chromatography-mass spectrometry (GC-MS) analysis. Further identification was confirmed using liquid chromatography with high resolution time of flight MS.

7AC.6

Environmental Factors Influencing Peroxyhemiacetal Chemistry in SOA. LINDSAY YEE, Jill Craven, Katherine Schilling, Christine Loza, Xuan Zhang, Matthew Coggon, Paul Ziemann, John Seinfeld, *California Institute of Technology*

Peroxyhemiacetals (PHAs) form from the heterogeneous reaction of semi-volatile hydroperoxides and aldehydes. There is increasing evidence that peroxyhemiacetal formation contributes to the chemical composition of secondary organic aerosols generated from a variety of volatile organic compounds under low-NO_x conditions. However, very little is known about the environmental conditions that affect PHA formation. In this study, we extend previously derived chemistry for the dodecane low-NO_x mechanism and other alkane systems to explore the additional effects of varying relative humidity and aerosol acidity on PHA formation. We simulate these conditions in the Caltech Atmospheric Chamber and we examine the evolving aerosol chemistry comparing complementary information from chemical ionization mass spectrometry and high-resolution time-of-flight aerosol mass spectrometry measurements to elucidate PHA formation chemistry. We use these chemical frameworks as tools for extension of PHA formation chemistry in other VOC systems and to the atmosphere where primarily low-NO_x and non-dry conditions exist.

7AC.7

O3-initiated Heterogeneous Oxidation of Linoleic Acid and its Dependence on Ambient Temperature and Relative Humidity. Guang Zeng, Yunhong Zhang, YONG LIU, *University of Colorado Denver*

Despite recent extensive studies towards heterogeneous oxidation of unsaturated organics (mostly oleic acid) initiated by ozone, little is known about effects of ambient temperature and relative humidity on chemical transformation of organic aerosols. In this work, we used ATR-IR flow reactor and linoleic acid (LA) as a proxy for atmospheric unsaturated organics to investigate its heterogeneous oxidation by O3 over a wide range of temperatures (257-313 K) and relative humidities (0-80% RH). Pseudo-first order rate constants and overall reactive uptake coefficients were acquired from absorbance changes in peaks located near 1743 cm-1; 1710 cm-1; 1172 cm-1 and 1110 cm-1, which can be assigned to C=O in ester; C=O in acid; C-C and C-O stretching modes, respectively. Experimental results showed that heterogeneous loss of O3 onto LA has an uptake probability close to 5×10-4 at 293K. It was found that uptake coefficients increased with increasing temperature, and within the temperature range studied here the O3 reactive uptake was enhanced by one order of magnitude. It was also noted such temperature enhancement effect on the reaction kinetics was much more effective at lower temperatures. For example, the Pseudo-first order rate constants increased nearly by 7-fold when temperature was changed from 257 K to 273 K. Such behavior can be explained by change in physical state of LA at lower temperatures which was confirmed by shifts of both CH2 and C=O stretching modes. A decrease in absorbance ratio of (A1743/A1710) with decreasing temperature was also observed, an indicative of a smaller amount of α-acyloxyalkyl hydroperoxide-related products formed during oxidation of LA with O3 at lower temperatures. In addition, RH study results showed that water vapor promoted heterogeneous reactive uptake of O3 on LA surface. Furthermore, water uptake studies showed that O3 initiated heterogeneous oxidation enhanced hydrophilicity of organic surface.

7AP.1

Crossover from Ballistic to Epstein Motion. William Heinson, CHRIS SORENSEN, Amit Chakrabarti, Flint Pierce, *Kansas State University*

We present a simulation of particle aggregation in the free molecular regime that undergoes a crossover from ballistic to Epstein diffusive motion where the frictional coefficient is proportional to the aggregate cross sectional area. The simulation starts with a dilute system of monomers all with mean free path (persistence length) of l_0. Persistence length of the aggregate l_a is found from the product of the Langevin characteristic time t_c and the Maxwell root mean square velocity v_{rms} which is $l_a=t_c\ v_{rms}$. We will show that $l_a=l_0N^{1/2\ -2x}$ where x=0.46. As the aggregates grow, the aggregate persistence length becomes smaller and the aggregate motion between collisions becomes more diffusive like. The kinetics of aggregation and aggregate size distributions show the expected BLCA and Epstein like behavior at early and late times, respectively. A significant crossover regime is found between these limits. The aggregation kernel homogeneity exponent evolves in a nonmonotonic manner from one regime to another.

7AP.2

The Evolution of Primary Particle Polydispersity in Aggregates During Sintering.

MAX L. EGGERSDORFER, Sotiris E. Pratsinis, *ETH Zurich*

Fractal-like aggregates consist of multiple particles that are connected by chemical (e.g. sintering) bonds. Such aggregates form by natural and man-made processes, typically at high temperatures, like fly ash from coal combustion as well as aerosol synthesis of ceramics (titania, fumed silica, alumina) and metals (Ni, Fe, Ag etc.). The morphology of such particles has critical implications in their performance. In nanoparticle synthesis by aerosol processes the sintering of aggregates during particle formation narrows their primary particle size distribution affecting mechanical and optical properties. The understanding of the evolution of primary particle size distributions during sintering is also important for the design of aerosol reactors by computational modelling. Furthermore, the fractal dimension, D_f, of agglomerates decreases steadily with increasing polydispersity of constituent primary particles [1].

Here a recently developed model for viscous sintering of amorphous [2] and crystalline (e.g. TiO_2 or Ag) [3] aggregates is used to elucidate the detailed evolution of their primary particle distribution during sintering. This model reproduces nicely the initial neck growth and evolution of particles center-to-center distance for equally sized pairs of particles and is compared to the classic models [4]. So the evolution of the radius of gyration and D_f of ensembles of irregular particles is presented as they asymptotically approach full compactness by sintering. It is shown that initially monodisperse primary particles become slightly polydisperse during sintering exhibiting even a small maximum in geometric standard deviation before converging to a fully coalesced sphere. Initially polydisperse primary particles monotonically reduce the breadth of their size distribution by sintering.

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[2] Eggersdorfer, M.L., et al., Langmuir 27 (2011) 6358-6367.
[3] Eggersdorfer, M.L., et al., J. Aerosol Sci. 46 (2012) 7-19.
[4] Coblenz, W.S., et al., Mat. Sci. Res. 13 (1980) 141-157.

7AP.3

Direct Simulation Monte Carlo (DMSC) Calculation of the Low Reynolds Number Drag on Aerosol Aggregates.

CHONGLIN ZHANG, Thaseem Thajudeen, Carlos Larriba, Thomas Schwartzentruber, Christopher Hogan Jr., *University of Minnesota*

The drag force experienced by aggregate aerosol particles at low Reynolds number governs aggregate motion and growth in a number of environments, and is therefore of critical importance. However, because of the morphological complexity of aggregates and the transition regime nature of gas molecule-particle momentum transfer for small particles, drag force prediction for aggregates is not commonplace. Here, we describe the use of direct simulation Monte Carlo (DMSC) for prediction of the drag force on model aggregates. In DSMC, the gas flow field is modeled by a number of interacting “simulation particles”, which impart drag to the particle. Unique about DSMC is that it permits simulation of gas flows in the transition regime, i.e. under conditions often encountered for aggregate aerosol particles with sizes in the 20-200 nm size range. Despite the suitability of DSMC for calculation of the drag force on aerosol particles, calculations suffer from high statistical variability for flow speeds which are small relative to the mean thermal speed of the background gas molecules. We discuss methods to address this statistical variability, and apply DSMC for drag calculation on spheres, dimers, and 20-mer aggregates with Knudsen numbers in the range 0.05-10. Results of calculations are compared to the drag force predicted from the results of dimensional analysis. Reasonable agreement (~10% difference) is found between DSMC calculated drag force and model predictions.

7AP.4

Break-up and Bounce of TiO2 and Cu Agglomerates Due to the Inertial Impaction. MIKA IHALAINEN, Terttaliisa Lind, Tiina Torvela, Kari Lehtinen, Jorma Jokiniemi, *Paul Scherrer Institut, Switzerland*

Impaction behavior plays a significant role in areas of nanoparticle technology, such as powder processing, nuclear safety and health research. Whether the agglomerates adhere onto the surface, bounce and/or break-up during inertial impaction under certain conditions remains a question to be answered. For this purpose agglomerate impaction behavior was studied.

A combination of a single stage Micro Uniform Deposit Impactor (MOUDI) and a low pressure sampling chamber was used to carry out the impaction studies. TiO2 and Cu agglomerates were impacted onto an impaction plate located in the MOUDI. The particles which deposited onto the impaction plate were studied using a Transmission Electron Microscopy (TEM). The TEM-grid for this purpose was located on the impaction plate. The bounced particles were collected from the sampling chamber for analysis with the TEM and a Scanning Mobility Particle Sizer (SMPS). The following parameters of the TiO2 agglomerates were varied to find out how they affect the impaction behavior: the primary particle size, agglomerate size and degree of sintering.

Both the primary particle size and the degree of sintering affected the break-up and bounce of the TiO2 agglomerates. For instance, the geometric mean diameter (GMD) of the bounced particles increased as the primary particle size was decreased indicating that the degree of fragmentation decreased. The degree of fragmentation represents the fraction of the bonds between the primary particles of the intact agglomerate that break-up during the impaction. The degree of fragmentation of the bounced particles also decreased as the degree of sintering of the agglomerates was increased. Further data analysis will be carried out to estimate the mass based bounced particle fraction of the impacted particles. Preliminary results show that there were no bouncing or de-agglomeration with the copper agglomerates.

7AP.5

Drag Measurements of Cylindrical Aerosol Particles in the Transition Regime. RANGANATHAN GOPALAKRISHNAN, Peter McMurry, Christopher Hogan Jr., *University of Minnesota*

Measurements of electrical mobility, and hence drag force, are commonly used to characterize submicrometer and nanometer sized aerosol particles. For spherical particles, Stokes law modified with the Knudsen number dependent slip correction factor can be used with confidence to link the particle diameter/radius to the observed drag force/electrical mobility. For non-spheres, however, questions remain regarding the correction approach to relate appropriate length scales describing the particle to the resulting drag force the particle experiences in a fluid flow. To address this issue we make measurements of the electrical mobility of well characterized high aspect ratio (cylindrical) aerosol particles in the momentum transfer transition regime, i.e. where the mean free path of the surrounding gas is on the order of the length scale of the particles. Two types of cylindrical aerosol particles are used for measurements. First, single walled carbon nanotubes are synthesized in an inverse diffusion flame, with diameters in the sub 10 nm range and lengths in the submicrometer to micrometer size range. Second, gold nanorods, synthesized in the liquid phase with both diameters and lengths in the sub 100 nm range, are aerosolized using an electrospray aerosol generator. A differential mobility analyzer (DMA) is used to isolate particles of a prescribed electrical mobility, and subsequently TEM analysis of mobility classified particles is used to precisely determine the particle length and diameter. From TEM measurements, theoretical prediction of the Knudsen number for such particles and subsequently their electrical mobilities are made using equations derived from dimensional analysis and Direct Simulation Monte Carlo (DSMC). The predicted electrical mobility for each analyzed particle is compared directly to its known electrical mobility under the measurement conditions, with the DMA transfer function and other experimental uncertainties accounted for.

7AP.6

The Effect of Orientation on the Mobility and Dynamic Shape Factor of Charged Axially Symmetric Particles in an Electric Field. MINGDONG LI, George Mulholland, Michael Zachariah, *University of Maryland*

The mobility of a nonspherical particle is a function of both particle shape and orientation. Thus unlike spherical particles the mobility, through its orientation, depends on the magnitude of the electric field. In this work, we develop a general theory, based on an extension of the work of Happel and Brenner (1965), for the orientation-averaged mobility applicable to any axially symmetric particle for which the friction tensor and the polarization energy are known. By using a Boltzmann probability distribution for the orientation, we employ a tensor formulation for computing the orientation average mobility rather than a scalar analysis previously employed by Kim et al (2007) for nanowires. The resulting equation for the average electrical mobility is much simpler than the expression based on the scalar approach, and can be applied to any axially symmetric structures such as rods, ellipsoids and touching spheres. The theory is applied to the specific case of nanowires and the results experimental results on the mobility of carbon nanotubes (CNT). A set of working formulas of additional mobility expressions for nanorods and prolate spheroids in free molecular, continuum and transition regimes are also presented . Finally, we examine the expression of dynamic shape factor common in the literature, and propose a clearer definition based on the tensor approach. Mathematica codes for the electrical mobility evaluations for five prototype cases (section 2.5.1. – section 2.5.5.) are provided in the Supporting Information.

7AP.7

Light Scattering Shape Diagnostics for Agglomerates. GEORGE MULHOLLAND, Lei Zhou, Michael Zachariah, William Heinson, Chris Sorensen, Amit Chakrabarti, *University of Maryland*

Motivated by light scattering experiments showing enhanced intensity of electric field aligned agglomerates vs. randomly oriented agglomerates, we address the theoretical basis for this effect by extending the theory of small angle scattering of clusters to oriented clusters and then applying the theory to clusters generated by classical diffusion–limited cluster-cluster aggregation (DLCA). Based on clusters with 30 monomers and with 100 monomers, the ratio of the slopes based on Zimm plots for the partially aligned (aligned along the major axis but free to rotate about that axis) and randomly oriented clusters is well correlated with a linear fit to the shape anisotropy, defined as the ratio of the square of the major to minor principle radii of gyration. It is also shown that state of the art small-angle aerosol scattering measurements would have the angular resolution required to measure the shape anisotropy for clusters with 30 to 1000 monomers for a size parameter of the monomer of about 0.15.

For large q for clusters with 30 to1000 monomers, it is shown from the simulations that S(q) for the partially aligned clusters does not follow the power law behavior observed for the randomly oriented clusters. Clusters with a fixed orientation are shown to result in a structure factor with multiple peaks, which could be used to obtain more detailed information about particle structure than shape anisotropy.

The measurements showing enhanced scattering for partially aligned soot agglomerates were for angle integrated measurements. Calculation of the integrated light scattering cross section for the same range of angles and polarization direction as the experiments indicate a significant enhancement of 70 % and 120 % for two representative aspect ratios. The smaller value overlaps with measured values of the scattering enhancement for oriented soot agglomerates in an electric field.

7CC.1

Comparison of n-Alkanoic Acid Surface Pressure Isotherms Determined for Microscopic Droplets and Macroscopic Solutions. CHRIS RUEHL, Kevin Wilson, Athanasios Nenes, Patrick Chuang, Allen H. Goldstein, *Univeristy of California, Berkeley*

Ambient organic aerosols can reduce the surface tension of macroscopic aqueous solutions, and often parameterizations based on these measurements are used to predict cloud condensation nuclei (CCN) activity for microscopic droplets. However, it is not known to what extent these parameterizations may need to be altered in response to the much higher surface:volume ratios of such droplets. Here we determine the surface tension of 1-2 micro-meter droplets formed at RH=99.9% from particles containing one of a series of n-alkanoic acids and NaCl. By varying the acid:NaCl ratio of the particles, we relate the reduction in surface tension to the maximum thickness of the organic film on the wet droplet. We compare the microscopic parameterization that we generate to previously-published macroscopic surface pressure vs. surface concentration relationships for the same compounds. The results provide a specific test to determine if macroscopic surface tension parameterizations are valid for microscopic droplets. We also discuss the general differences in droplet surface tension obtained with a bulk parameterization (e.g., the Szyskowski equation) and a surface parameterization, and show that the latter is preferable for calculating CCN activity.

7CC.2

Hygroscopicity Trends of Secondary Organic Aerosol Generated from Ozonolysis of 1-Alkenes. RYAN SULLIVAN, Markus Petters, Aiko Matsunaga, Sarah Suda, Lorena Minambres, Annelise Faulhaber, Paul Ziemann, Sonia Kreidenweis, *Carnegie Mellon University*

Secondary organic aerosol (SOA) can potentially influence cloud properties and climate by absorbing water and contributing to cloud condensation nuclei populations. Alkenes are gaseous precursors of SOA that are emitted from a variety of anthropogenic and biogenic sources. We produced SOA from the oxidation of a series of 1-alkene homologs to investigate the relationships between the alkene precursor structure, the measured aerosol hygroscopicity, and the chemical composition of the chamber-generated aerosol. The effect of Criegee radical scavenger structure and polarity on the resulting aerosol properties was explicitly investigated through the addition of water vapor, alcohols, aldehydes, or inorganic acids to the chamber. The observed aerosol hygroscopicity was found to decrease with increasing precursor chain length and increasing product molecular volume, as expected from Köhler theory. Shorter-chain and more polar Criegee scavengers increased the hygroscopicity of the aerosol compared to longer-chain and less polar scavengers, also as expected. A new analysis method coupled HPLC polarity-based separation of organic compounds with scanning flow rapid CCN analysis to determine the hygroscopicity of individual compounds in the complex organic aerosol. This provided new insights into the distribution of compound hygroscopicity and composition as a function of chamber reaction conditions. This new tandem method revealed that the aerosol was composed of two modes of compound hygroscopicity, characterized by a hygroscopicity parameter (kappa) of ~0.02 and ~0.2. We present an analysis of the measured net hygroscopicity as well as the relative fractions of each hygroscopicity mode, and compare these to expected values based on known reaction mechanisms and rates. We anticipate that these results will help improve our ability to accurately predict SOA hygroscopicity from known precursors.

7CC.3

Cloud Condensation Nuclei Activity of Secondary Organic Aerosol: Investigation of Hygroscopicity and Activation Kinetics. KATE CERULLY, Lea Hildebrandt Ruiz, Andrea Paciga, Tomi Raatikainen, Neil Donahue, Spyros Pandis, Athanasios Nenes, *Georgia Institute of Technology*

Cloud condensation nuclei (CCN) activation is dependent on both aerosol size and chemistry. Thus, the investigation of CCN behavior of secondary organic aerosol (SOA) as it undergoes transformation in the atmosphere is complex and important. SOA from toluene was formed during Carnegie Mellon University chamber experiments. A suite of instruments, including a cloud condensation nuclei counter (CCNC), thermodenuder (TD), and high resolution time-of-flight aerosol mass spectrometer (AMS), were used to measure CCN activity, aerosol volatility, and aerosol composition and oxidation, respectively.

In this study, we investigate the hygroscopicity of SOA and specifically, the difference in hygroscopicity of denuded versus non-denuded as well as fresh versus aged aerosol. While the hygroscopicity parameter, kappa, is on average approximately 0.2, there are apparent trends in kappa during SOA formation and aging. In addition, we use Threshold Droplet Growth Analysis (TDGA), comparing the size of activated droplets against a standard of uninhibited activation such as ammonium sulfate, as well as a CCNC instrument model to investigate aerosol kinetics of size-selected SOA. By operating the CCNC in Scanning Flow CCN Analysis (SFCA) mode, we are able to investigate both the condensation and evaporation kinetics of aerosol. Aerosol condensation kinetics are similar to that of ammonium sulfate.

7CC.4

Water-Soluble VOCs and Aerosol CCN Activity: A Tale of Three Surfactants. Neha Sareen, Allison Schwier, Greg Drozd, Joseph Woo, Terry Lathem, Athanasios Nenes, V. FAYE MCNEILL, *Columbia University*

The uptake of water-soluble volatile organic compounds (WSVOCs) by wet atmospheric aerosols can lead to the formation of secondary organic aerosol material (SOA). We have performed a series of laboratory studies in order to quantify of the impact of WSVOC uptake and aqueous-phase SOA formation on aerosol cloud condensation nuclei (CCN) activity. Deliquesced, acidified submicron ammonium sulfate aerosols at >60% RH were exposed to ppb levels of gas-phase methylglyoxal, acetaldehyde, or alpha-pinene oxide (aPO) in a continuous-flow aerosol reaction chamber (residence time = 3-5 h). Aerosol size, composition, and CCN activity was monitored at the reactor outlet via scanning mobility particle sizer (SMPS), continuous-flow streamwise thermal gradient chamber (CFSTGC), and aerosol chemical ionization mass spectrometry (Aerosol-CIMS), respectively.

Methylglyoxal and acetaldehyde are known to form SOA and suppress surface tension in bulk aqueous aerosol mimics, but both of these species have relatively low Henry's Law constants. We found evidence that adsorption of these species from the gas phase to the gas-aerosol interface significantly impacts aerosol CCN activity, by directly altering the aerosol surface tension. Up to 15% reduction in critical dry diameter for activation was observed without any detectable particle growth due to bulk uptake of organics.

In contrast, aPO is efficiently taken up by the deliquesced aerosols. No detectable change in aerosol CCN activity was apparent at a given dry particle diameter, despite significant aerosol organic content detectable via Aerosol-CIMS and a 20% increase in particle volume. Kohler theory analysis indicates a surface tension of 68 mN/m, commensurate with previous analysis of total WSOC from alpha-pinene. This surface tension depression offsets the expected decrease in hygroscopicity due to the increase in aerosol organic content.

The need for future experiments and modeling studies to further quantify the impacts of WSVOCs on cloud formation and precipitation will be discussed.

7CC.5

The Ice Nucleating Potential of Amorphous Secondary Organic Aerosol to Form Cold Clouds. BINGBING WANG, Andrew Lambe, Paola Massoli, Timothy Onasch, Paul Davidovits, Douglas Worsnop, Daniel Knopf, *Stony Brook University*

Secondary organic aerosol (SOA) generated from the oxidation of organic gases are ubiquitous in the atmosphere, but their interaction with water vapor and their ice cloud formation potential at low temperatures remains highly uncertain. We report on measurements of water uptake and ice nucleation of laboratory-generated SOA that exhibit similar behavior to ambient organic particles. Water uptake above 230 K is governed by the oxidation level of the SOA, followed by moisture-induced phase transitions and immersion freezing. For temperatures from 200 to 230 K, the SOA nucleate ice from supersaturated water vapor independent of oxidation level. We show that particle phase and viscosity govern the particles' response to temperature and relative humidity and provide a straightforward interpretation for the observations of both laboratory and ambient organic particles. Since SOA undergo glass transitions, these observations suggest that atmospheric SOA are potentially important for ice cloud formation and climate.

7CC.6

Hygroscopicity of Amine Secondary Aerosol – Mixtures of Organic and Inorganic Components. XIAOCHEN TANG, David R. Cocker III, Kathleen Purvis-Roberts, Akua Asa-Awuku, *University of California Riverside*

Aliphatic amines are emitted from both biogenic and anthropogenic sources and contribute to the formation of secondary organic aerosol in reactions with OH, O3 and NO3. However, the cloud condensation nuclei (CCN) ability of amine aerosol has not been explored yet. Here, we study the hygroscopicity of aerosol formed from three amines (trimethylamine, diethylamine and butylamine) in the UCR environmental chamber. NO3 is a dominant night time oxidant and can react with amines in acid-base and/or oxidation reactions. The secondary aerosol formed are composed of both organic and inorganic components. The ability of these particles to uptake water is measured with a hygroscopic tandem differential mobility analyzer (HTDMA) and CCN counter. Results show that aerosol formed from diethylamine and butylamine with NO3 are very hygroscopic (kappa~0.3). Conversely, when amines were oxidized by OH, no inorganic components were detected in the particle phase and were subsequently less hygroscopic. Hence aminium nitrates formed in acid-base reactions greatly improve hygroscopicity of NO3-initiated aerosol.

Presence of water vapor during the NO3-initiated reaction also promoted formation of aminium salts, which correspondingly enhanced CCN activity of formed aerosol. Highest salt fraction is measured in humid reaction between butylamine and NO3, in which kappa value reached as high as 0.8. This is the first research into the hygroscopicity of aliphatic amine aerosol. Our results will significantly impact the estimation and role of amines in atmospheric chemistry and global climate models.

7CC.7

Kinetics of Water Transport in Amorphous Aerosol. JAMES F. DAVIES, Allen E. Haddrell, Rachael E.H. Miles, Jonathan P. Reid,*University of Bristol*

Aerosol particles are often assumed to establish an instantaneous equilibrium composition with the surrounding gas phase. However, the kinetics of water transport can be limited by diffusion in the gas phase, in the particle bulk or by surface accommodation. For example, the slow transport of water within glassy or amorphous aerosol particles can lead to particles that approach an equilibrium state over timescales that are much longer than is accessible to most analytical instruments. Studies of water transport in single particles using optical or electrodynamic traps over timescales in excess of 10,000 seconds can provide robust methods for investigating the kinetics of water transport in amorphous states and for benchmarking models.

Measurements made using a new electrodynamic balance technique will be described, comparing the timescales for water transport during evaporation or condensation from solution droplets, surfactant coated droplets, glassy aerosol and aerosol consisting of a two-phase gel. Aerosol particles are injected into a gas flow which can be rapidly cycled (second timescale) between high and low relative humidity (dry and >90 % RH). Droplet sizes are recorded from elastic light scattering with a time-resolution of as low as 2.5 ms. Droplets of two different compositions can be studied in sequence, monitoring the time-dependence of one and then the second in quick succession, allowing the kinetics of water transport in amorphous aerosol to be compared precisely to inorganic aerosol.

The kinetics of water transport limited by bulk and surface transport processes will be reported and the influence of amorphous phases on the timescale for equilibration of water in atmospheric aerosol assessed.

7HA.1

Airborne Biopolymer Analysis and Toxicity Potential Associated with Hydrocarbon Weathering on Shorelines Impacted by the Deepwater Horizon Oil Spill. ALINA M. HANDOREAN, Kevin McCabe, Jane Turner, Alison L. Ling, Benjamin J. Miller, Mark T. Hernandez, *University of Colorado at Boulder*

The atmosphere carries biochemical hallmarks of life – both in primary and weathered forms. The contribution of the most primary biopolymers — DNA, lipids, carbohydrates and proteins — to the pool of atmospheric organic carbon associated with weathering oil, remains relatively unknown.

We investigated coastal aerobiological loads in conjunction with the petroleum hydrocarbon releases in the Gulf of Mexico, following the 2010 Deepwater Horizon accident. Airborne particulate matter was analyzed for its carbohydrate and DNA content, as well as its genotoxicity potential between contaminated beaches in Louisiana (Grand Isle), and geologically similar but pristine beaches on the eastern Texas Coast (Port Arthur). Size segregated aerosol samples (8 hour composites; PM2.5 and PM10) were collected with ultra-clean technique on filters mounted in teflon cassettes. Particulate matter was immediately eluted from these filters into sterile, pyrogen-free water, and aliquots stored for subsequent biopolymer, genetic and toxicity analyses.

Carbohydrates were measured using a sensitive colorimetric assay of phenol-conjugated monosaccharides. The mass and organic carbon fraction of these biopolymers was presented as a surrogate index for total bioaerosol loads, which was juxtaposed to the types of microorganisms present in air. Airborne genomic DNA was precipitated, amplified (PCR of 18s/16s RNA), sequenced and compared to the NCBI database for genus level identification.

Elevated levels of carbohydrates were observed in aerosols above oil contaminated beaches, with respect to their pristine counterparts. QIIME analysis resulted in a total of 14,925 sequences; patterns reveal variation in taxa abundance in the presence of weathering oil. Acinetobacter sp., and Legionella sp. were proeminent in many Louisiana aerosol samples. Flavobacteria were consistent in their distribution between both the sampling sites. A genetically engineered bacterial strain of Salmonella thyphimurium (TA 1535) exposed to filter eluents suggests that some aerosols collected above the Louisiana beaches had the potential to induce genotoxic cellular stresses.

7HA.2

Release of Bioaerosol Genomic DNA Due to Membrane Damage During Aerosolization and Sampling. HUAJUN ZHEN, Taewon Han, Donna Fennell, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Bioaerosol particles are exposed to great stresses during aerosolization and sampling, which results in rapid loss of viability. Here we demonstrate for the first time that the stress due to aerosolization and sampling could be so strong that it damages cell membranes of the bioaerosol particles resulting in the release of their genomic DNA.

We investigated cell membrane damage of gram-negative Escherichia coli and gram-positive Bacillus atrophaeus bacteria for different aerosolization and sampling methods. The cells with their membranes intact and the damaged cells in each sample were quantified by epifluorescence microscopy and quantitative polymerase chain reaction (qPCR), respectively. The results are reported as a ratio of the DNA quantity released due to cell damage with the DNA quantity remaining within the intact cells.

When E. coli culture suspension was aerosolized by a Collison nebulizer, the ratios were found to significantly increase over 60 minutes. The use of the Collison nebulizer with a polycarbonate jar instead of a glass jar reduced the ratio from 0.17 ± 0.080 to 0.093 ± 0.032. For E. coli collected for five-minute with Button Aerosol Sampler, Anderson Impactor and BioSampler, the ratios had ranges of 0.054-0.094, 0.19-0.58 and 0.06-0.32, respectively. Application of our new electrostatic collector is expected to yield low ratios due to low stress. B. atrophaeus had similar amount of membrane damage when sampled by Button Aerosol Sampler and BioSampler, but significantly lower than E. coli when sampled by Anderson Impactor. The magnitude of cell membrane damage to bioaerosols aerosolized by C-Flow PFA concentric nebulizer, Liquid Sparging Aerosolizer and Single-Pass Aerosolizer is under investigation.

Our results strongly suggest that quantification of microorganisms using the methods that rely on intact cells would underestimate bioaerosol concentrations. It also provides guidance for selecting optimal aerosolization and sampling methods to preserve the physiological status of microorganisms.

7HA.3

Effect of Aerosolization and Sampling Time on the Activity of a Purified Neuraminidase from Clostridium Perfringens as Viral Neuraminidase Model. MARIE-JOSÉE TOULOUSE, Nathalie Turgeon, Jim Ho, Dongqing Li, Caroline Duchaine, *Université Laval, Canada*

Several viruses such as Influenza can be transmitted by the airborne route. However, little is known about their aerosolization, propagation, and detection in aerosol state. Apart from specific but time consuming and costly assays like PCR, there are few if any generic approaches to assess viral presence in air. We have already developed and validated a rapid and cheap screening test for the presence of certain viruses by using a virus-specific neuraminidase substrate. Here, we studied the effect of aerosolization and sampling on the neuraminidase activity.

A purified neuraminidase from Clostridium perfringens (SIGMA) was our model for this study. It was aerosolized using a TSI model 9302 atomizer into a GenaMini aerosol chamber (SCL MedTech). Alexa fluor 555 was aerosolized with the enzyme to assess the capture efficiency of the samplers. Air sampling was performed using a Biosampler (SKC) at 12.5 liters per minute for 20 minutes and 0.8 micro-meter polycarbonate filters (SKC) at 10.0 liters per minute for 25 minutes. 250 liters of air were collected by each sampler.

The analysis of the Alexa fluor 555 collected in our samples demonstrated that the Biosampler was more efficient than 0.8 micro-meter polycarbonate filters to collect the particles generated in our system. Moreover, this sampler causes 10 times less damage to the enzyme than sampling on filters.

The Biosampler is a good sampler to collect microorganisms that possess neuraminidase because it preserves the activity of the enzyme more than dry sampling on filters. Those results will have to be confirmed with airborne viruses (Orthomyxoviridae, Paramyxoviridae, Togaviruses). Early detection of viral presence in air would permit measurement of potential threats, for example in hospitals, agricultural buildings or military establishments where soldiers are housed. It would allow the quick implementation of measures to reduce the spread of the infection, like quarantine and vaccination.

7HA.4

Viable Approach for the Detection and Sampling of Mycobacteria Species Contamination by Aerosol and Surface Sampling. Pamela Murowchick, DAVID ALBURTY, Alec Adolphson, Michael Hornback, Benjamin Cobb, Brian Dable, *AlburtyLab, Inc.*

Testing was recently conducted in the AlburtyLab test chamber. The goal of this evaluation was to demonstrate an initial version of the Areté Associates BioSS integrated environmental health monitoring system, including the Areté TRAP biomonitor detector/collector, InnovaPrep LLC backpack surface extractor (BSE) and Epistem Ltd. Genedrive polymerase chain reaction (PCR) identifier. The system successfully demonstrated “point of interest” detection, surface sample extraction and biological ID in less than 1 hour. The system, as tested, demonstrated detect/collect/identify (DCI) capability individually and as a system met or exceeded the test objectives.

A modified strain of Escherichia coli bacteria was disseminated in the aerosol test chamber and used for trigger detecting with the biomonitor. The E. coli strain harbors a plasmid that contains a rifampicin resistant rpoB variant cloned from a clinical sample of Mycobacterium tuberculosis, which the follow-on confirmatory identification node’s assay is designed to detect.

When the aerosolized bacteria were detected in the test cloud at a suitable concentration to alarm, the biomonitor triggered collection of a dry filter sample. Following the completion of sampling, the dry filter sample was extracted and loaded into an assay for identification. In parallel to the dry filter collection, a portable surface sampler, BioSS Backpack Surface Extractor (BSE), was used to collect the bacteria from test coupons exposed to the same E. coli test cloud. The extracted eluent from the surface collector was directly loaded into an assay for identification. The progress of the hardware systems was monitored in real-time with the status communicated to an off-site database where the results can be aggregated from several pieces of equipment. For this test evaluation, the components of the BioSS were operated in independent steps as a proof-of-concept.

7HA.5

Investigation of an Optimized Single-Stage Electrostatic Precipitator for Bioaerosols. TAEWON HAN, Donna Fennell, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

We recently developed an electrostatic collector for bioaerosols, where biological particles are electrostatically deposited onto a 3.2 mm electrode covered by a hydrophobic substance and then removed and collected by rolling water droplets (20 or 40 micro-liter) to achieve high sample concentration rate. As part of the further development of the collector, it was integrated with a new electrical charger based on carbon fiber brushes. The new integrated sampler was made of static dissipative material (e.g., Delrin) and has a shape of a closed half cylinder. Its top round top part contains carbon fiber brushes, while its flat bottom holds a narrow collection electrode. The objective of this research was to optimize the charger and collection electrode for maximum performance of the sampler. We tested the sampler with various configurations of carbon brushes comprising the charger and different materials of the collection electrode. The total bioaerosol particles number collected by a water droplet was determined by microscopy and the reference concentration was monitored by a Grimm optical particle counter.

Surprisingly, electrode material had a great effect on collection efficiency: copper (19%), brass (30%), plain steel (46%), zinc plate steel and high carbon steel (50%), alloy steel (51%), stainless steel (79%), pressed carbon fiber (87%). A combination of the charger with eight carbon brushes and carbon fiber electrode yielded virtually no particle losses and collection efficiency of 84% when sampling E. coli bacteria at 10 L/min for 10 min. The efficiency was the same for 20 and 40 micro-liter droplets. When sampling for 60 min, the actual collection efficiency was 70% due to a reduced particle removal from the electrode. This bioaerosol sampler will be optimized for higher flow rates, but it already shows great promise and could be a part of various applications, including Homeland security.

7HA.6

Validation of Five Bacteriophages Models for the Study of Airborne Viruses. NATHALIE TURGEON, Marie-Josée Toulouse, Sylvain Moineau, Caroline Duchaine, *Université Laval, Canada*

Bacteriophages (bacterial viruses) represent good models for the study of airborne viruses as they are safe to use, some of them display features similar to human and animal viruses, and they are relatively easy to produce in large quantities. Accordingly, several studies have used phages as viral models in aerosol studies. Surprisingly, only few studies have compared the effect of aerosolization and sampling on different phages in order to validate their use as models. It has been demonstrated that aerosolization and sampling conditions can negatively affect virus infectivity, but this will vary from one virus to another. Thus, several viral models are needed to study these parameters and to eventually apply them to eukaryotic viruses.

The aim of this study was to compare the effect of aerosolization and sampling on viral infectivity of five tail-less bacteriophages: MS2 (ssRNA), Phi6 (segmented dsRNA), PhiX174 (ssDNA), PM2 (dsDNA), and PR772 (dsDNA). We tested two nebulization buffers: a salt solution and a salt solution complemented with organic matter. The aerosols were collected using a liquid cyclone (Biosampler) and a dry cyclone (the National Institute for Occupational Safety and Health 2-stages cyclone bioaerosols sampler). Samples were analyzed by plaque assay and qPCR.

Our results demonstrated that the five phages are indeed affected differently by aerosolization and sampling. Phages MS2 and PhiX174 are more resistant to aerosolization and sampling in dry condition than the three others. We also revealed that the presence of organic matter in the aerosol preserves the infectivity of sensitive phages throughout aerosolization and sampling with dry cyclones. These results will help in the selection of the appropriate phage model to mimic the behavior of human and animal viruses in aerosols.

7HA.7

Investigation of Structural Modifications of a Common Cold Virus at Elevated Temperature in the Gas-phase with GEMMA.PETER KALLINGER, Victor Weiss, Dieter Blaas, Günter Allmaier, Wladyslaw Szymanski, *University of Vienna*

During the last decade, the GEMMA technique (Gas-phase Electrophoretic Molecular Mobility Analyzer, a combination of a nano electrospray, DMA, and a particle detector) has proven useful for detection and size-determination of intact viruses. Human rhinoviruses (HRVs) are members of the picornavirus family and the main cause of the common cold. They are nearly spherical of icosahedral shape with a diameter of about 30 nm. On incubation at T > 50 °C, the infectious virus loses its innermost capsid protein VP4 together with its single stranded RNA genome; the resulting subviral particle is about 4% bigger than the native virion. It has been shown previously with GEMMA that subviral particles obtained on incubation at elevated temperature exhibit a change of the size spectrum with respect to the size spectrum of native virions; subviral particles, together with oligomers of the VP4 capsid protein, were detected. In order to investigate these conformational modifications online under the influence of heat, we have now used a different approach, namely heating the virus in the gas-phase. We constructed a device that can be operated at atmospheric pressure at predetermined temperature and humidity. It was integrated in the GEMMA system between the nano electrospray and the charge conditioning device in front of the DMA. Since changes of size and conformation of a given virus occur at characteristic temperatures, this apparatus might become useful for the fast online detection and study of thermal stability of viruses and other bio-nanoparticles. We shall present first results on heat-induced conformational modifications of the HRV2 capsid in the gas-phase and compare it with results of experiments carried out in solution.

7IM.1

Device and Method for Generation of Aerosol Distributions with Tuneable Geometric Mean Diameter down to 5 nm. JAMES FARNSWORTH, Jason Johnson, *TSI Incorporated*

Polydisperse test aerosols are prepared for a variety of reasons including inhalation research, filter media testing, and instrumentation development. Nebulization is a simple and useful means for generating test aerosols. However, it is difficult to obtain distributions of mean sizes below 25 nm, as droplet diameters produced in nebulization are large and dissolved residue in the diluent interferes with the size distribution of interest. Flame and furnace methods can be used to generate sub-25 nm aerosols, but these techniques have disadvantages related to easy of use, repeatability, and potential health concerns. All generation methods typically struggle with controlling size while maintaining constant output concentration and geometric standard deviation (GSD).

Here we present a device and method for generating a lognormally-distributed aerosol distribution with an adjustable mean diameter, prepared from a single dissolved solution, while maintaining good stability of concentration and GSD. An aqueous solution of 10 percent NaCl was prepared, and the new TSI Model 3485 Nanoparticle Nebulizer was used to generate aerosols over a range of mean diameters using the 1000X dilution capabilities of the instrument. The mean diameter range of the device was further extended by adjusting droplet impaction distance, thus varying droplet diameter. The aerosol size distribution was measured using a TSI 3936 SMPS. The resulting aerosol was lognormally distributed with a mean diameter tuneable over the range 5-30 nm geometric mean number diameter (10-130 nm geometric mean volume diameter). The GSD for these particle distributions was 1.5 ± 0.2 and number concentration ranged from 10^6 to 10^7 #/cc for all generated distributions.

These results demonstrate the use of a nebulizer such as the TSI 3485 for generation of concentration-stable challenge aerosols over a wide size range, and offer a cheaper and safer alternative to furnace or flame nanoparticle generation techniques for obtaining sub 20nm aerosols.

7IM.2

Characterization of a Device for Measuring Electrical Mobility Size and Concentration of Nanoparticles. JASON JOHNSON, Axel Zerrath, Rob Caldow, Melissa Grose, Sean Morell, Erik Willis, Daniel Jensen, *TSI Incorporated*

A device has been developed to meet the need for a small, portable instrument to measure the size, concentration, and potential exposure to nanomaterials or environmental and laboratory nanoparticles. This instrument (the TSI Model 3910 NanoScan SMPS) is capable of measuring particle size distributions in a portable form-factor. It uses miniaturized components and the basic measurement principles of a Scanning Mobility Particle Sizer (SMPS) and is able to achieve a size measurement range of 10 to 420 nm, with 8 channels per decade of resolution and a total integrated number concentration to at least 1x10^6 particles/cm3. The instrument may be powered with Li-ion batteries for use in applications such as workplace monitoring, or with AC power for extended remote or laboratory measurement applications.

As configured, the device is a multi-component system, combining a cyclone inlet selector for removal of large particles, a patented, non-radioactive, unipolar corona discharge aerosol diffusion charger (Kaufman, et al. 2000), a radial differential mobility analyzer (RDMA), (Pourprix 1994), an isopropanol -based condensation particle counter (CPC), and a mobile computing platform for on-board data analysis and data logging, enabling either tethered or stand-alone operation.

The performance of this instrument was characterized and compared to reference SMPS systems (TSI Models 3936N76 and 3034) with various polydisperse aerosols such as sodium chloride, silver and poly-alpha olefin (PAO) and was shown to yield number concentration measurements that are within 99% ± 6% of those of the reference system. It was also characterized for its ability to measure differential mobility analyzer (DMA)-classifed monodisperse aerosols and the results of these tests will be presented. Additionally, the results of ambient measurements made in parallel with optical particle sizer (OPS) measurements will also be presented.

7IM.3

Development and Evaluation of a Personal Sampler for Nanoparticle Exposure Assessment. JOHN VOLCKENS, Dan Miller-Lionberg, Anthony Marchese, Hank Lentz, Matt Zock, Kristin Bunker, Traci Lersch, John Mastovich, Gary Casuccio, *Colorado State University*

Global research involving nanotechnology revolves around the manipulation of size, shape, and compositionally tunable properties of engineered particles having at least one dimension in the sub-100 nm size range, and includes the development of new manufacturing techniques that utilize these nanostructures. Engineered nanoparticles possess unique properties that may present potential health risks to the workers who manufacture materials and products containing engineered nanoparticles, and to consumers who are directly or inadvertently exposed to engineered nanoparticles. Monitoring personal exposures to these engineered nanoparticles is necessary to evaluate potential health risks.

This work describes prototyping and testing of a personal, thermophoretic aerosol sampler designed to collect airborne nanoparticles in the breathing zone of individuals. The objective was to make the device small and lightweight so that it can be used as a personal sampler, and efficient at collecting airborne nanoparticles for subsequent quantification and identification of engineered nanoparticles using electron microscopy and energy dispersive X-ray spectroscopy (EDS).

The design of the personal sampler incorporates the thermophoretic force generated from an applied temperature gradient, orthogonal to the aerosol flow, to separate particles from a moving airstream. By placing a transmission electron microscope (TEM) grid on the cold-plate side of the channel, particles can be collected upon media that can be placed directly in an electron microscope to allow measurement of size, shape, and elemental composition. The ability to perform electron microscopy directly on sampling media collected in the sampler eliminates the need for specialized sample preparation and allows for more efficient differentiation among engineered, biogenic (naturally produced) and incidental (anthropogenic, non-engineered, such as those from fossil-fuel combustion) nanoparticles. Results, including electron microscopy images and EDS spectra, will be presented from laboratory and field measurement programs. The particle concentration (particles/cc) results will be compared to direct-reading instruments.

7IM.4

Design and Performance of a Thermophoretic Precipitator Nanoparticle Sampler. ART MILLER, Chris Wendel, Alek Marinos, Grant King, Aleksandar Bugarski, *NIOSH*

Researchers at the National Institute for Occupational Safety and Health (NIOSH) are developing methods for characterizing diesel particulate matter in mines. Introduction of novel engine and exhaust aftertreatment technologies in underground mines is changing the nature of diesel emissions, and alternative metrics to the traditional mass-based measurements are being investigated with respect to their ability to capture changes in the properties of diesel aerosols. The emphasis is given to metrics based on measurement of number and surface area concentrations, but analysis of collected particles using electron microscopy (EM) is also employed for detailed particle characterization. To collect samples for EM analysis at remote workplaces, including mining and manufacturing facilities, NIOSH is developing portable particle samplers capable of collecting airborne nano-scale particles. This paper describes the design, construction, and testing of a prototype thermophoretic precipitator (TP) particle sampler optimized for collection of particles in the size range of 1-300 nm. The device comprises heated and cooled metal plates separated by a 0.8 mm channel through which aerosol is drawn by a pump. It weighs about 2 Kg, has a total footprint of 27x 22 cm and the collection plate size is approximately 4 x 8 cm. Low power consumption and enhanced portability were achieved by using moderate flow rates (50–150 cm3/min) and temperature gradients (10–50 K/mm with ΔT between 8 and 40 K). The collection efficiency of the prototype, measured with a condensation particle counter using laboratory-generated polydisperse submicrometer NaCl aerosols, ranged from 14–99%, depending on temperature gradient and flow rate. Analysis of transmission electron microscopy images of samples collected with the TP confirmed that the size distributions of collected particles determined using EM are in good agreement with those determined using a Fast Mobility Particle Sizer.

7IM.5

Evaluation of a Compact Electrostatic Nanoparticle Sampler. HE JING, Ta-Chih Hsiao, Siqin He, Qisheng Ou, Da-Ren Chen,*Washington University in St. Louis*

A new compact nano-aerosol sampler for particle SEM (Scanning Electron Microscope) analysis has been designed and its performance has been experimentally evaluated. The new sampler collects particles via the electrostatic deposition. Two chambers for aerosol charging and particle collection are included in the sampler. The charger used in the NSAM (Nanoparticle Surface Area Monitor, TSI Inc.) is used in the particle charging chamber of the sampler. Charged particles are then electrically deposited on the SEM stub in the particle collection chamber. In this study the performance optimization of the sampler was first carried out. The optimized charger voltage, total flow rate through the sampler and aerosol/ion carrying flow rate ratio were 4.5 kV, 1 lpm and 1:1 respectively. The sampler's performance when operated at the above-identified optimal condition was then further evaluated. Fluorescent particles in the sizes ranging from 60 to 400 nm were used to evaluate the particle deposition distribution in the sampler via the fluorescence analysis. The effect of particle material on the particle collection was examined with PSL (Polystyrene Latex) particles, solid (i.e., potassium chloride) and liquid (i.e., oleic acid) particles. The testing particle size ranges for PSL particles, potassium chloride particles and oleic acid particles were from 100 to 1000 nm, from 10 to 500 nm and from 50 to 500 nm respectively. The detail of this study will be discussed in the presentation.

7IM.6

Environmental Particle Collector and Detector System for Continuous Sampling of Ultrafine Aerosols. MARIA D. KING, Victor Ugaz, John Haglund, Ray Pierson, Yassin Hassan, *Texas A&M University*

Environmental exposure to aerosolized particulate matter less than 10 micrometer aerodynamic diameter is widely associated with adverse respiratory and cardiovascular health effects. Despite their high toxicity and mutagenic potential, few existing methods are capable of sampling and characterizing large airspace volumes for extended periods of time. We have established a real time in-line collection and detection method for nanosize aerosol particulates. Different concentrations of Al_2O_3 nanoparticle suspensions were aerosolized in a laboratory flow cell and collected with the low cutpoint WWC at 200 L/min using 0.01 % Tween-20. The collected WWC effluent was then co-injected into a microchannel with an aqueous 0.033 mg/mL fluorescein solution. A relatively linear concentration dependence of interfacial fluorescence is observed up to ~1 wt%, beyond which the intensity reaches saturation. Decreasing flow rate increases the intensity due to increased residence time for complexation. The WWC results display a clear correlation between nanoparticle concentration and fluorescence intensity that is in good agreement with the control suspensions (comparable concentrations but not aerosolized and collected by the WWC), verifying the potential for our microchannel-based method to enable continuous nanoparticle detection. Output liquid flow rates from the WWC of 0.04 – 0.2 mL/min are within the bounds of our experiments. Scanning Mobility Particle Sizer (SMPS) analysis confirmed that we were able to easily detect the lowest environmental particle concentration of ~200 microgram/meter^3 (4 – 160 nm particle size range). Samples taken before and after WWC collection were also analyzed using a Nanosight system, which confirmed that the post-collection size distribution in the WWC did not deviate significantly from that of the aerosolized material. Each hydrosol sample from the WWC with the 102 mm reference filter suspensions was quantitated by gravimetry and inductively coupled mass spectrometry (ICP-MS) for Al_2O_3 content. We observed high levels of nanoparticle recovery (~75%) in all tests.

7IM.7

Quantifying Ligand Adsorption to Nanoparticles using Tandem Differential Mobility – Mass Analysis.

SUVAJYOTI GUHA, Xiaofei Ma, Michael Tarlov, Michael Zachariah, *University of Maryland, College Park*

Quantification of ligands adsorbed to different bionanoparticles is important in the context of drug delivery and therapeutics. Here we present a new approach for ligand quantification by combining differential mobility analyzer (DMA) with aerosol particle mass analyzer (APM). This approach is advantageous compared to other existing techniques because it can be applied to heterogeneous samples and is independent of bionanoparticle property, ligand morphology and conformation. We demonstrate this approach with two examples, adsorption of different concentrations of bovine serum albumin to gold nanoparticles and adsorption of rituxan, a monoclonal human antibody to polystyrene latex spheres at different pH. Our results appear to be in excellent agreement with literature. Thus we anticipate that this hyphenation of DMA with APM can become an important method for quantification of ligands in the near future.

7SA.1

Impact of Updated Emission Inventories on Source Apportionment of Fine Particle and Ozone Over the Southeastern U.S.

WEI WANG, Shiang-Yuh Wu, Kai Wang, Yang Zhang, Hiroaki Minoura, Zifa Wang, *North Carolina State University, Raleigh, NC, USA*

Various source apportionment techniques have been developed to estimate source contributions (SC) to major pollutants for emission control, which are largely affected by updates in the National Emission Inventory (NEI). SCs of 10 major source categories to fine particulate matter ($PM_{2.5}$) were previously estimated over the southeast U.S. for 2002 based on the 1999 NEI version 2 (NEI99v2) using the Community Multiscale Air Quality modeling system with the Brute Force Method, which calculates SCs based on predictions using baseline emissions and a set of emissions with one category zeroed-out one at a time. New simulations with the 2005 NEI (NEI05) are conducted and compared with previous simulations to examine changes in SCs. $PM_{2.5}$ concentrations increase by 9.1% in January and 19.2% in July. In January, miscellaneous areas (MISC), biomass burning (BIOM) and coal combustion (COAL) remain the top 3 contributors to $PM_{2.5}$ but with different ranking and higher SCs, due to increased primary $PM_{2.5}$ (PPM) emissions in NEI05 and increases in relative contributions of MISC and COAL to emissions of PPM, NH_3 and SO_2. In July, COAL, MISC and industrial processes (INDUST) remain the top three with higher SCs for similar reasons. SCs from diesel and gasoline vehicles (DV and GV) decrease in both months, due to decreased GV contributions to SO_2 and NH_3 emissions and DV contributions to NO_x and PPM emissions. Compared with NEI99v2, SCs from other combustion and BIOM are higher in Florida, due to substantial increases in formaldehyde and PPM emissions in NEI05, resulting from higher wildfire emissions and state emission updates. SCs from INDUST increase and those from DV and GV decrease in urban areas. SCs of O_3 from most sources in July increase due to a large increase in their contributions to NO_x emissions. These results have important policy implications to emission control strategies.

7SA.2

Organic Aerosol Source Apportionment in the United States. BENJAMIN MURPHY, Kristina Wagstrom, Spyros Pandis, *Carnegie Mellon University*

The contribution of specific sources, both anthropogenic and biogenic, to atmospheric pollution varies widely throughout space and time. The relationship between these sources and ambient receptors is complicated by variability in the sources themselves, meteorological conditions, and chemistry that occurs during the pollutants' atmospheric lifetime. The Particulate Matter Source Apportionment Technology (PSAT) algorithm has been applied to the regional-scale CTM, PMCAMx-2008 to study the source-receptor relationships organic aerosol (OA) components, major contributors to the particulate matter (PM) mass composition.

PMCAMx-2008 treats primary organic aerosol (POA) evaporation upon dilution in the atmosphere as well as the multi-generation OH oxidation of vapor-phase organic constituents in equilibrium with aerosol phase. This phenomenon can alter the volatility of these compounds and over time have an effect on their atmospheric transport and fate. We investigate this relationship by quantifying contributions to OA loadings from local, short range, mid range and long-range sources at several receptor sites in the US. We also explore the impact of these sites as sources on the surrounding domain. Finally, we assess the average chronological age of OA mass throughout the US domain. For all of these analyses we perform model runs with and without evaporative POA and aging of OA vapors to understand the effects these assumptions have on model predictions. In previous work, a uniform representative volatility distribution was applied to OA mass from all sources. We investigate the sensitivity of our model's results to this assumption by varying this uniformly applied distribution for a set of runs.

The analysis from this study confirms the highly regional nature of OA pollution. We also find that implementing OA aging has some effect on the average predicted particle age, but very little effect on its average predicted transport distance or extent of impact.

7SA.3

Characterization of Organic Carbon Sources in Pasadena and Bakersfield, CA During CalNex 2010. PUNITH NALLATHAMBY, Rebecca Sheesley, John Offenberg, Michael Lewandowski, Tadeusz Kleindienst, Mohammed Jaoui, *Baylor University*

The California Nexus (CalNex) field study in 2010 focused on the nexus of air quality and climate change in Southern California; field sites in Bakersfield, CA and in Pasadena, CA were operated synoptically in May-June 2010. The Pasadena site will be used as a proxy for the greater Los Angeles urban signal, while the Bakersfield site likely represents a mix of urban and agricultural sources. Source apportionment of particulate organic and elemental carbon (OCEC) is of high interest in characterizing the air quality during the campaign. Correlations between OC and EC at the two sites show R^2 values of 0.65, 0.49 and 0.39 for OC, EC and OC:EC respectively. Back trajectory analysis will be applied to further assess whether Bakersfield is impacted by the greater Los Angeles urban plume during the field study. Organic tracer analysis by accelerated solvent extraction and gas chromatography/mass spectrometry will be presented for PAHs, alkanes, hopanes, steranes, levoglucosan and aromatic acids. Preliminary hopane measurements indicate similar levels as reported for Riverside, CA during the SOAR campaign in 2005 (approximately 0.2 ng m^{-3}). Source apportionment of primary emissions (motor vehicles, biomass burning etc.) using organic molecular marker Chemical Mass Balance (CMB) for OC and EC at both sites will be used to discuss regional differences in Southern California emission contributions. In addition, concentration of aromatic acids will be used to estimate potential contribution of motor-vehicle associated secondary organic aerosol.

7SA.4

Daily Trends of Ultrafine Particulate Matter at Sacramento, California. Toshihiro Kuwayama, Chris Ruehl, MICHAEL KLEEMAN, *UC Davis*

Ultrafine particulate matter (PM0.1) represent a potential health risk, but very little monitoring data exists for source contributions to PM0.1 over an annual cycle. The present study investigates the 2009 daily trends of ultrafine particulate matter emissions with aerodynamic diameter between 0.056-0.1 micro-meter at Sacramento, California, using Positive Matrix Factorization (PMF) version 3.0. Samples were collected with Micro Orifice Uniform Deposit Impactors (MOUDIs) followed by analysis for organic carbon (OC) and elemental carbon (EC) using thermal-optical analysis and metals analysis using ICP-MS.

PM0.1 chemical composition changed as a function of season, with higher concentrations of EC during the winter months and lower concentrations during the summer. Metals such as Na, K, Fe, and As also followed a similar seasonal pattern, pointing to the importance of reduced mixing depth during winter months along with new sources associated with home heating. Wind direction and wind speeds also affected the collection of Ni, Cu, and Pb since point sources dominated these emissions.

Contributions to PM0.1 mass were identified from major sources including diesel truck emissions, railway traffic, background mixed highway traffic emissions, and residential wood burning emissions using PMF. PM0.1 factors for diesel trucks and railway traffic were lower than factors for residential wood burning emissions and background mixed highway traffic emissions at the sampling site. PM0.1 source contributions displayed significant seasonal variation, with the majority of PM0.1 biomass combustion observed during the cooler winter months.

The time-series of PM0.1 composition and source apportionment results provides a basis for future comparisons to PM0.1 predictions from regional grid models. This technique of model predictions and comparisons to point measurements represents the most plausible methods for PM0.1 epidemiological analysis in the coming years.

7SA.5

Coarse Particles in the Desert Southwest: Final Results and Policy Insights. ANDREA CLEMENTS, Matthew Fraser, Pierre Herckes, Kale Walch, Paul A. Solomon, *Arizona state University*

Many arid regions of the desert Southwest have been designated non-attainment of the National Ambient Air Quality Standard (NAAQS) for PM10. Within this size range, coarse particle (PMc, particles with an aerodynamic diameter [AD] between 2.5 and 10microns) concentrations often exceed that of fine particles (PMf, particles with AD less than or equal to a nominal 2.5microns) and primarily drive exceedences. However, PMc has not been widely studied separately from the PMf fraction of PM10 and improved information about the spatial and temporal particle composition, source categories, and relative source strength can aide in improved PM10 control measures.

Pinal County, Arizona was chosen as an ideal study location to further our understanding of particle sources impacting arid environments. With population growth as a result of urban sprawl into the traditionally rural region, attainment of the PM10 standard is a pressing concern in Pinal County. A year-long characterization study was conducted at three different locations on a 1-in-6 day schedule yielding a rich dataset characterizing both fine and coarse particles in terms of mass, ions, elements, bulk elemental and organic carbon, and some organic species concentrations. These data were used for source appointment modeling of the aerosol.

Several metrics confirmed the dominance of crustal sources. Spatial analysis, temporal variation, and modeling results suggest variable influences from agricultural sources, road dust, and the cattle feedlots with more minor contributions from secondary aerosol formation and regionally-transported particles. Results indicate control of crustal sources may affect the greatest change in overall mass concentrations and that the close proximity of the cattle feeding operations greatly influences the mass measurements at one of the regional compliance monitors. Future policy implications insights are being discussed with the Pinal County Air Quality District and some proposals may be applicable to other counties within the desert Southwest currently in non-attainment of the federal NAAQS.

7SA.6

Sources of Organic Aerosol in Eastern Iowa. ELIZABETH STONE, Chathurika Rathanyake, Thilina Jayarathne, *University of Iowa*

Atmospheric aerosols are micron-sized particles in the atmosphere that have significant consequences on human health and in the regulation of global climate. The climate and health effects of aerosols depend partially on their chemical composition, which is largely determined by the contributing aerosol sources and atmospheric transformations. The ambient atmosphere in Eastern Iowa provides a unique setting to study industrial, motor vehicle, agricultural influences on aerosol composition. Very few aerosol measurements have been made in the Midwestern United States outside of polluted urban areas; this study presents the first detailed characterization of organic aerosol in the state of Iowa. At a natural location in Johnson County approximately 40% of fine particulate matter with diameter less than 2.5 microns (PM2.5) was found to be comprised of carbonaceous material. In this study, the sources of carbonaceous aerosol are explored by the measurement of molecular markers that are unique tracers for aerosol sources. Molecular markers for gasoline vehicles, diesel engines, coal combustion, biomass burning, primary biogenic materials and secondary organic aerosol were measured by solvent-extraction followed by gas chromatography mass spectrometry (GCMS) analysis. The resulting data were used in a chemical mass balance source apportionment model to evaluate the relative contributions of these aerosol sources to ambient measurements.

7SA.7

Development of a New SMP Model Satisfying All Known Physical Constraints in Aerosol Source Apportionment Study.BONG MANN KIM, *AQMD*

A new multivariate receptor model, SMP (Solver for Mixture Problem), has been developed that satisfies all known fundamental natural physical constraints identified in aerosol source apportionment study. Previously, Nonnegative Matrix Factorization (NMF) models have been developed and applied successfully in chemometrics and PM source apportionment study. NMF/PMF models were developed based on nonnegativity constraints of loading and scores (equivalent to source compositions and source apportionments in receptor modeling). However, more physical constraints need to be satisfied in addition to nonnegativity constraints of source compositions and source apportionments. A new model has been developed based on alternating primal-dual interior point nonlinear programming, subject to the inequality constraints of all known physical constraints. Although many multivariate receptor models attempt to estimate both source compositions and source apportionments from the ambient data alone, the SMP model is the first model that can estimate both source apportionments and source compositions. Source compositions estimated by the SMP model can be used in other CMB analysis. The SMP model has been applied to an error free data set to examine its capability of estimating source compositions and source apportionments. Three simulations were conducted, and the results will be compared and discussed.

8AP.1

Aerosol Aggregation in the Transition Regime. THASEEM THAJUDEEN, Suhrid Deshmukh, Christopher Hogan Jr., *University of Minnesota*

As aggregates form frequently in aerosol synthesis processes, it is important to understand how the exact morphology of aggregates arises, such that their shape can be predicted in a given synthesis system. Unfortunately, most prior studies investigating the mechanisms of aerosol aggregation have focused solely to either the continuum or free molecular regimes, which are specific limits of transport. Owing to the characteristic sizes of the common aerosol particles, the mass and momentum transfer processes leading to aggregation occur in the transition regime for both momentum transfer (drag) and mass transfer (collisions). Therefore, the morphology of produced aggregates is dependent on the Knudsen number (the momentum transfer scaling parameter) and diffusive Knudsen number (the mass transfer scaling parameter). It is presently unknown how these numbers (which decrease as aggregation occurs) explicitly evolve and influence subsequent aggregate growth. In this study we model aggregate formation across different mass and momentum transfer regimes, with to date the most rigorously correct model of the physics involved. Through scaling arguments it is shown that the mass transfer processes involving aggregates can indeed be fully described using aptly defined Knudsen number and diffusive Knudsen number, both of which depend on two different size descriptors, namely the Smoluchowski radius and the orientationally averaged projected area. On non-dimensionalizing the equations of motion for aggregates, it is further found that both the diffusive Knudsen number and Knudsen number influence the motion of the aggregates/particles. Brownian dynamic-based cluster-cluster aggregation simulations are performed, for which the inputs are the initial Knudsen number, initial diffusive Knudsen number, and particle volume fraction. It is shown that these three parameters fully govern the time evolution of aggregates.

8AP.2

Potential Enhanced Particle Growth in the Transition Regime. HUI OUYANG, Ranganathan Gopalakrishnan, Christopher Hogan Jr., *University of Minnesota*

Interparticle van der Waals potentials play an important role in aerosol particle growth by coagulation and can enhance the growth rate in many circumstances by a factor of 2-3. In spite of this, such interactions are often unaccounted for in solutions to the general dynamic equation for particle growth, mainly due to the mathematical complexities involved in dealing with such potentials. In this work, we use a combination of dimensional analysis and mean first passage time simulations to develop an accurate yet simple approach to account for such interactions. Through these two approaches we show that for realistic van der Waals interactions that a dimensionless collision rate coefficient, H, can be expressed solely as a function of the diffusive Knudsen number, KnD, and that the dimensionless H(KnD) relationship effectively describes the collision rate (and hence coagulation rate) between particles with van der Waals forces accounted for in the mass transfer continuum, free molecular, and transition regimes. The observed relationship is compared to the more traditional predictions of flux matching theory, which are found to underpredict the collision rate for the largest van der Waals potentials. Using the newly developed collision rate function, the general dynamic equation for particle growth is solved used constant number Monte Carlo simulations. These simulations demonstrate that the dynamics of a coagulating and initially monodisperse system are solely dependent upon the ratio of the van der Waals energy to the thermal energy, the initial diffusive Knudsen number, and the initial Knudsen number.

8AP.3

Diffusion Charging of Non-Spherical Aerosol Particles from Brownian Dynamics Simulations. RANGANATHAN GOPALAKRISHNAN, Thaseem Thajudeen, Christopher Hogan Jr., *University of Minnesota*

To correctly determine the size distribution of aerosol particles from electrical mobility analysis, it is necessary to know precisely the charged fraction of aerosol particles as a function of particle “size”. Much work has thus been done to determine the diffusion charging rate, i.e. the rate at which ions collide with and transfer charge to aerosol particles, for spherical particles, such that upon introduction to an environment of equal positive and negative ion concentrations, the particles arrive at a known diameter-dependent steady state charge distribution. For non-spherical particles, however, the diffusion charging rate remains unknown, leaving ambiguities in all electrostatic based analyses of non-spherical particles.

In this work we examine theoretically the diffusion charging of non-spherical particles (using ensembles of aggregated spheres as test particles) employing a combined approach of dimensional analysis and mean first passage time simulations. We show that although non-spherical particle diffusion charging is a complex process, the dimensionless diffusion charging rate for particles of any shape can nonetheless be expressed as a function of the diffusive Knudsen number, i.e. the ratio of the colliding ion persistence distance to a clearly defined descriptor of the particle size, and a ratio of the surface potential energy of the particle to the thermal energy of the background gas. Particle-shape independent dimensionless functions are found which describe the particle-ion collision rate, enabling calculation of the steady-state charge distribution on any particle, provided its geometry can be mathematically described and the background gas and ion properties are known. These calculations additionally link the non-spherical particle diffusion charging rate to calculations of vapor condensation onto non-spherical particles, non-spherical particle collision rates, and diffusion charging, condensation, and coagulation for spheres in the transition regime.

8AP.4

Tandem DMA Measurement of the Evaporation of Sub 5nm Metal Nanoparticles. CARLOS LARRIBA, Santiado Ruiz-Valdepeñas, Christopher Hogan Jr., *University of Minnesota*

The evaporation rate of small particles (< 5 nm) is theoretically expected to increase due to the Kelvin effect. If the particles are charged, conversely, with further decreasing size, the evaporation rate is expected to slow, as the predicted vapor pressure of charged clusters decreases to negligibly small values as the cluster size decreases (the Thomson effect). The Kelvin and Thomson effects are also the bases for classical nucleation theory (the Kelvin effect) as well as ion-induced nucleation theory (the Kelvin and Thomson effect combined), and are therefore of considerable importance. However, the actual validity of these theoretically derived effects for small particles remains in question. We use tandem differential mobility analysis (DMAs) to examine the evaporation of sub-5 nm diameter silver particles, produced with a hot wire generator. In these experiments, the evaporation of mobility classified silver particles is facilitated by a temperature controlled microfurnace. The DMAs employed, 1/2 mini DMAs, are of modest to high resolving power (~12-25) and are capable of mobility classifying singly charged particles up to 10 nm diameter down to the sizes of individual molecular ions. To our knowledge, this is the first time that such experiments have been performed for such small sized particles, with a combined experimental and theoretical effort to quantitatively monitor dissociation (evaporation) kinetics of ionized metal clusters.

8AP.5

Determining the Proton Affinity of Atmospheric Molecular Ions. KAI RUUSUVUORI, Theo Kurten, Ismael Kenneth Ortega Colomer, Hanna Vehkamäki, *University of Helsinki*

Understanding the birth and interaction mechanisms of atmospheric aerosols is essential if we are to understand e.g. climate change and the health effects of aerosols. While the role of ion-induced nucleation is not believed to be dominant in the atmosphere (Kulmala et al., 2007), understanding the role of charge in the first steps of nucleation is important.

Proton affinity describes the ability of a molecule to accept a proton and is an important thermodynamic quantity. However, absolute gas-phase proton affinities are hard to measure, which makes theoretical methods a valuable tool in determining these absolute values. Our aim is to study the absolute values of proton affinities using quantum chemical methods. These methods will be applied to several positively charged molecular ion species that have been observed by Ehn et al. (2010).

Based on benchmarking calculations using several different quantum chemical methods, the CBS-QB3 method was chosen for the proton affinity calculations. Calculations have been performed using Gaussian 09 and the obtained values have been compared to results listed in the National Institute of Standards and Technology (NIST) database when possible. Intermediate results show good agreement with NIST values.

8AP.6

Parameterization for Nanoparticle Growth. SILJA HÄKKINEN, Hanna Manninen, Joonas Merikanto, Maija Kajos, Tuomo Nieminen, Markku Kulmala, Ilona Riipinen, *University of Helsinki*

We present a simple parameterization for atmospheric nanoparticle growth using extensive field data acquired from several measurement stations around Europe. The parameterization includes particle condensational growth by sulfuric acid, secondary organics from monoterpene oxidation and additional unknown condensing species. To capture the size dependency of condensation particle growth in three size classes (1.5 to 3 nm, 3 to 7 nm and 7 to 20 nm) was determined. The performance of the proposed parameterization was investigated using particle growth rates calculated from long-term particle number size distribution measurements over Europe. The longest time series of 7 years (2003 to 2009) was acquired from a boreal forest site in Hyytiälä, Finland. The long-term measurements made it possible to test how well the parameterization captures the seasonal pattern of particle growth relevant for climate and air quality studies. The results from the model-measurement comparison were encouraging and suggest that the proposed parameterization of nanoparticle growth can be further used to describe the growth process of freshly nucleated particles in large-scale atmospheric models.

8AP.7

Measurement of Momentum Accommodation Function Using Free Nanoparticles. HAESUNG JUNG, Koohee Han, George Mulholland, Jung Kim, *University of Seoul*

To understand the movement of nanoparticles, many authors have studied the friction phenomena of nanoparticles at the free molecule regime. Generally, the Stokes-Cunningham expression has been used to predict the drag force of particles. After Millikan reported the slip correction coefficient obtained from his oil drop experiment, many researchers proposed different coefficient for the expression. With the experimental investigations, mathematical formulas for nanoparticle transport were also studied using the gas kinetic theory. Epstein considered gas-nanoparticle scattering to derive mathematical formula of drag force for particles combining the Diffuse and specular reflection for the free molecule regime. However, the discussion for the gas-nanoparticle scattering was not based on the experimental understanding of the slip phenomena. Recently, Zhigang Li and Hai Wang reported that increased gas-particle binding energy causes increased molecular absorption on particle surface. They argued that this absorption enhances the diffuse reflection, and results in the specular to diffuse transition. In this work, with the experimental study of the electrical mobility for PSL, SiO2, Au nanoparticles at low pressure conditions, we discuss that increased gas-nanoparticle interactions enhance the diffuse reflection ratio. The verification of specular to diffuse reflection transition is clearly seemed in our data. Especially, strong intermolecular potential of metal particle shows distinct discrepancy of diffuse reflection ratio to the PSL, and SiO2 particles. These results agree well with the numerical study of Zhigang Li and Hai Wang.

8AP.8

The Effects of Unresolved Scalar Fluctuations on the Formation of Particles from Vapor. NATHAN MURFIELD, Sean Garrick,*University of Minnesota*

The effects of the subgrid-scale (SGS) scalar interactions on nanoparticle nucleation are investigated via a priori analysis of direct numerical simulation data. The formation of dibutyl-phthalate (DBP) particles via homogeneous nucleation is simulated in a planar wake. Classical nucleation theory is used to model particle nucleation and the Navier-Stokes equations are coupled with the scalar transport equations to provide the fluid, thermal, and chemical fields. The data shows that particle nucleation is initially confined to the thin interfacial region or shear layers, where molecular diffusion is dominant. As the flow becomes turbulent nucleation increases significantly and the rate of particle formation increases by several orders of magnitude. To assess the effect of SGS scalar interactions on DBP particle nucleation, the temperature and mass-fractions are filtered and the resulting quantities are used to compute the nucleating particle field. Two filter widths are used to obtain varying levels of SGS interactions. Particle size distributions are computed to examine the particle fields produced. This work shows that the effects of SGS interactions are significant and have two distinct trends. In the proximal region of the wake, the unresolved interactions act to decrease particle formation. However, as the flow transitions or becomes turbulent the effect of the SGS interactions act to increase particle formation. Additionally, statistical analyses reveal that vapor dilution and cooling occurs where the SGS fluctuations increase.

8AP.9

The Effects of Leaf Area Density Variation on the Collection Efficiency of Ultrafine Particles (UFP). CHENG-WEI HUANG, Ming-Yeng Lin, Andrey Khlystov, Gabriel Katul, *Duke University*

The removal of ultrafine particles (UFP) by vegetated surfaces remains a subject of active research in many applications pertinent to climate, cloud physics, human health and respiratory related diseases. Vegetated surfaces are known to be a sink for UFP, prompting interest in the relationship between leaf area and UFP collection efficiency. A number of models have tackled the UFP collection efficiency by vegetation for an isolated leaf or uniformly distributed leaf area; however, up-scaling these theories to the ecosystem level must confront the problem of how spatial gradients in leaf area density impact the collection efficiency. This question is explored by setting up three scenarios in a wind tunnel: (1) Juniperus Chinensis branches that are uniformly distributed within the test section (uniform LAD); (2) LAD that is linearly increasing with downwind distance and (3) LAD that is decreasing with downwind distance. The total leaf area index (LAI) remains the same in all three cases. Particle concentrations were measured at multiple locations within the vegetated volume for a range of sizes of UFP (12.6-102 nm) using Scanning Mobility Particle Sizer. The measured concentration can be used to evaluate the performance of size-resolving model that couples the turbulent flow field and the collection efficiency for the variable LAD. The model assumes that (i) the mean longitudinal momentum balance is controlled by the interplay between drag force, the pressure gradient and the horizontal advection term, and (ii) the dominant collection mechanism is Brownian diffusion. Hence, other collection mechanisms such as inertial impaction, interception and phoretic effects are ignored. The agreement between the model calculations of the UFP collection efficiency by the vegetation and the wind tunnel measurements for all three cases is discussed for a wide range of wind speeds and particle diameters.

Keywords: Canopy turbulence, leaf area density, size-resolving model, wind tunnel experiments, ultrafine aerosol particles.

8AP.10

Modeling Cross-flow Aerosol Mixing under Moderate Reynolds Number. MATTHEW BROWN, Yi-wen Huang, Daniel Cziczo, Suresh Dhaniyala, *Clarkson University*

Aerosol experiments often require the conjoining or mixing of two flows – typically a particle-laden flow and a clean sheath flow or sometimes two particle laden flows. Examples of such flow systems include: the aerosol injection region in the DMA, where aerosol and sheath flows mix, aerosol sheathing flow, such as in optical instruments, or mixing of aerosol and clean flows in aerosol diluters. The interaction of such flows is often under conditions of moderate Reynolds numbers of less than 1000. While there is sufficient fundamental understanding of the behavior of flows at low Reynolds numbers and there is some experimental knowledge of turbulent behavior of aerosols under very high Reynolds number, our knowledge of flow mixing behavior at moderate Reynolds numbers and their implication for aerosol mixing is largely unknown. In the present study, experiments and computational modeling are used to determine the influence of flow mixing conditions, such as velocity ratios and bulk flow Reynolds numbers, on particle dispersion characteristics. Experiments are conducted with a bench-top setup to inject size-selected particles perpendicularly into a clean flow and the radial distribution of particles is determined from multi-angle concentration measurements downstream of the mixing region. Initial results suggest that, even under moderate Reynolds numbers, turbulent mixing of particles is possible when the velocities of the cross-flow streams are comparable. By matching computational particle transport modeling results with experimental data for identical operating conditions, particle size-dependent turbulent interaction parameters are determined. Details of the experiments and modeling approach used in the current study will be presented and implications for design of aerosol mixers and sheath flow devices will be described.

8AP.11

Effect of Sub Grid Scale Turbulence Fluctuations on Particle Deposition in Duct Flows. Behtash Tavakoli, GOODARZ AHMADI, *Clarkson University*

The rate of particle deposition in a vertical turbulent duct flow was investigated using the Large Eddy Simulation (LES) approach. In most earlier LES simulation the effects of the subgrid scale (SGS) turbulence fluctuations on particle dispersion and deposition are neglected. In this study, particular attention was given to the effect of sub-grid scale (SGS) velocity fluctuations on particle transport and deposition. Particles are tracked using the one way coupled Lagrangian approach. In order to consider the effects of SGS turbulence fluctuations on particle deposition, a Gaussian fluctuating random field model using the SGS root-mean square velocity fluctuation as velocity scale and local grid size as length scale was used. The instantaneous SGS velocities were generated, and added to the simulated large eddy velocity field.

The particles deposition rate in LES model was compared with the predictions of the Reynolds Stress Transport Model (RSTM). In the RSTM analysis, a Discretized Random Walk (DRW) model with the time scale of eddy life time was implemented to consider the effect of velocity fluctuations on particle dispersion and deposition. Comparison of the numerical simulations for particle deposition velocity with the experimental data showed that the inclusion of the SGS turbulence fluctuations led to more accurate predictions of particle deposition rates.

8AP.12

Effect of Fractal Dimension and Prefactor on Aggregate Heat Conduction in the Free-Molecular Regime. FENGSHAN LIU, Gregory Smallwood, *National Research Council Canada*

One of the importance processes during laser-induced incandescence of soot is heat conduction cooling shortly after the laser pulse. Soot in general appears as mass-like fractal structure in flames as a result of particle aggregation. There is a shielding effect in aggregate conduction cooling due to the partial blocking of some primary particles in the interior of the aggregate from collision with the surrounding molecules. There have been very few studies investigating the cooling rate of fractal aggregates and these studies were conducted for specific fractal dimensions and prefactors. Quantitative studies for the shielding effect over a range of fractal dimension and/or prefactor have not been reported in the literature.

In this study, direct simulation Monte Carlo (DSMC) calculations were carried out for several pairs of fractal dimension and prefactor to investigate how these fractal parameters affect the shielding effect. Fractal aggregates of different fractal dimension and prefactor were numerically generated using a combination of tunable particle-cluster and cluster-cluster aggregation algorithm.

DSMC calculations of aggregate heat conduction were conducted in the free-molecular regime. Results were presented as a correlation of the heat conduction equivalent sphere diameter.

8AP.13

Large Eddy Simulation of Compressible Gas-particle Two-phase Flows in a Square Duct. XINYU ZHANG, Lin Tian, *Mechanical Engineering, Univ. of Nottingham, Ningbo, China*

A three-dimensional large eddy simulation is performed on compressible gas-particle two-phase flows in a square duct. A 3D Cartesian-grid finite volume scheme and a code developed by Chernousov A. A. is used for the simulation of gas phase. The governing equations for gas phase are Favre filtered compressible Navier-Stokes equations without nonlinear terms. It is assumed that subgrid turbulence behavior is analogous to molecular dissipative mechanism. Particle motions are evaluated using a Lagrangian trajectory analysis procedure. The discrete phase equations used included drag, lift, buoyancy, and virtual mass forces. Particle-particle and particle-wall interactions are accounted for by the hard sphere model. The effects of particles on gas phase is neglected. The transient flow characteristics of the gas-particle two-phase flows are studied. The results show that the particle size plays an important role in compressible gas-particle two-phase flows.

8AP.14

Modeling Plume Dispersion of Diesel Truck Exhaust in a Wind Tunnel. JONATHAN STEFFENS, Max Zhang, *Cornell University, Ithaca, NY, USA*

The Comprehensive Turbulent Aerosol Dynamics and Gas Chemistry (CTAG) model has been used to model plume dispersion of a diesel truck. Experimental data was collected by researchers at the newly constructed five meter by five meter wind tunnel at West Virginia University. Two sets of instruments were positioned such that one remained stationary upwind of the truck and the other was mounted to a mobile platform to sample the plume at various downwind locations. The instruments measured wind speed, particle size distributions, temperature, CO2 and NOx. The CTAG model was applied to the scenario in order to validate its effectiveness in characterizing vehicle emissions plumes.

8AP.15

UV-Visible Absorption of Wood Smoke Particles with Photochemical Oxidation. MIN ZHONG, Myoseon Jang, *University of Florida*

Biomass burning is an important source of black carbon (BC) and organic carbon (OC) which affect the radiative balance of Earth by absorbing and scattering solar radiation. Photochemical oxidation produces significant amount of secondary organic aerosol, which might coat on the surface of preexisting wood smoke particles and change the light absorption properties of these particles. In addition, aging process also occurs in the primary organic aerosol. Thus, UV-visible absorption of wood smoke particles might dynamically change in the presence of sunlight. In this work, outdoor chamber (104m3) experiments will be conducted to investigate the dynamics of light absorption in wood smoke particles. The preliminary results show that light absorption of wood smoke particles increases as the reaction time increases, indicating the evolution of chemical species due to photochemical oxidation. The measured spectra are further decoupled into the spectrum of BC, primary OC and SOA. Since BC is stable under ambient conditions, the change of light absorption is mainly due to OC which account for more than 98% of the total mass of wood smoke particles. The light absorption of primary OC is stronger than that of SOA which appears in yellowish.

8AP.16

Linear Multiplexed Electrospray Atomizers Micro-machined from Metal and Polymers. BRANDON LOJEWSKI, Weiwei Yang, Weiwei Deng, *University of Central Florida*

Multiplexed electrospray is a promising aerosol generation technique to produce high throughput monodisperse droplets in the nanometer and micron size range. Here we report the design, fabrication, analysis and performance of a linear electrospray (LINES) system. The fabrication of the nozzle array is based on a precision CNC micromachining platform with 1-micron resolution. This rapid prototyping approach offers the flexibility of creating devices from a wide range of materials including metals and polymers with packing densities on par with silicon microfabrication at 20 sources/cm for LINES devices and 460 sources per square cm for the two-dimensional array. The LINES device uses a slot extractor design to simplify alignment and enhance operation robustness. We also used dummy nozzles to offset edge effect on electric filed and improve droplet size uniformity. We derived the approximate spray expansion model from first principles. We applied the line-of-charge approximation to establish scaling laws for prescribing operating conditions. The devices show excellent droplet size uniformity from source to source, with relative standard deviation (RSD) <3%.

8AP.17

Strictly Monodispersed Droplets Generated by External Electro-hydrodynamic Perturbations on Liquid Jets. HONGXU DUAN, Weiwei Yang, Johan Rodriguez, Jing Gu, Weiwei Deng, *University of Central Florida*

The ordered break-up of liquid jets is an effective way to produce highly monodispersed droplets. Here we report a new approach to apply periodic electro-hydrodynamic (EHD) perturbations on liquid jets of modest Webber numbers. Two perturbation modes are demonstrated: radial mode and axial mode. When the perturbation is near the 50% and 100% of the Rayleigh frequency, liquid jets experience highly ordered break-up which results in strictly monodispersed droplets with typical standard deviation of 0.01. We found that the electric stress gradient, instead of the magnitude of electric stress, near the jet surface must be sufficient to introduce the short wavelength perturbation. We extended the Rayleigh jet model and back calculated the magnitude of initial perturbation, which could be as small as a few nanometers. We termed the periodic perturbation source as “EHD chopper”. The design and implementation of EHD chopper is scalable for generating highly monodispersed droplets from multiple jets.

8AP.18

Three Dimensional Characteristics of Mineral Dust using Atomic Force Microscopy. XIN XIN WOODWARD, Ashima Chhabra, Will Cantrell, *Michigan Technological University*

Mineral dust in the atmosphere plays a role in Earth's climate through its ability to absorb and scatter radiation (both solar and terrestrial) and through its part in the hydrological cycle as cloud condensation and ice nuclei. The three dimensional characteristics of dust are particularly important for their part in Earth's radiative balance and, perhaps, for their role as ice nuclei. As examples, the optical properties of mineral clay aerosol are best fit by assuming that they are highly eccentric oblate spheroids (Meland et al., 2012) and the surface roughness of dust may determine their efficacy as ice nuclei (Hoose and Mohler, 2012).

Most sizing methods capture one or two dimensions for particles. In contrast to differential mobility analyzers, scanning electron microscopes and other devices, atomic force microscopes acquire information in three dimensions. We have investigated individual aerosol particles of both Arizona Test Dust and kaolinite and find that the asphericity is quite pronounced. The height of most particles is typically a factor of five to ten smaller than the average dimension in the projected area. We will present analysis of detailed, three dimensional images of both Arizona Test dust and kaolinite. In particular, we will show the asphericity for the dusts as well as discuss the surface roughness for each.

8AP.19

Estimates of Non-Ideal Effects on the Agglomerate Dynamics. WEONGYU SHIN, George Mulholland, Seong C Kim, Jing Wang, Jacob Scheckman, David Pui, *Chungnam National University*

Several characteristics of silver agglomerates are not incorporated in existing models for agglomerate dynamics. Existing models assume chain-like agglomerates with open structure. Silver agglomerates can be aligned in the electric field and have necking between primary particles. Primary particles on silver agglomerates are polydisperse and the primary sphere size are variable. Estimates of these features on the agglomerate dynamics were computed as perturbations to the Chan-Dahneke agglomerate model. The variable primary sphere size effect results in the largest change from the idealized model with about a 10% increase in scaling exponents for both friction coefficient – number of primary particles (η) and mass-mobility diameter (Dfm). The second largest change is a 4% decrease in the exponent η and a 4% increase in the exponent (Dfm) from the alignment in the electric field. The effects of necking between particles and polydispersity of the primary particles are negligible for the two exponents. Adjusting the model by this amount provides a significant improvement in the agreement between the model and silver agglomerate measurements for the dynamic shape factor.

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8AP.20

Mobility Behavior of Nanoparticle Fractal Agglomerates. WEONGYU SHIN, Jin Hyoung Kim, George Mulholland, David Pui,*Chungnam National University*

For diffusion limited cluster agglomerates the ratio of the mobility radius to the radius of gyration Rm/Rg vs. N and the ratio of the mobility radius to the radius of primary particle Rm/a are determined over a range of Knudsen numbers extending into the transition region where there is a lack of data. It was found that in the large N slip regime ($100 < N < 400$), datapoints are found to be between the two asymptotic lines for the continuum and free molecular regimes as those datapoints are plotted in both Rm/Rg vs. N and Rm/a vs. N.

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012-0004006).

8AP.21

Effect of In-Plume Aerosol Processing on the Efficacy of Marine Cloud Albedo Enhancement from Controlled Sea-Spray Injections. Stuart Geoff, ROBIN STEVENS, Dominick Spracklen, Hannele Korhonen, Jeffrey Pierce, *Dalhousie University*

The intentional enhancement of cloud albedo via controlled sea-spray injection from ships has been proposed as a possible method to control anthropogenic global warming (1); however, there remains significant uncertainty in the efficacy of this method due to uncertainties in aerosol and cloud microphysics. A major assumption used in multiple recent studies (2,3) is that all sea-spray was emitted uniformly into some oceanic grid boxes, and thus did not account for sub-grid aerosol microphysics within the sea-spray plumes. However, as a consequence of the fast sea-spray injection rates which are proposed, in the order of 10^{17} s^{-1} (1), particle concentrations in these plumes may be quite high and particle coagulation may significantly reduce the number of emitted particles and increase their average size. Therefore, it is possible that the emissions necessary to reach a desired cooling may be even larger than currently assumed.

We explore the evolution of these sea-salt plumes using a multi-shelled Gaussian plume model with size-resolved aerosol coagulation. We determine how the final number and size of particles depends on the emission rate and size distribution of the emitted sea-spray plume and local atmospheric conditions, including wind speed and boundary-layer stability. Under the injection rates reported in (1) and typical marine conditions, we find that the number of aerosol particles is reduced by about 40%. This fraction decreases for decreasing emission rates or increasing wind speeds due to lower particle concentrations in the plume. Finally, we make suggestions for effective size-resolved emissions for use in climate models.

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8AP.22

Differential Light Scattering by Dye Coated Silica Microspheres. Matthew Hart, PAUL LANE, Jay Eversole, *Naval Research Laboratory*

We report the use of elastic scattering spectroscopy for single, threat agent aerosol particle detection and discrimination. Dispersion of the refractive index results in light scattering that is dependent upon the wavelength of incident light, as well as the particle size and shape. A test bed was developed that consists of a quadrapole trap into which monodisperse silica microspheres are injected via electrospray ionization. The microspheres traverse coincident laser beams at two separate wavelengths, generating a differential scattering signal. The results of Mie scattering theory to experimental results are compared. Preliminary measurements showing the effect of an organic dye coating on differential scattering will also be presented.

8CA.1

The Effect of Model Spatial Resolution on Secondary Organic Aerosol Predictions. CHRIS WAINWRIGHT, Jeffrey Pierce, John Liggio, Kevin Strawbridge, Annie-Marie Macdonald, Richard Leaitch, *Dalhousie University*

Between 20-90% of submicron aerosol mass throughout the continental boundary layer consists of secondary organic aerosol (SOA) mass. As such, the ability of chemical transport models to accurately reproduce the continental boundary layer greatly depends on their ability to predict SOA. Although there has been much recent effort to better describe SOA formation mechanisms in models, little attention has been paid to the effects of model spatial resolution on SOA predictions. The Whistler Aerosol and Cloud Study (WACS 2010), held between June 22nd and July 28th, 2010 and conducted at Whistler, BC, Canada provides a unique data set for testing simulated SOA predictions. The study consisted of intensive measurements of trace particles and gases in the atmosphere in a mountain valley. We test the ability of the global chemical transport model GEOS-chem (www.geos-chem.org) to predict the aerosol concentrations during this event and throughout the campaign. Simulations were performed using three different resolutions of the model: 4ºx5º, 2ºx2.5º and 0.5ºx0.667º. Predictions of organic aerosol concentrations at Whistler was greatly dependent on the resolution; the 4ºx5º version of the model significantly under predicts organic aerosol, while the 2ºx2.5º and 0.5ºx0.667º versions are much more closely correlated with measurements. In addition, we performed a comparison across North America between the 3 versions of the model. 0.5ºx0.667º simulations predicted 19% more SOA than 2ºx2.5º (time anddomain averaged) and 32% more than 4ºx5º. This increase in SOA with resolution is largely due to sub-grid variability of OA that leads to an increase in the partitioning of organic matter to the aerosol phase at higher resolutions. Aerosol lifetime and biogenic emissions have smaller, but non-negligible, changes with resolution. These results suggest that a portion of the traditional under-prediction of SOA by models may be due to coarse grid resolution.

8CA.2

Short-Term Storm Responses of Soil CO2 Efflux and Hydrologic Organic Carbon Export in a Forested Watershed in the Haean Basin, South Korea. YITAYEW A. WORKINEH, Ji-hyug Park, *Kangwon National University*

Increasing rainfall variability and extremes as a consequence of climate change can affect carbon (C) storage in forest soils by altering rates of soil C losses via soil respiration and hydrologic carbon export. To investigate short-term dynamics and controlling mechanisms of soil C losses during rainfall events, we conducted high-frequency monitoring of soil CO2 efflux and streamwater export of dissolved (DOC) and particulate organic carbon (POC) in a forested watershed in the Haean Basin, South Korea. Highest increments in soil CO2 efflux relative to the rate expected from the temperature-respiration relationship occurred during spring rainfall events following the dry period. As soil moisture increased over the monsoon period, storm responses from the expected carbon flux values became weaker, particularly during small size events. Variations in soil moisture explained 33% of variations in CO2 efflux increases relative to the rate expected from the temperature-respiration relationship. DOC and POC export corresponded to storm intensity. 90% and 66% of the variations in DOC and POC exports during storm events were explained by stream discharge, respectively. The results suggest that while DOC and POC export are strongly regulated by storm-induced changes in discharge, storm responses of soil respiration are determined by complex factors including antecedent hydrologic conditions and the magnitude and intensity of storm events.

Keywords: Climate change, Dissolved organic carbon, Extreme events, Particulate organic carbon, Soil carbon, Soil respiration

8CA.3

Real-Time Measurements of Water-Insoluble Fractions and Black Carbon Concentrations With Water and Butanol Based Particle Counters. DANIEL SHORT, Michael Giordano, Yifang Zhu, Andrea Polidori, Akua Asa-Awuku, *University of California, Riverside*

Particle number and size information is important for anthropogenic combustion effects on air quality, climate, and health. The composition of particles from vehicular fuel combustion, may contain water insoluble black carbon (BC) and other insoluble material that modify particle nucleating properties. Conversely, the soluble fraction is important for particle water–uptake and wet deposition processes. Long Beach, California has heavy commercial traffic which includes the Port of Los Angeles as well as many freeways and railways.

For this study, ambient aerosol was sampled from the South Coast Air Quality Management District (SCAQMD) instrument station located 15 m from the I-710 freeway in Long Beach, California. A water-based condensation particle counter (CPC) and a butanol-based CPC provided particle number concentration data. Both instruments were coupled with a Scanning Mobility Particle Sizer (SMPS) and particle number and size were recorded. Our novel measurement and analysis technique exploits the differences in particle distributions from the CPCs to infer insoluble particle mass fractions from real-time emissions. The data is correlated with BC measurements obtained with a Multi-Angle Absorption Photometer (MAAP). The contribution of insoluble mass from insoluble BC is determined. These differences show that the presence of BC has a significant effect on the particle activation ability of water-based CPCs at diameters below 30nm. Real-time insoluble mass fractions are presented.

8CA.4

Carbon Enrichment in Windblown Sediment on the Columbia Plateau. BRENTON SHARRATT, Laurel Graves, Shelley Pressley,*USDA-ARS*

Sediment flux into the atmosphere from agricultural soils during high wind events can impact resource management and the environment. For example, nutrients in sediment represent a loss of fertilizer from soils that must be replenished for sustained crop production. In addition, sediments that are laden with nutrients and transported downwind can degrade air and water quality. Although flux of sediment has been quantified during high wind events in the Columbia Plateau, no information is available that characterizes nutrients in windblown sediment. Windblown sediment and soil samples were collected from agricultural fields in eastern Washington from 1999 to 2006. Sediment was collected using creep and Big Spring Number Eight (BSNE) samplers; the BSNE samplers were installed at various heights above eroding fields. Carbon content of the soil and collected sediment was determined using a LECO TruSpec analyzer. Enrichment, or a ratio of C in the windblown sediment to soil of greater than one, was observed in about half of the years. For nearly all high wind events, C content of sediment transported by creep was greater than sediment transported by saltation or suspension. This study suggests that wind erosion can result in loss of C from agricultural soils.

8CA.5

The Correlation of Organic Carbon and Total Protein Parts in Atmospheric Aerosol of Southwestern Siberia. ALEXANDR SAFATOV, Galina Buryak, Sergei Olkin, Irina Reznikova, Valerii Makarov, Svetlana Popova, *FBRI SRC VB Vector*

Literature data show that atmospheric aerosol always contains a certain amount of organic (OC) and elemental carbon (EC) as well as components of biological origin. The aim of this study was to analyze long-term data on ground level of OC and total protein (TP, universal marker of components of biological origin) in atmospheric aerosol in Southwestern Siberia.

Aerosol sampling was performed in the vicinity of Novosibirsk by pumping the air at the volumetric rate of 13 m3/h for a day through fiber filters of AFA-HA-20 type and glass fiber filters. Four series of observations for each season lasted for 30 days. The weight of deposited aerosol was determined by the gravimetric method. The concentrations of OC and EC were determined by the thermal method. The masses of total protein in the samples were determined using a fluorescent dye.

The analysis of results demonstrates that average annual concentration of aerosol tends to increase with a slight reduction during recent years of observations. The average annual concentration of OC in the atmosphere also tends to increase, whereas the average annual concentration of TP remains nearly constant. At the same time, the portion of OC in the total aerosol particles mass also tends to increase during the observation period, while the portion of TP remains practically constant. The seasonal changes in OC, TP, and TC concentrations were revealed also.

8CA.6

Tunable Laboratory Generated Aerosols: Linking Experimental Data to Field Measurements and Theory. CHRISTOPHER ZANGMEISTER, Xiaofei Ma, Michael Zachariah, *National Institute of Standards and Technology*

This study focuses on the use of aerosolized graphene oxide (GO) generated from aqueous solution as a model for atmospheric brown and black carbon. We demonstrate that we can control the size, shape, composition, and the absorption and extinction cross-sections of GO. We can tune the shape of GO aerosol from crumpled sheets to nanoscopic spheres using various solution conditions. By thermally processing GO it is reduced to a graphene like material that mimics many of the properties of soot. Optical measurements were made using cavity ring down and photo acoustic spectroscopies, and when coupled to an atmospheric particle mass analyzer we show that GO and reduced GO aerosol are suitable surrogates for absorbing carbonaceous aerosol in the terrestrial atmosphere.

8CA.7

Contribution of Biomass Burning and Traffic Emissions to Aerosol Optical Properties at a Rural Site in Southeast England During the Winter ClearfLo IOP. Paola Massoli, Allison Aiken, Kyle Gorkowski, Scott Herndon, Edward Fortner, John Jayne, William Brooks, Puneet Chhabra, Leah Williams, Nga Lee Ng, Timothy Onasch, Jonathan Franklin, Mavendra Dubey, Douglas Worsnop, ANDREW FREEDMAN, *Aerodyne Research, Inc.*

We present results on the optical characterization of aerosols during the ClearfLo (Clean Air for London) Intensive Operating Period that took place from mid-January to mid-February, 2012 at a rural site southeast of London, England. The site, situated at the Kent Showground in Detling, is located approximately 50 km southeast of central London. Data were collected from two separate inlets that were outfitted with 2.5 micron cutoff impactors. The first inlet was routed to a CAPS PMex (Aerodyne Research, ARI) particle optical extinction monitor and a Multi-Angle Absorption Photometer (MAAP) (ThermoFisher), both operated a nominal wavelength of 630 nm. The second inlet was routed to a CAPS PMex monitor operated at 450 nm and a Photo-Acoustic Soot Spectrometer (PASS-3) (Droplet Measurement Technologies) which provided particle absorption at three wavelengths (780 nm, 532 nm and 405 nm). The second inlet also contained a provision for alternately routing the air sample flow through a ARI particle denuder operated at temperatures up to 250 ºC. Optical extinction, absorption and the single scattering albedo (SSA) were measured at several wavelengths over a period of approximately three weeks. Over the course of the campaign, the sampled air masses were of local (traffic emissions, biomass burning), regional (Thames Estuary) or distant (continental European) origin. This works reports on the contribution of the various types of air masses to the measured aerosol optical properties.

8CA.8

Fuel Based Fine Particulate and Black Carbon Emission Factors from Atlanta railyards. BORIS GALVIS, Michael Bergin, Armistead Russell, *Georgia Institute of Technology*

Railyards have the potential to influence local fine particulate matter ($PM_{2.5}$) concentrations through emissions by diesel locomotives and diesel truck activity. This is of concern in urban areas, where railyards are in close proximity human populations. This is particularly true of Atlanta, where the Inman and Tilford railyards are located near both K-12 schools and residential neighborhoods. It is worthwhile to point out that the concentration of $PM_{2.5}$ near the railyards measured by the Georgia Environmental Protection Division (EPD) has the highest annual average reported at any of the state run monitoring sites, suggesting that railyard associated emissions play an important role in local air quality. In order to determine the impact of railyard emissions on fine particulate matter concentrations we estimate the fuel based black carbon (BC) and $PM_{2.5}$ emission factors for the Inman and Tilford railyards northwest of Atlanta, Georgia. This was done by making continuous measurements of BC, $PM_{2.5}$, CO_2, wind speed and direction at two locations on either side of the railyards. The emissions factors (i.e. the mass of BC or $PM_{2.5}$ per gallon of fuel burned) are estimated by both using an upwind/downwind method as well as an event-based approach. Based on our estimates, the railyards emit approximately 2.6 g of BC and 5.5 g of $PM_{2.5}$ per gallon of diesel fuel burned. We also found that the railyards are responsible for approximately 1.7 micro-grams/m^3 of $PM_{2.5}$ and approximately 0.7 micro-grams/m^3 of BC at the study sites. Overall, the results indicate that the railyards have a significant impact on local air quality, and furthermore this new data set provides useful information to policy makers on the emission factors from an urban railyard.

8CA.9

Modeling of Regional Age Distribution of Black Carbon. HONGLIANG ZHANG, Qi Ying, Michael Kleeman, *Texas A&M University*

Black carbon (BC) containing particles in the atmosphere, emitted from incomplete combustion of fuels, coal and biomass, have significantly affect air quality and climate because of their ability to absorb/reflect solar radiation and to affect cloud formation. To evaluate the impacts of BC on regional and global scales it is necessary to have accurate descriptions of the mixing status of BC particles and their spatial and temporal evolutions.

In this study, the source-oriented externally mixed 3D CIT/UCD model is enhanced to represent the age distribution of particles so that it is not only possible to determine the temporal and spatial variations of the particles and their source-origins but also their "aging" status (chemical compositions, optical properties). The source and age resolved 3D CIT/UCD model is applied to study the age distribution of BC in Southeast Texas. The model correctly predicts the overall concentrations of BC when compared to a base case simulation without age-resolved particle representation. Age-resolved simulation suggests that BC emitted within 0-3 hours contribute approximately 70-90% in urban Houston and about 20-40% in rural areas. Significant diurnal variations in the relative contributions to BC are predicted by the model. Highest contributions of fresh particles occur at morning and early evening traffic hours due to increased emission and lower mixing. The high level of fresh BC in the Southeast Texas area means that they could have a strong regional impact on aerosol optical and hygroscopic properties, and thus affect cloud formation and radiation balance.

8CA.10

The Correlation between Positive Sampling Artifacts and Organic Aerosol Volatility. ANDREW A. MAY, Albert A. Presto, Allen Robinson, *Carnegie Mellon University*

Collecting organic aerosol on bare quartz filters can often lead to a positive sampling artifact -- organic vapors that adsorb onto the filter. This is particularly true in source tests, which often have high concentrations of low-volatility organic vapors. These adsorbed organic vapors result in over-estimated particulate organic carbon on the quartz filter. The adsorbed vapors can be partially accounted for by collecting samples on quartz-behind-Teflon (QBT) filters in parallel to the bare quartz filters and calculating the difference (Q-QBT). Recent work has indicated that the relative amount of the positive sampling artifact associated with source testing of light-duty gasoline-powered vehicles is related to gas-particle partitioning.[1] Furthermore, recent work has indicated that the quantity of sampling artifact is not constant across a volatility distribution. This work compares the volatility distribution inferred using thermal desorption-gas chromatography-mass spectrometry[2] on bare quartz filters and QBT filters for light-duty gasoline-powered vehicles, a gas-turbine engine, and ambient samples collected during the Pittsburgh Air Quality Study. The results indicate that the sampling artifact is closely related to the volatility distribution of the organic aerosol for source testing; it is hypothesized that this relationship will also be observed for ambient sampling. The implications of this study are that accurate positive sampling artifact corrections require knowledge of the volatility distribution of both the sample collected on the bare quartz filter as well as the QBT filter.

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8CA.11

Interpreting Thermal Denuder Data with an Optimizing Comprehensive Instrument Model. JAMES HITE, Kate Cerully, Athanasios Nenes, *Georgia Institute of Technology*

In this study, we develop a method of determining the volatility distribution of an aerosol sample through the use of a fully characterized thermal denuder (TD) instrument model. The first model component resolves the temperature and parabolic laminar flow field of the TD while the second resolves the mass transfer associated with aerosol evaporation inside the instrument. This is advantageous as the model can in effect be applied to TDs of varying geometry, requiring only a few direct measurements of the centerline temperature profile at certain temperatures which are then scaled to any desired temperature setting. The evaporation module (mass transfer component) simulates the evolution of aerosol with a given condensed-phase volatility distribution in the TD using a volatility basis set (VBS) approach as described in (Donahue et. al. 2006).

A volatility tandem differential mobility analyzer (VTDMA) setup is used to gather data which are then interpreted by the modeling framework. Measured particle number concentration and size (organic aerosol mass concentration, C_{OA}) before the TD inlet are used to determine aerosol partitioning into the VBS which then, along with the flow characteristics, drives the mass transfer in the model. An iterative optimization routine coupled with the TD instrument model is utilized to determine the bulk volatility distribution of a given aerosol sample by minimizing a cost function with number of terms proportional to the number of observations. The TD model is tested against data collected for laboratory-generated aerosol composed of single compounds and mixtures thereof. In benchmarking the model, properties of each species derived from model analysis of TD experiments are compared against literature values (e.g., saturation concentrations and density). The retrieval of the volatility distribution of mixtures generated in the lab is thoroughly assessed for consistency with the single-compound experiments and the published literature.

8CA.12

Comprehensive Characterization of Particulate Matter Using Sequential Thermal Extraction/Pyrolysis with On-line Gas Chromatography/Mass Spectrometry. Josef Beranek, Allison Coffman, Evguenii Kozliak, ALENA KUBATOVA, *University of North Dakota*

High-molecular weight (HMW) species may represent a significant portion of unidentified total organic matter in air particulate matter (PM). In order to recognize and characterize HMW species in PM and to determine its contribution to total organic carbon (OC), we developed and optimized a novel analytical method. The method is based on a stepwise (with 100 degreeC increments) thermal extraction (TE) performed up to 300 degreeC followed by stepwise pyrolysis (Py) at 400–800 degreeC with on-line gas chromatography/mass spectrometry (GC/MS). To prevent ambiguities in the assignment of evolving low molecular weight (LMW) compounds to pyrolyzed HMW species, it was important to remove (i.e., vaporize) all volatile LMW compounds using a combination of solvent extraction and TE (at 200 and 300 degreeC) prior to the pyrolysis. In addition, the complete vaporization of LMW OM was hindered by the analyte-matrix interactions in bulk wood smoke and urban PM when the procedure was conducted without the prior solvent extraction.

The developed method yielded specific thermal signatures/patterns of eluting organic species for two PM samples of different origin. The HMW constituents identified in pyrolyzed fractions (400–800 degreeC) were attributed to 1) pyrolysis products of unburned lignin residues in wood smoke PM, and to 2) biopolymers and large non-volatile hydrocarbons in urban PM. A significant contribution of HMW species was also observed in the aqueous extracts of wood smoke PM.

Apart from the ability to characterize HMW species in PM, sequential TE/Py-GC/MS has potential to improve the understanding of traditional thermal optical analysis for organic and elemental carbon by enabling a direct MS detection of thermally evolved species.

8CA.13

The Spatial and Temporal Variability in Bioaerosol Community Struture in Urban and Rural Colorado. Robert Bowers, NICHOLAS CLEMENTS, Allison Moore, Michael Hannigan, Christine Wiedinmyer, Noah Fierer, *University of Colorado at Boulder*

The Colorado Coarse Rural-Urban Sources and Health (CCRUSH) study is investigating the health impacts of $PM_{10-2.5}$ in arid rural and urban environments. To compliment the health study, one year of sixth-day 24-hour filter samples were collected with a dichotomous ($PM_{2.5}$ and $PM_{10-2.5}$) medium-flow sampler at four locations in Colorado. Two sites are located in urban Denver, CO and are characterized as industrial-residential and urban-residential. One site, Alsup Elementary, is near the intersection of 4 major roadways and adjacent to a gravel pit operations. The other two sites are located 50 km northeast of Denver in Greeley, CO, a rural city near major agricultural operations, including animal feeding operations. Greeley sites are classified as rural-residential. Quartz samples were analyzed for microbial community composition using a high-throughput bacteria specific barcoded illumina sequencing procedure, and a multi-domain (bacteria, fungi and other microbial eukaryotes) barcoded pyrosequencing procedure. With such a massive microbial community dataset measured in parallel with particulate speciation and meteorological variables, we can begin to unravel the physical parameters that structure the airborne microbial communities, which will ultimately increase our understanding of the potential health risks, and quite possibly, the health benefits that the airborne microbial community may provide. Airborne communities are also compared to known communities of potential sources, such as leaves and soil.

8CA.14

Volatility of Ambient Organic Aerosol at an Urban and a Remote Site in Europe. ANDREA PACIGA, Lea Hildebrandt Ruiz, Gabriella Engelhart, Evangelia Kostenidou, Monica Crippa, Andre Prévôt, Urs Baltensperger, Spyros Pandis, *Carnegie Mellon University*

The composition and volatility of ambient organic aerosol were measured in a major urban (Paris, France) and a remote area (Finokalia, Greece) during five month-long campaigns. The measurements were performed combining CMU's variable residence-time thermodenuder, the Aerodyne Aerosol Mass Spectrometer and a Scanning Mobility Mass Spectrometer.

The OA measurements in Paris were part of the MEGAPOLI campaigns and were collected in the summer of 2009 and winter of 2010, providing contrasting meteorological conditions. During the summer the OA concentrations were relatively low, with mostly aged OA that was transported to the site from other areas. Half of the OA evaporated at 90 degrees Celsius and 90 percent at 190 Celsius at a centerline residence time of 25 seconds. During the winter the OA levels were higher with local sources becoming more important. The OA volatility was higher than in the summer with half of the OA evaporating at 80 degrees Celsius.

The most recent FAME campaign took place in October 2011 in a remote site on the island of Crete, Greece. This dataset is added to the collection of studies at Finokalia performed during the summer of 2008 and winter of 2009. This particular site is far from local emission sources, allowing the aerosol to reach a highly aged, oxygenated state. During periods with intense sunlight the aged OA has quite low volatility (requiring a temperature of 120 degrees Celsius to evaporate half of its mass at a centerline residence time of 15 seconds). During periods with lower photochemical activity the OA volatility increased with half the OA evaporating at 100 degrees Celsius.

A dynamic mass transfer model is used to estimate the OA volatility distribution for the different areas and seasons, evaluating changes in O:C of the OA, photochemical conditions, and OA sources (using positive matrix factorization).

8CA.15

Effect of Ammonia on the Volatility of Dicarboxylic Acids. ANDREA PACIGA, Ilona Riipinen, Spyros Pandis, *Carnegie Mellon University*

Dicarboxylic acids are major components of ambient organic aerosol in most areas throughout the year. Often the concentrations, of especially the smaller ones in the particulate phase, are a lot higher than what their vapor pressure and the corresponding gas-to-particle equilibrium partitioning would allow. One possible explanation for this preference of the dicarboxylic acids for the particulate phase is the reaction with ammonia and the formation of the corresponding salts. We use using a tandem differential mobility analyzer – thermodenuder system to measure the volatility of a small (ammonium oxalate) and a medium size (ammonium adipate) salt. The evaporation of these dicarboxylates is studied for several particle sizes and two heating residence times. The particles do not reach equilibrium in the thermodenuder and therefore a dynamic mass transfer model is used for the interpretation of the results and the estimation of the saturation vapor pressure and enthalpy of vaporization of the dicarboxylates.

The solid state saturation vapor pressure of ammonium oxalate is estimated to be more than five orders of magnitude lower than that of oxalic acid. Ammonium adipate, however, did not show an appreciable difference in saturation vapor pressure or enthalpy of vaporization when compared to adipic acid. These results suggest that the dominating presence of oxalate in the particulate phase is at least partially due to its ability to form strong-low volatility salts with ammonia in the atmosphere.

8CA.16

Molecular Characterization of Cloud Water Using Ultrahigh-Resolution FT-ICR Mass Spectrometry. YUNZHU ZHAO, Parichehr Saranjampour, Anna Gannet Hallar, Lynn Mazzoleni, *Michigan Technological University*

Clouds act as a medium for interactions between gaseous and particulate phase substances altering the composition of atmospheric organic matter (AOM). To investigate this further, samples of supercooled clouds were collected at Storm Peak Laboratory in Colorado (3220 m asl). Approximately, 5000 molecular formulas were assigned to AOM isolated using a reverse phase extraction procedure and analyzed by electrospray ionization ultrahigh-resolution FT-ICR mass spectrometry ($100 < m/z < 700$). The components have a wide range of double bond equivalents (DBE = number of rings and double bonds), ranging from 0 to 19, an average oxygen-to-carbon ratio (O/C) of 0.58 ± 0.09, and an average hydrogen-to-carbon ratio (H/C) of 1.5 ± 0.24. The values indicate that the compounds range from aliphatic to aromatic, however a majority of them are aliphatic. The compounds assigned with only carbon, hydrogen and oxygen from cloud water AOM were compared to assigned formulas from other studies [1-3]. The comparison of aerosol water soluble organic carbon (WSOC) indicated 34-66% of the WSOC components were in common with the cloud water AOM. However, a large number of unique compounds in cloud water AOM were also observed. The unique compounds have aliphatic and highly oxidized elemental ratios ($H/C \geq 1.5$ and $O/C \geq 1$). The comparison of cloud water AOM and rainwater AOM [4] showed higher similarity with respect to the ranges of the observed elemental ratios but differ substantially with respect to the number of assigned molecular formulas. Compounds with high O/C ratios were observed in both cloud water and rainwater samples, but were not observed in the aerosol samples, indicating the importance of aqueous phase reactions in forming more highly oxidized AOM compounds.

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[2]Schmitt-Kopplin et al., AnalChem, Vol. 82, 2010.
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[4]Altieri et al., AtmosChemPhys, Vol. 9, 2009.

8CA.17

Advanced Molecular Speciation of Aircraft Engine Soot by Nano Desorption Electrospray Ionization Mass Spectrometry.JEREMY CAIN, Alexander Laskin, Julia Laskin, Edwin Corporan, David Blunck, William Roquemore, *Air Force Research Laboratory/Propulsion Directorate*

Aircraft are the major source of black carbon in the upper troposphere and lower stratosphere. Aircraft particulate matter (PM) may impact the atmospheric environment through alteration of cloud forming processes and heterogeneous kinetics. As alternative fuels are explored to supplement the current fuel feedstock, it is important to assess the environmental impact of PM emissions relevant to these fuels. Soot particles from an Allison T63-A-700 turboshaft engine were deposited on aluminum foil inside an inertial cascade impactor and subsequently analyzed by nano-desorption electrospray ionization mass spectrometry (nano-DESI MS). The engine was operated at three power settings: low-speed idle, intermediate and cruise. Six fuels were tested: a JP-8, Fischer-Tropsch (F-T) and four alternative fuel surrogates (n-dodecane blends). Micro-FTIR spectroscopy results in a parallel investigation showed that aliphatic C-H and C-O groups are present in significant quantities. Advanced molecular speciation of those functionalities is performed here in both positive and negative modes for two solvents (acetonitrile and acetonitrile/toluene) over a mass range m/z = 150-900. Comparisons for this data set are made among particle size, fuel type and solvent. Additional comparisons are made for soot produced with a flat flame burner combusting a simple gaseous fuel (C_2H_4).

8CA.18

Simulating Black Carbon Mixing State in the Planetary Boundary Layer with a Particle-Resolving Single-Column Model.JEFFREY H. CURTIS, Nicole Riemer, Matthew West, *University of Illinois at Urbana-Champaign*

The chemical reactivity, cloud condensation nuclei activity, radiative properties and health impacts of black-carbon-containing particles depend crucially on the aerosol mixing state. The recently developed particle-resolving aerosol box model PartMC-MOSAIC has allowed unique insight into the evolution of aerosol mixing state as it tracks per-particle evolution for an aerosol population undergoing coagulation, condensation, dilution and emission in a Lagrangian air parcel. However, so far, spatial resolution was lacking.

Here we present a new model, PartMC-1D, which couples the aerosol box model PartMC-MOSAIC with the single-column version of the Weather Research and Forecast (WRF) model. The resulting spatially resolved model predicts the per-particle size and composition as well as transport processes driven by local meteorology to provide detail on the evolution of the aerosol mixing state as the planetary boundary layer develops during the day.

In this presentation we first explain the newly developed, particle-based stochastic algorithm for turbulent diffusion, and show results of code verification. We then present spatially- and particle-resolved simulation results of black carbon aging in a polluted boundary layer. These results indicate that while the bulk concentration of black carbon is well-mixed in the boundary layer during the day, there is a strong dependence of black carbon mixing state on height with fresh black carbon particles existing in only the lowest layers. Based on these results we quantify the implications for cloud condensation nucleation activity and optical properties of black-carbon-containing particles.

8CA.19

Light Absorption Properties of Brown Carbon from Fresh and Photo-chemically Aged Biomass Burning Emissions. RAWAD SALEH, Christopher Hennigan, Gavin McMeeking, Wayne Chuang, Hugh Coe, Neil Donahue, Allen Robinson, *Carnegie Mellon University*

To date, climate forcing calculations treat black carbon (BC) and dust as the only particulate light absorbers. Recent studies have shown that some organic aerosols, referred to as brown carbon (BrC), also absorb light. BrC has been identified in biomass burning emissions, however, its light absorption properties are poorly quantified. We determined imaginary refractive indices (absorptivity) of organics in fresh and photo-chemically aged biomass burning emissions from both household wood burning (oak) and fuels commonly consumed in wildland and prescribed fires in the US (pocosin pine and gallberry). A core (BC) – shell (organic) light absorption model based on Mie theory was used to determine the imaginary refractive index of the organic shell that best fits absorption coefficients measured using an aethalometer. The organic carbon in both primary emissions and aged (secondary) aerosol was brown, with absorption efficiencies comparable to BC at short visible wavelengths. This is the first direct demonstration that secondary organic aerosol produced by photo-oxidation of biomass burning emissions is brown. The values of imaginary refractive indices at 550 nm and their wavelength dependence were: 0.45 and lambda$^{-2.2}$ for primary oak, 0.3 and lambda$^{-1.55}$ for secondary oak, 0.1 and lambda$^{-3.5}$ for primary pocosin pine, 0.06 and lambda$^{\wedge}$(-2.9) for secondary pocosin pine, and 0.04 and lambda$^{-2.7}$ for primary gallberry. The common current assumption that biomass burning emissions consist of BC cores and non-absorbing (instead of brown) organic coatings may result in a considerable underestimation of their climate forcing.

8CA.20

Oxidation of C60 Aerosol by Ozone. ANDREA TIWARI, Alec Wagner, John Morris, Linsey Marr, *Virginia Tech*

Manufactured carbonaceous nanoparticles, such as C_{60} fullerenes, will enter the atmosphere during production, use, and disposal. There, they will be subject to physical and chemical transformations which could modify their properties and ultimately their fate, transport, and toxicity within the environment. The objective of this research is to determine the products and rates of reaction of aerosolized C_{60} with atmospherically relevant concentrations of ozone. Batch reactions were carried out in a 6-m^3 Teflon chamber at ozone mixing ratios of 45 – 120 ppb. C_{60} aerosols were introduced into the chamber through dispersion of powdered C_{60}.The resulting concentration was 9.3 +/- 2.6 x 10^4 particles cm^{-3}, and the size distribution peaked around 100 nm. Following exposure to ozone, aerosols were collected onto filters, gold slides, and copper grids for analysis by high performance liquid chromatography (HPLC), reflection absorption infrared spectroscopy (RAIRS), and transmission electron microscopy (TEM). Results indicate that the reaction proceeded within minutes and appeared to be complete in less than 1 h. It did not depend on initial ozone mixing ratio. After 1 h, the C_{60} aerosols took up 11 +/- 3 ppb of ozone, and C_{60} concentrations decreased by 10-20%. Reaction products included the primary ozonide ($C_{60}O_3$), a C_{60} epoxide ($C_{60}O$), as well as higher oxides and may also have included an oxygen-linked C_{60} polymer. The majority of the aerosols remained soluble in toluene, but this fraction decreased with exposure time. The reaction products were not appreciably soluble in water. These results suggest that at atmospherically relevant ozone levels, C_{60} is rapidly oxidized and that this process may affect its fate and transport in the environment. Other carbonaceous nanomaterials such as carbon nanotubes may be subject to similar transformations.

8CA.21

Black Carbon Trends over Several Decades at Multiple Locations. CHELSEA PREBLE, Odelle Hadley, Liang Liu, Tami Bond, Thomas Kirchstetter, *University of California, Berkeley*

Archived air quality data in the U.S. and Europe can be used to reconstruct past trends in black carbon (BC), an indicator of fossil fuel combustion and biomass burning. Here, we consider coefficient of haze (COH) data that was extensively measured in California, New Jersey, and other North American locations from the mid-1960s to the turn of the century. We reinstated COH monitors alongside aethalometers in Vallejo and San Jose, California, and after two years of air monitoring determined that COH is proportional to and, thus, can be used to infer past concentrations of BC. Analyzing COH data sets, we found that BC concentrations markedly decreased from 1965 to 2000 in both California and New Jersey. The opposing trend of increasing energy consumption over the same period indicates successful regulatory control of sources and a shift from dirtier to cleaner fuels. As air quality improved over four decades, a seasonal trend of maximum BC concentrations in winter persisted in California but, somewhat surprisingly, disappeared in New Jersey. A strong weekly cycle of lowest BC concentrations on weekends was evident in California and New Jersey, suggesting that diesel traffic, which exhibits a similar weekly cycle, has been a major source of BC in both states. Our extended analysis will include BC trends in other regions of North America and Europe and will be applied to understand BC radiative forcing in California and deposition of pollutants in the Arctic.

8CA.22

Regional Multi-generation Secondary Organic Aerosol Production from Major Anthropogenic and Biogenic Precursors.JINGYI LI, Qi Ying, *Texas A&M University*

Primary emitted volatile organic compounds (VOCs) produce semi-volatile organic compounds through a multi-generation oxidation process where intermediate reaction products further react with oxidants to generate a newer generation of VOC products with different volatility than the parent species. However, this multi-stage oxidation process is neglected by most regional aerosol models using a lumped gas phase chemical mechanism that only loosely coupled with the secondary organic aerosol modules. In this study, the most recent version of the Master Chemical Mechanism (MCM, version 3.2) is implemented in the CMAQ model to predict the multi-generation production of semi-volatile organic compounds. The amount of secondary organic aerosol (SOA) produced from these products is calculated using an online equilibrium partitioning SOA model. The CMAQ-MCM-SOA model is applied to a two-week air quality episode in southeast Texas in August and September 2006. Regional distributions of SOA as a function of generation and precursor are calculated and compared with results using a volatility basis set (VBS) approach to test the parameters used in the VBS.

8CA.23

The Dual-Spot Aethalometer: Application of Real-Time Source Apportionment Algorithm for Black Carbon and Carbonaceous Aerosols. LUKA DRINOVEC, Grisa Mocnik, Peter Zotter, Andre Prévôt, Christian Ruckstuhl, Anthony D.A. Hansen,*Aerosol d.o.o., Slovenia*

Filter-based measurements of aerosol optical absorption are widely used to determine Black Carbon (BC) concentrations in real time. Measurements at multiple wavelengths make the separation of contributions of BC from different combustion sources possible. These methods can suffer from non-linearity due to 'loading' effects of increasing aerosol deposit on the filter (Gundel 1984, Weingartner 2003, Arnott 2005, Virkkula 2007). Static algorithms to compensate for the effect, either by post-processing of the data or fixed in the instrument firmware, fail to capture the details and potential variability of these aerosol optical properties, and thus impact source apportionment using the data.

We have developed a new Aethalometer® AE33, in which two parallel sampling channels are operated at different loading rates. Combining the data from the two parallel analyses allows the measurement of BC with no loading effects, and yields a dynamical value of the non-linearity parameter. These analyses are performed for multiple optical wavelengths spanning the range from 370 nm to 950 nm and with a time resolution as rapid as 1 second. The results show greatly improved analytical performance for measurement of BC. The instrument is network-ready and is designed for both research and routine monitoring operations.

We present the use of this new instrument in urban and rural measurement campaigns in Switzerland, Austria and Slovenia showing absence of loading artefacts, and an application allowing on-line source apportionment similar to Sandradewi 2008.

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8CA.25

Secondary Organic Aerosol Formation from Dilute Small Off-Road Engine Emissions. DANIEL S. TKACIK, Albert A. Presto, Allen Robinson, *Carnegie Mellon University*

Internal combustion engines are a major source of particulate matter (PM) in urban areas. A complex mixture of organics contributes 20 – 90% of fine PM mass. Organic PM results from emission of primary organic aerosol (POA) and formation of secondary organic aerosol (SOA). Small off-road engines (SOREs) are one class of sources that have been subject to much less regulation and therefore are much more polluting than on-road sources. For example, nearly 11% of total US hydrocarbon emissions come from handheld two-stroke engines (EPA 2005), even though these engines account for very little in terms of national fuel consumption.

In this study, we investigate SOA formation from dilute two-stroke and four-stroke SORE emissions via photo-oxidation under a range VOC:NOx ratios. Particle number and volume concentrations are measured using a scanning mobility particle sizer (SMPS) and particle composition is measured using an Aerodyne high-resolution aerosol mass spectrometer (HR-AMS). Gas-phase measurements are made using an online gas-chromatograph with a mass selective detector (GC-MS). SOA/POA ratios from both types of emissions range from 0.11 to 22. POA and SOA mass spectra are separated using positive matrix factorization (PMF). SOA resulting from the photo-oxidation of two-stroke SOA SORE exhaust is found to be more oxidized than SOA from four-stroke exhaust. SOA production from dilute two-stroke SORE emissions, which is calculated on a fuel-consumption basis, is found to be orders of magnitude larger than most on-road sources. This suggests that SOREs, especially two-stroke engines, may be a significant source of SOA.

8CA.26

Volatility and Activity Coefficients of Levoglucosan in Artificial and Quasi-Ambient Organic Aerosols. ANDREY KHLYSTOV, Suqi Huang, Ming-Yeng Lin, *Research Triangle Institute*

Source apportionment models use tracer compounds to determine contribution of different sources to aerosol concentration measured at a receptor site. In order to be a reliable tracer, the compound needs to be specific for a certain source category and be conserved in the atmosphere, i.e. should not change significantly by reactions or volatilization during transport from the source. In this study, volatility of a wood smoke tracer, levoglucosan, was investigated both in pure form and in mixtures with monocarboxylic acids and aqueous extracts of ambient aerosol. Basic thermodynamic properties of levoglucosan and its activity coefficients in the mixtures will be presented. It will be sown that levoglucosan is a semivolatile compound which volatility depends on the polarity of the mixture.

8CA.27

Black Carbon Hygroscopicity at a Rural Site in the UK. JAMES ALLAN, Dantong Liu, Michael Flynn, Dominique Young, James Whitehead, Gordon McFiggans, Hugh Coe, Zoe Fleming, *University of Manchester*

Black Carbon (BC) is recognised as a highly potent climate forcing agent, particularly on regional scales, however the exact magnitude of its forcing potential is highly uncertain, partly due to uncertainties in its atmospheric lifetime. It is therefore important to understand the atmospheric processes and timescales by which hydrophobic BC particles obtain hygroscopic coatings, which makes them more susceptible to scavenging and in turn, wet deposition. In order to study these processes, an intensive campaign was carried out at the Weybourne Atmospheric Observatory, a coastal, rural site in the UK during the summer of 2011. During this period, the site was influenced by a variety of polluted airmasses of different ages from the UK and mainland Europe.

As part of a suite of measurements, a hygroscopicity tandem differential mobility analyser (HTDMA) coupled with a single particle soot photometer (SP2) was used to study the growth factors of particles while quantifying their BC content and compared to composition data measured using a Soot Particle Aerosol Mass Spectrometer (SP-AMS). The growth spectra of BC-containing particles at 90% RH showed an expected non-hygroscopic mode corresponding to unmodified soot particles and an additional ‘more hygroscopic’ mode with a growth factor of up to 1.5. This mode sometimes became dominant during periods of high ammonium nitrate concentrations. Attempts at quantitatively predicting the growth based the available composition data and the Zdanovskii-Stokes-Robinson (ZSR) mixing rule produced satisfactory results within the limitations of the measurements. These data demonstrate the importance of nitrate in the atmospheric BC lifecycle and can be used to inform approaches used in higher-level modelling.

8CA.28

Contribution of Alkanes and Polycyclic Aromatic Hydrocarbons to Organic Aerosol. HAVALA PYE, George Pouliot, Michael Lewandowski, John Offenberg, Tadeusz Kleindienst, *U. S. Environmental Protection Agency*

Intermediate volatility organic compounds, such as long-chain alkanes and small polycyclic aromatic hydrocarbons (PAHs), are thought to contribute significantly to ambient organic aerosol as a result of their low volatility and ability to reduce their vapor pressure to the semivolatile range with minimal functionalization. In this work, we develop a parameterization for SOA formation from different length and structure alkanes and use that as a basis for the Community Multiscale Air Quality (CMAQ) model to simulate the contribution of C8 and larger alkanes to secondary organic aerosol over the United States. The contribution of PAHs is included based on previously published work. Alkanes are predicted to be a more significant source of secondary organic aerosol than PAHs due to their relatively higher emissions, and the aerosol from alkane oxidation is predicted to be well correlated with odd oxygen. The possible implications of missing long-chain alkane emissions are highlighted.

8CA.29

Carbonaceous Superaggregates in Souteast Asian Outflow. NICHOLAS BERES, Rajan Chakrabarty, Hans Moosmuller, Frida Bender, Veerabhadran Ramanathan, *Desert Research Institute*

Light absorption due to aerosols in the atmosphere is dominated by black carbon (BC) particles emitted from combustion sources. BC particles in the atmosphere have been observed to exist as sub-micron sized fractal-like aggregates, and several studies have been conducted to characterize BC fractal morphologies and their influence on radiative forcing. In this poster, we report our observation of BC “superaggregates” (SAs) in the long-range transport of pollutants during the 2012 CARDEX (Cloud, Aerosol, and Radiative forcing Dynamics EXperiment) campaign based on the island of Hanimaadhoo in the Republic of Maldives. Scanning electron microscopy (SEM) images reveal occurrence of SAs in abundance on the filter substrates. These particles have a mean mobility diameter of ~3 micrometers and a fractal dimension (D_f) of ~2.64 - consistent with the prediction by gelation/percolation theory of aggregation. Back-trajectory analysis indicates that these SAs originated from South East Asian biomass burning episodes during February 27 - March 01, 2012. The knowledge of SA physical characteristics makes it possible to estimate their optical properties and contribution to short-wave radiative forcing.

8CA.30

Evidence and Quantitation of Aromatic Organosulfates in Ambient Aerosols in Lahore, Pakistan. Shuvashish Kundu, Tauseef Quraishi, Ge Yu, Catalina Suarez, Frank Keutsch, ELIZABETH STONE, *University of Iowa*

Organosulfates are important components of secondary organic aerosol (SOA) in ambient atmospheres, yet their structures, abundances, and formation processes are not well understood. In this study, a new type of organosulfate with an aromatic carbon backbone is identified and quantified in fine particulate matter (PM2.5) in the heavily polluted megacity of Lahore, Pakistan. An authentic standard of benzyl sulfate was synthesized and confirmed the presence of this unique compound in aerosol samples using high-resolution time-of-flight tandem mass spectrometry. Benzyl sulfate was quantified using ultra-performance liquid chromatography (UPLC) with negative electrospray ionization triple quadrupole mass spectrometry (ESI-MS/MS). The highest monthly-average benzyl sulfate concentrations were recorded in January and November 2007 (0.50±0.11 ng m-3), whereas the lowest concentration was observed in July (0.05±0.02 ng m-3). Seasonal trends were consistent with synoptic meteorology, with maxima occurring during the dry season and minima during the monsoonal summer. Matrix effects were evaluated by comparison of results obtained by external calibration and the method of standard addition; a minor deviation was observed (<10%) and matrix effects were determined to be insignificant in benzyl sulfate quantitation. Although benzyl sulfate contributions to organic carbon were relatively small (<0.001%), it may be an important tracer for organosulfates derived from anthropogenic volatile organic compounds.

8CA.31

Measurement of Gas and Particulate Amines at Agricultural Facilities using an Ambient Ion Monitor. PHILIP SILVA, *USDA - Agricultural Research Service*

Agricultural facilities are the source of particles and gases that can exhibit an influence on air quality. Particle influences from agricultural sources can include both primary emissions and secondary particle formation through the emission of gaseous precursors. Reports showing amines as particle forming precursors have lead to a need for new measurements of amines from these types of operations.

The ambient ion monitor (AIM) is composed of a parallel plate denuder, aerosol steam generator, and two ion chromatographs equipped with conductivity detectors to provide semi-continuous air quality monitoring capability. We previously reported the adaptation of this method to detect amines and other organic ions important in the field of agricultural emissions.

Here we will discuss recent field deployments of the AIM instrument to detect alkyl amines at agricultural facilities. We show that the AIM instrument detects a number of amines at concentrations relevant to agricultural emissions. Trimethylamine is detected in the highest concentration and is present in both the gas and particle phase. Other amines detected include methylamine, dimethylamine, and butylamine, though not all are observed in the particle phase.

8CA.32

Characterization of Atmospheric Aerosols Impacted by the Iowa City Landfill Tire Fire. Jared Downard, ELIZABETH STONE,*University of Iowa*

On May 26, 2012 the Iowa City Landfill liner caught on fire, burning an estimated 1.3 million tires across 7 acres for more than two weeks. Fine particulate matter (PM2.5) samples were collected approximately two miles northeast of the fire and were impacted by the plume on six days. Organic species were measured in PM2.5 using gas chromatography mass spectrometry (GCMS). Ambient PM2.5 contained elevated concentrations of elemental carbon and polycyclic aromatic hydrocarbons (PAH). Benzo[a]pyrene, a Group 1 carcinogen, increased to levels 37 times greater than the background reaching a maximum 24 h average concentration of 1.4 ng/m3. The tire fire plume also contained high concentrations of volatile organic compounds (VOC) such as isoprene, limonene, benzene, and toluene, which may have contributed to secondary organic aerosol (SOA).

8HA.1

Use of Two Samplers for Determination of Quantitative and Qualitative Bioaerosols In Tijuana, Mexico, Air Basin. LILIA HURTADO, Guillermo Rodriguez, *Universidad Autonoma de Baja California, Tijuana, Mexico*

Air pollution is a risk factor for health, most of the studies are related to particles and gases while some infectious diseases attributed to air pollution are by microorganisms which include bacteria, fungi, yeast and viruses. Bacteria are transported and dispersed in air as microbial consortia, bonded to plants particles, animals, pollen and soil particles called bioaerosols, which have adapted by their self or associated to others to survive. This ability can be estimated through quatitative and qualitative evaluations in time and space with procedures that allow to obtain viable microorganisms.

In this work the microbiological characterization in Tijuana, Mexico, air basin was coducted using two types of microorganisms air samplers, one of them by impact (M air T Millipore) and the other by centrifugation (Biotest Hycon). Nine sampling sites was selected along the city, including three air quality monitoring stations, samples were collected in 2011-2012 in the morning and afternoon, microbiological analysis provided information of colony forming units (CFU), genera and species. The above data is correlated with climatic factors, gases (CO, NOx, O3) and particulate matter, to establish the influence of air pollutants in microorganisms survival. Counts in the range of 1000 to 100,000 CFU were obtained per 100 liters of air, time and space variation was observed on microbial count. We detected some potentially pathogenic bacteria such as Escherichia coli, Pseudomonas aeruginosa, Streptococcus faecalis and Staphylococcus aureus, among others. There was no significant difference between the two types of samplers.

8HA.2

Laboratory Studies of Humidity-Induced Pollen Rupture to Produce Respirable Particles. QIAN ZHOU, Richard Flagan, Timothy M. VanReken, *Washington State University*

Many types of pollen contain allergenic material that has been linked to asthma and other respiratory ailments. However, the physical mechanism by which pollen induces the asthma response is unclear- the pollen grains themselves are too large to reach the lower airways where the asthma response occurs. Recent work has suggested a likely explanation. When exposed to high relative humidity, pollen has been observed to rupture and produce fine particles. The pollen rupture is probably the result of osmotic swelling; water from the surrounding environment is absorbed into the pollen grain until the grain wall fails and the cytoplasm is released. Previous studies have shown that the resulting particles are of respirable size (<2 micrometer) and include allergenic material that can trigger human immune response.

Our focus in this research is to quantify the dependence of pollen rupture on water vapor exposure. For the study, we assembled a small humidity-controlled environmental chamber that can be mounted on a microscope stage. For each experiment, several grains of pollen are placed on a microscope slide, and then exposed to a constant relative humidity for up to several hours. Time-lapse imagery was recorded throughout each experiment. By analyzing the time-lapse images, the relationship between relative humidity, exposure time, and pollen rupture can be determined. These results can then be used to develop a parameterization to allow better model predictions of the allergenic risks from pollen release. The present work focuses on wheat pollen, but future efforts will turn to species more closely linked with allergic response.

8HA.3

Development and Optimization of ATP Bioluminescence Method for Rapid Bioaerosol Quantification. TAEWON HAN, Srishty Subramanian, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Measurement of Adenosine Tri-Phosphate (ATP) using bioluminescence method has been used in a variety of applications as a good indicator of microbial contamination. We recently explored application of the ATP method to rapidly obtain detailed information on the collection efficiency and losses of liquid-based samplers challenged with actual bioaerosols. However, the previous study did not investigate robustness of the ATP bioluminescence method. Thus, to widen the use of ATP-based bioluminescence in bioaerosol applications, we analyzed the effect of various factors affecting the intensity and consistency of the luminescence signal resulting from ATP reaction with bioaerosols: decay in reagent activity due to storage (e.g., BacTiter-Glo reagent needed to produce luminescence), microorganism culture period, bioaerosol sampling methods (e.g., filtering, liquid-based and electrostatic) and others.

A freshly received BacTiter-Glo reconstituted reagent was subdivided into equal portions and stored in the freezer (at -20°C) from 1 to 14 days. Every day a vial was thawed out, mixed with an ATP standard (10 micro-mol) at 0, 1, 2, 4, and 6 hours after thawing out, and the Relative Luminescence Units (RLU) of the reaction indicative of the total ATP content were measured. The results show that within 1 hour of thawing out the reagent its luminescence intensity decreased on average by 36%. However, the luminescence intensity did not change substantially for 5 hours after that indicting a time window when bioaerosol experiments should be performed. Reagent storage in a freezer for 14 days did not affect the reactions. Our results also show that microorganism species commonly used as test particles in bioaerosol work, such as E. coli, B. subtilis, and P. fluorescens, exhibit an optimum growth period producing strongest bioluminescence signal. Bioaerosol sampling method was also found to affect the intensity of ATP-based bioluminescence reactions, with inertia-based collection usually resulting in weaker bioluminescence signal.

8HA.4

Evaluation of Antimicrobial Durability on Natural Product Nanoparticle-Deposited Air Filter. GI BYOUNG HWANG, Bo Mi Kwon, Chu Won Nho, Jae Hee Jung, Gwi Nam Bae, *Korea Institute of Science and Technology*

Bioaerosols contain airborne viruses, fungi, bacteria, and fragments of organisms. They can cause a variety of disease including infections, hypersensitivities, and toxic reactions and spread widely with air stream. Thus, it is important to control the concentration and viability of bioaerosols in order to protect human health. Recently, the air filtration treatment using natural products has been considered as the most practical way because some of natural products are lethal to microorganism as well as relatively less harmful to human comparing with other antimicrobial substances. In this study, we evaluated the antimicrobial durability on natural product nanoparticle-deposited air filter for four months.

Nanoparticles of Sophora flavescens were deposited on the surface of filter fiber through the thermal-nebulization process. Sophora flavescens is known to have various biological activities such as antibacterial or antifungal function and anticancer. The fabricated filters were stored at 20oC and relative humidity of 25%. Every month we confirmed the inactivation efficiency of the filter against E coli bacterial bioaerosol and the quantitative change on major chemical components (kurarinone, sophoraflavanone G, and kuraridin) of Sophora flavescens. In addition, the morphology change of the nanoparticles on filter was investigated using SEM.

The inactivation efficiency of the antimicrobial filter where natural product nanoparticles were deposited for 3min was approximately 90% and the efficiency kept for 3 months. And, during the same period, the major chemical components did not change. After three months, however, the inactivation efficiency decreased to 44%, and the amount of major chemical components reduced by 32.5%. The morphology of the nanoparticles did not change for four months.

8HA.5

Applying Real-Time Quantitative Polymerase Chain Reaction to Monitor the Airborne Streptococcus Pneumonia in a Daycare Center. MIAO-CHING CHI, Lin Meng-Chih, Chen Min-Li, *Department of Respiratory Care, Chang Gung University of Sci*

Streptococcus pneumoniae causes a range of diseases such as pneumonia, otitis media, arthritis, sinusitis, septicemia, and meningitis. In order to prevent the health of young children and older adults from infection, it is important to evaluate the environments at a high risk exposed to S. pneumoniae. Therefore, the aim of this study was to develop an optimized real-time qPCR method for analyzing the concentrations of S. pneumoniae. To optimize the analytical conditions for the real-time qPCR, several factors including detection limit, extraction time (30 sec, 60 sec, 120 sec, and 180 sec), storage temperature (4 degree centigrade, -20 degree centigrade, and -80 degree centigrade), and storage time (0 day, 3 day, and 7 day) were determined. Aerosol samples in a daycare center were collected for examining the concentrations of S. pneumoniae in use of the determined real-time qPCR. The results indicated the detection limit of this method was as low as 6.1copies/micro-liter with a value of correlation coefficient 0.999. In terms of extraction time, the optimal S. pneumoniae DNA recovery was one minute. Moreover, the results of this study indicated that storage in low temperature could reduce the biological activity of S. pneumoniae and damage its DNA. Therefore, it is suggested to analyze the samples immediately after air sampling. The indoor concentrations of airborne bacteria, fungus, and S. pneumoniae were measured in the range from 6.64×10^2 CFU/m^3 to 2.36×10^3 CFU/m^3, 5.51×10^2 CFU/m^3 to 4.02×10^3 CFU/m^3, and 9.62×10^3 copies/m^3 to 2.38×10^4 copies/m^3, respectively. Conclusions: The results showed the existence of airborne S. pneumoniae indoors. In the future, real-time qPCR method can be applied to monitor the airborne S. pneumoniae for assessing its relationship with the prevalence of nasopharyngeal carriage.

8HA.6

Association of Virus Content with Its Carrying Particle Size. ZHILI ZUO, Thomas Kuehn, Sunil Kumar, Yogesh Chander, Sagar Goyal, Jessica Appert, Peter Raynor, Song Ge, David Pui, *University of Minnesota*

Airborne transmission of viral diseases heavily depends on the size of the virus-carrying particles, since particle size governs many aspects such as the transport of virus aerosol in air, deposition within the human respiratory tract, and control by filtration. A primary mode in the submicron size range has been found for the size distribution of human expiratory particles. However, how the virus is distributed among particles of different sizes is not well understood.

The objectives of this laboratory study were to quantify virus content as a function of particle size and to determine virus survivability in the airborne state. Five surrogate viruses (MS2 bacteriophage, human adenovirus, transmissible gastroenteritis coronavirus, swine influenza virus, and avian influenza virus) were aerosolized, size-selected (100-450 nm) using a differential mobility analyzer, and collected onto gelatin filters. Uranine dye was also nebulized with the virus, serving as a chemical tracer. The resulting particle size distribution was determined using a scanning mobility particle sizer. The collected samples were analyzed by infectivity assays, quantitative PCR, and spectrofluorometry.

Results using MS2 bacteriophage suggest that the viable and total virus distributions are better represented by the particle volume rather than the number distribution. The amount of virus per particle increased with particle size, which could be described by a power-law relationship. However, the survivability of airborne virus was not significantly affected by particle size. These results will help better understand disease transmission by virus aerosols. Experiments are ongoing with the four animal viruses and the comparison of the five viruses is presented.

8HA.7

Survival of Four Bacteriophages Virus Models Under Relative Humidity and Temperature Aerosol Stresses. MÉLISSA MARCOUX-VOISELLE, Nathalie Turgeon, Daniel Verreault, Sylvain Moineau, Caroline Duchaine, *Université Laval, Canada*

The spread of viruses in the air is still a misunderstood phenomenon. Many questions remain unanswered regarding their aerosolization, transport and survival over time, in various environmental conditions. The development of standardized models for the study of viral aerosols would lead to major advances in this field. The study of aerosolized bacteriophages offers a very interesting opportunity as models. Indeed, they are safe, inexpensive and even some have morphologies similar to eukaryotic viruses.

In this study, we aimed to evaluate the effects of relative humidity (RH) and temperature over the time on viral bioaerosols using a rotating chamber. We used four tailless bacteriophages: MS2 (ssRNA), Phi6 (segmented dsRNA), PhiX174 (ssDNA) and PR772 (dsDNA). The phages were aerosolized using a Collison 6-jet into a 50 liters drum, rotating at one rpm. The aerosols were maintained in the desired conditions for 0, 6 and 14 hours and sampled with a Biosampler. The experiments were conducted at 18°C and at three RH levels (20, 50 and 80%), as well as at 30°C and 80% RH.

We obtained four different responses for the survival of those phages in the conditions tested: 1) at 18°C, MS2 is resistant to all levels of RH, 2) Phi6 is less affected at low levels of RH, 3) PhiX174 and PR772 are more stable at high levels of RH, 4) PR772 seems less resistant to long distance transmission, mimicked by long term aerosol state. The selected phages could be good models for the study of airborne transmission of viruses as they exhibit various behavior and resistance to stresses.

8HA.8

Transient Deposition Functions Applicable to Inhaled Pharmaceutical Aerosols. Philip Ophus, CARLOS LANGE, *University of Alberta*

Single breath devices, which have strong transient effects, are becoming more common in the delivery of aerosol medications. Most current mathematical functions used to predict the deposition of inhaled aerosol particles in the human lung are based on Lagrangian models of particle flow. These models work well for certain particle effects that occur during respiration, but they are ill-suited for modelling instantaneous time-dependent effects. The alternative to Lagrangian models is Eulerian models, which can handle transient effects much more easily, though they are difficult to create. Deposition functions truly based on Eulerian models are needed to accurately simulate the short-term single-breath effects of a typical breathing pattern and thus provide better dosage estimates.

In the interest of developing such Eulerian deposition models, mathematical techniques were employed to develop fully time-dependent Eulerian deposition functions. These methods were used to describe the velocity fields of simple particle flows. Analytic expressions describing the time-dependent flow of particles through a curved pipe were created and solved numerically. The results compared well with classical analytical and experimental results for the steady-state case. Numerical simulations with the new functions were used to determine which flow regimes required the use of Eulerian modelling for deposition prediction. Solutions to simple cases such as this will provide the functional form for more complicated geometries and flows, such as that in the mouth/throat region or the flow past a bifurcation in the lung pathways.

8HA.9

Development of Controlled Condensational Growth for Aerosol Delivery During Nasal High Flow Therapy. GENG TIAN, Yoen-Ju Son, Michael Hindle, Worth Longest, *Virginia Commonwealth University*

Non-invasive ventilation methods including high flow therapy (HFT) through a nasal cannula interface are becoming increasingly popular as a way to provide breathing support and help move patients off of endotracheal tubes faster. However, an effective method to deliver pharmaceutical aerosols to patients receiving HFT is not currently available. The objective of this study is to quantify performance of controlled condensational growth for pulmonary aerosol drug delivery during HFT considering the effects of a realistic nasal cannula interface, transient inhalation, and the inclusion of hygroscopic excipients. Controlled condensational growth during HFT is a newly proposed strategy in which submicrometer aerosols are delivered to one nostril and warm air saturated with water vapor is delivered to the other nostril. The small particle size allows the aerosol to easily penetrate the delivery lines, cannula, and narrow nasal passages. Aerosol size increase due to condensation and hygroscopic growth beginning in the nasopharynx and continuing into the lungs result in micrometer-size droplets (2-4 micrometers) that will deposit by impaction and sedimentation within the lower airways. In vitro experiments with a characteristic nasal airway model extending through the trachea are used to evaluate transport and deposition of hygroscopic and non-hygroscopic aerosols. Computational fluid dynamics simulations are validated based on the in vitro experiments and used to explore local drug deposition as a result of including the nasal cannula and transient inhalation. Including a hygroscopic excipient to enhance and better control the final particle size is also explored. Results indicate very low nasal depositional losses, the need for on-demand aerosol generation during inhalation, and aerosol growth to 2 micrometers and above within the trachea. Ultimately, the proposed technology will provide a highly effective method for delivering pharmaceutical aerosols to patients, for local or systemic therapy, without interruption of their ventilatory support.

8HA.10

Losses of Cigarette Smoke Particles in Oral Cavities.

BAHMAN ASGHARIAN, Owen Price, Jeff Schroeter, Colin Dickens, John McAughey, *Applied Research Associates, Inc.*

Accurate prediction of the dose of inhaled cigarette smoke particles to the lungs is directly affected by losses in oral cavities. Coagulation and condensational growth of cigarette smoke particles during the puffing and subsequent mouth-hold may result in appreciable losses in the oral cavities by sedimentation. Recent measurements of particle deposition in the oral cavities have indicated a higher fraction of losses than computational predictions due to gravitational settling during the initial mouth-hold of the puff. Visualization of the cigarette puff suction into the oral cavities demonstrated a strong free shear flow initiating through the lips, travelling through the oral cavities, hitting the back of the mouth, and finally mixing with the initial air residing in the mouth. Additional deposition of cigarette smoke particles on the back of the mouth is feasible if particles gain adequate inertia during the puff. To investigate the significance of impaction losses, idealized flow calculations were conducted where the flow in the oral cavities was assumed to be uniform at the lips but developed axially during the travel in the mouth. The flow then impinged on a flat surface, representing the back of the mouth. The axial and tangential components of the flow profile were used in particle transport equations to calculate particle trajectories and deposition on the impaction plate. Model predictions showed small losses that varied with the suction flow rate and initial size of particles. Together with losses during the subsequent mouth-hold, the total loss of cigarette smoke particles can be described by impaction and sedimentation in oral cavities. This study was funded by British American Tobacco.

8HA.11

Particle Transport During Ventilation in Upper Airways.

Chang Liu, Donna Meyer, ZONGQIN ZHANG, *University of Rhode Island*

The phenomena of bi-directional flow streaming can be found in zero-mean-velocity oscillating flows in a wide range of channel geometries. Study of aerosol transport patterns under normal breathing and high-frequency ventilation conditions has many applications in the fields of inhalation toxicology and aerosol medicine delivery. In this study, we investigate the phenomena of particle transport patterns during flow streaming in symmetrical bifurcating channels using computer simulations and experimental verifications. Computer generated streaming flow distribution patterns agree well with the patterns shown in the experimental photographs under the same geometry and flow conditions. Results of computer simulations show that oscillation amplitude is the dominant effect on particle transport velocity during streaming in channel networks. It is found that the diameter ratio of mother tube to daughter tube has significant effects on particle distribution patterns. New streaming flow patterns in bifurcating channels are identified. Simulation results provide some useful guidance in design and manipulating the streaming particle transport in bifurcation networks.

Keywords: flow streaming, respiratory flow, bifurcation, particle transport

8HA.12

Development of a Wick Electrospray Pharmaceutical Aerosol Generator. LANDON HOLBROOK, Worth Longest, *Virginia Commonwealth University*

A novel wick-based electrospray system (WES) is presented and developed with the goal of delivering submicrometer pharmaceutical aerosols to mechanically ventilated patients at very high efficiencies. In the WES system, a porous polymer wick is placed in a reservoir containing a dissolved drug model and liquid vehicle. An electrical potential is applied between the wick and a counter electrode ring to create the submicrometer aerosol. The device is connected in the inspiratory arm of a mechanical ventilation circuit and driven by an external power supply. One significant innovation of this system for respiratory drug delivery is that both the microprocessor-controlled syringe pump and capillary are replaced with readily available low-cost polymer wicks. The objective of this developmental study is to evaluate initial performance of the WES device for delivering pharmaceutical aerosols to infants on mechanical ventilation. In vitro experiments are used to quantify aerosol production rates and depositional losses in the device, on the counter-electrode, and in the connective tubing. Outlet aerosol size is quantified using an optical particle counter and cascade impaction. Computational fluid dynamics simulations are used to optimize the counter-electrode geometry and inlet co-flow air to minimize depositional losses. Through modifying the solution surface tension, wick configuration, counter-electrode, and field strength, aerosols in the submicrometer range are generated. Deposition within the system is found to be within an acceptable range indicating the potential usefulness of this device in therapeutic applications.

8HA.13

Influence of Morphometry and Airway Constriction on Response to Inhaled Methacholine. MICHAEL OLDHAM, Rodney Clinkenbeard, Owen Moss, *University of California, Irvine*

For some individuals, the degree of response to inhaled allergens or efficacy of inhaled pharmaceuticals may be influenced by their lung morphometry and normal state of airway constriction. Such a relationship was investigated by obtaining lung images before and after human subjects were exposed to a bronco-constrictor.
Fourteen healthy, non-smoking subjects received a computed tomograph (CT) scan just prior to performance of a methacholine challenge. Following the methacholine challenge and bronchodilation all subjects received a second CT scan. CT scans were reconstructed for the first six tracheobronchial airway-generations and airway length, diameter, branch angle and inclination to gravity dimensions were obtained. A typical path airway model of the first six tracheobronchial airway generations was used to calculate airway circumference and surface area. The product of airway circumference and surface area was incorporated into an airway volume factor, inversely proportional to the fractional decrease in airway circumference due to deposited methacholine.

Comparison of airway dimensions from the two CT scans indicated all subjects started the study with each airway generation having some degree of constriction (2% to 33%). Six subjects did not respond to the methacholine challenge while 8 subjects responded with a greater than 3% decrease in their forced expiratory volume in one second. Compared to the non-responders, these responders had smaller airway volume factors (about the same in airway generation 1 to 36% smaller in airway generation 5). They also entered the study with a greater degree of airway constriction (The largest difference was in airway generation 5; 28% compared to 13% constricted in the non-responsive).

All subjects entered the study with upper airway constriction. Eight subjects showed responses that reflected lung morphometry and airway surface dose effects; and six subjects with the smallest normal state of airway constriction and the largest airways did not respond to inhaled methacholine.

8HA.14

Physical and Chemical Properties of Iron Oxide Nanoparticles that Contribute to Cellular Toxicity and Acellular Production of Hydroxyl Radical.

JESSICA CHARRIER, Christoph Vogel, Aamir Abid, Ian Kennedy, Cort Anastasio, *University of California, Davis*

Engineered nanoparticles are increasingly used in consumer products causing more frequent human exposure to these materials. The potential health risks of nanomaterials – and, especially, the physical and chemical properties that increase toxicity - are not well understood. One likely mechanism of toxicity of nanoparticles is their ability to produce reactive oxygen species, such as hydrogen peroxide and hydroxyl radical (˙OH), which can induce oxidative stress, inflammation, and cell death. To investigate which properties of nanoparticles are associated with toxicity, we quantified accelular production of ˙OH and the upregulation of markers of inflammation and oxidative stress in macrophage cells from six iron oxide nanoparticle types. The iron oxide nanoparticles have varying physical properties (e.g., surface area and surface charge) and different ratios of iron oxidation state (Fe(0), Fe(II) and Fe(III)). We will report on the relationship between the chemical and physical properties of Fe nanoparticles, acellular ˙OH production, and upregulation of inflammatory and oxidative stress-related markers in macrophage cells. We will also discuss the relation between the cell-free ˙OH results and in-vitro cellular oxidative response.

8HA.15

Worker and Environmental Assessment of Potential Unbound Engineered Nanoparticle Releases.

GARY CASUCCIO, Randall Ogle, Kristin Bunker, Keith Rickabaugh, *RJ Lee Group, Inc.*

To satisfy the DOE policy and to address the uncertainties inherent in a rapidly developing technological field, a multiphase pilot study has been conducted at the Lawrence Berkeley National Laboratory (LBNL) to evaluate the potential for emissions of unbound engineered nanoparticles (UNP) to the outdoor environment and assess the need for appropriate controls. The work conducted as part of the study represents a first effort to evaluate the environmental release of UNP in research environments, with a focus on determining whether emissions from building exhaust are acceptable or compliant. Based on the results obtained, the controls currently used by researchers during work with UNP met or exceeded the validated, recommended control level based on a control band approach. It was also determined that high-efficiency particulate air (HEPA) filtration was not required for the research processes evaluated.

The final phase of the study provides a plan for implementing an ongoing environmental program for emissions of UNP to the outdoor environment. The plan involves several steps including identification of possible UNP hazards to workers by using LBNL’s Baseline Exposure Assessment (BEA), an equivalent work planning and control process, or other industrial hygiene information and assessments. The plan includes the use of a control band matrix to identify appropriate control options, discussion of options with researchers and subject matter experts, and any necessary performance of periodic monitoring of long-term research. The plan discusses documentation that will be developed and maintained. The plan also considers potential future changes in the monitoring approach that may be appropriate as the technology for ensuring nanomaterial safety evolves.

8HA.16

Toxicological Assessment of Emerging Diesel Fuel Emissions: The EMITTED Study. JOSEPHINE COOPER, Krystal J. Godri, Naomi Zimmerman, Terry Jung, Cheol-Heon Jeong, Greg J. Evans, James S. Wallace, *SOCAAR, University of Toronto*

Vehicle emissions contribute significantly to urban ambient particulate matter, and exposure to these emissions has been associated with adverse cardio-respiratory effects. As light-duty diesel vehicle use across North America increases, and new emission treatment technologies and diesel fuel types are introduced, there is a growing need for toxicologically relevant measures of diesel exhaust characteristics.

One aim of the EMITTED (Exhaust Measurement and Inhalation Toxicology Testing of Emerging Diesel fuels) study is the development of a realistic in vitro model to explore airway exposure to diesel exhaust particulates (DEP). Biomarkers representative of the airway's immunological response were used to elucidate toxicologically relevant responses to DEP.

An in vitro model of the airway was constructed using the Calu-3 human bronchial epithelial cell line in an air-liquid mono-culture. The model was exposed to liquid solutions of suspended iron dust and carbon black (positive and negative control, respectively), or liquid impinged and filter extracted DEP solutions of <200nm in diameter. DEP was generated by a heavy-duty diesel engine, which was fitted with a diesel oxidation catalyst and particulate filter. The engine was operated under 25% and 75% full loads with diesel fuel types: soy, animal fat, and commercially available ultra-low sulphur diesel.

Changes in extracellular and intracellular concentrations of the cytokines: GM-CSF, IFN-gamma, IL-1alpha, IL-1beta, IL-6, IL-8, and VEGF were quantified by 'multiplexing' using Millipore's Luminex instrument. As DEP effects have been attributed to its oxidative properties, DCFH oxidation by reactive oxygen species in the cell was measured in parallel. To ensure the model was viable throughout DEP exposures, cell cytotoxicity was also assessed through resazurin reduction.

DEP exposure induced the airway's protection, adaptation and inflammation responses through elevation of reactive oxygen species and immunomodulatory protein concentrations. Further investigation of these pathway activations should reveal the mechanisms by which DEP exposure causes airway toxicity.

8HA.17

Assessment of the Pre-Toddler Inhalable Particulate Environmental Robot's Ability to Mimic Dust Resuspension by Children. Gediminas Mainelis, ZUOCHENG WANG, Kathleen Black, Marta Hernandez, Stuart Shalat, *Rutgers, The State University of New Jersey*

Young children spend most of their time indoors, often playing on the floor. Activities on the floor have been shown to resuspend particulate matter (PM). Children's activities and the proximity of their breathing zones to the floor can elevate children's exposure to PM and may cause respiratory problems.

Personal sampling is impractical for very young children. As an alternative, a robotic sampling surrogate PIPER (Pre-Toddler Inhalable Particulate Environmental Robot) has been developed to measure children's exposure to PM. PIPER motion profiles have been developed to replicate the floor activities of young children. Here, two OPCs (TSI 8220) were used to evaluate the particle resuspension ability of PIPER under 6 different activity profiles in 65 homes. The effect of floor type on particle resuspension was also investigated. One OPC was set up as a stationary sampler. The mobile OPC was mounted on PIPER. Real time particle concentration was measured during two time periods, during the first PIPER was motionless while during the second, PIPER was moving around, mimicking the floor motion of young children.

The data from mobile OPC show that due to PIPER's motion the airborne concentration of particles >10 micro-meters can increase by up to 500% on carpeted floor and 250% on bare surface floor. The resuspension caused by PIPER's motion was also detected by the stationary OPC in the same room, but to a lesser extent. For particles > 10 micro-meters, the particle concentration increase detected by stationary OPC was up to 100% on a carpeted floor and 55% on a bare floor. Different motion profiles did not have a significant effect on particle resuspension. Results suggest that since personal monitors provide better exposure estimate compared to stationary ones PIPER may better approximate young children's exposure.

8HA.18

Assessing the Impact of Hazardous Air Pollutants Emitted from Phosphate Fertilizer Plants Ambient Air Quality and Human Health. HSING-WANG LI, Nima Afshar-Mohajer, Chang-Yu Wu, Jean-Claude J. Bonzongo, Vito A. Ilacqua, Yongsuk Choi, Brian Birky, *University of Florida*

The United States is the second largest producer of phosphate fertilizers in the world. Phosphate products are widely used around the world for fertilizer, detergents, animal feed and food. In Central Florida, there are several phosphate fertilizer manufacturing plants that are potential sources for Hazardous Air Pollutants (HAPs) that have potential adverse health effects. In this study, three types of models (AERMOD View 7.6.1, Chemical Mass Balance (CMB, V8), and EPA's Human Exposure Model-3 (HEM3) were used to investigate the potential impact of the HAP emissions. The objective of this study was to evaluate ambient HAP concentrations resulting from such emissions and to estimate the corresponding human exposures and health risks.

AERMOD - Six receptor locations were evaluated: four urban areas (Zephyrhills, Plant City, Tampa, Lakeland) and two ambient air monitoring sites (Tower Dairy, Sydney) The maximum annual ground level concentration among the six receptors was found in Sydney, and the concentrations ranged from 0.190-0.617 pg/m3 for Be, Co, Cd, Sb; 1.10-2.07 pg/m3 for Se, Hg, As; and 3.35-5.58pg/m3 for Cr, Mn, Pb, and Ni. In addition, the maximum ground level concentration of Pb (5.44 pg/m3) was much lower than National Ambient Air Quality Standards (150 ng/m3). CMB - According to the source contribution estimated by CMB, three dominant contributions for total metals were from marine (38.8%), coal-fired power plant (27.9%) and lime (12.9%) for the Sydney site, while the phosphate fertilizer plants contributed only 1.41-2.45%. For Cr, phosphate processing facilities contributed 19.9% while other major sources were vehicles (43.9%), coal-fired power plant (25.5%) and soil (7.08%). HEM3 - The maximum off-site risk for Cr (1.4×10-6) and Cr6+ (1.1×10-6) from Facility A were slightly higher than acceptable in standard practice (1×10-6) in the northeast of Facility A (0.25 miles from the stacks). One possible source for the Cr in phosphate emissions is the milling balls made of chromium used in the production process.

8HA.19

Genotoxic Potential of Organic Extracts from Particle Emissions of Diesel and Rapeseed Oil Powered Engines. JAN TOPINKA, Alena Milcova, Jana Schmuczerova, Martin Mazac, Martin Pechout, Michal Vojtisek-Lom, *Institute of Experimental Medicine AS CR, Prague, Czech Repu*

The study was performed to identify genotoxicity induced by organic extracts from particulate matter in the exhaust of two typical diesel engines run on diesel fuel and neat heated fuel-grade rapeseed oil: A Cummins ISBe4 engine tested using the World Harmonized Steady Cycle (WHSC) and modified Engine Steady Cycle (ESC) and a Zetor 1505 engine tested using the Non-Road Steady Cycle (NRSC). In addition, biodiesel B-100 (neat methylester of rapeseed oil) was tested in the Cummins engine run on the modified ESC cycle. Diluted exhaust was sampled with high-volume samplers on Teflon coated filters. Filters were extracted with dichlormethane and DNA adduct levels induced by extractable organic matter (EOM) in an acellular assay of calf thymus DNA coupled with 32P-postlabeling in the presence and absence of rat liver microsomal S9 fraction were employed. The results suggest that diesel emissions contain substantially more total PAHs than rapeseed oil emissions (for the ESC cycle) or that these concentrations were comparable (for the WHSC and NRSC cycles), while c-PAHs levels were comparable (for the ESC cycle) or significantly higher (for the WHSC and NRSC cycles) for rapeseed oil emissions. DNA adduct levels induced by diesel and rapeseed oil derived EOM were comparable, but consistently slightly higher for diesel than for rapeseed oil. Highly significant correlations were found between 12 priority PAHs concentrations and DNA adduct levels (0.980; $p<0.001$). Metabolic activation by the microsomal S9 fraction resulted in several fold higher genotoxicity, suggesting a major contribution of PAHs to genotoxicity. Generally, DNA adduct levels were more dependent on the type of engine and the test cycle than on the fuel. Our findings suggest that the genotoxicity of particulate emissions from the combustion of rapeseed oil is significant and is comparable to that from the combustion of diesel fuel. Support: LIFE10 ENV/CZ/651 (MEDETOX).

8HA.20

Discerning the Chemical Composition and Mutagenic Effects of Soy Biodiesel PM. DAVID NASH, Esra Mutlu, William Preston, Michael Hays, Sarah Warren, Charly King, William Linak, M. Ian Gilmour, David DeMarini, *U.S. EPA*

Exhaust particles from the combustion of traditional diesel fuel have been shown to lead to increases in adverse health effects such as impaired lung function, respiratory distress, and cardiovascular disease. This has resulted in an effort to find alternative fuels, such as soy-based biodiesel, that can replace traditional diesel. In the present study, the chemical composition and mutagenic effects of 0, 20, and 100% soy biodiesel (B0, B20, B100) PM emissions from a Yanmar L70 diesel engine and Pramac E3750 generator were examined. As expected, GC/QQQ analysis of the B100 extract shows more than 50% less polycyclic aromatic hydrocarbons (PAHs) than are found in B0 and B20 per particle mass. The B100 extract was also shown to be less mutagenic than B0 and B20 when evaluated using the Salmonella (Ames) assay. However, the B20 extract contained ~40% more PAHs and was more mutagenic than B0. Hopanes, alkanes, organic acids and methyl esters were identified and are also presented for each biofuel blend. This study shows that PAHs are the main mutagenic driver and can be used to predict relative mutagenic potency of various biofuel blends. [Abstract does not necessarily reflect the policy of the US EPA.]

8HA.21

Development and Implementation of Techniques to Investigate the Physiological Response of Bacteria to Aerosolisation.RICHARD THOMAS, Janine Jordan, David Cleary, *Dstl*

Bacteria can be aerosolised into the atmosphere due to a number of activities such as man-made and natural (e.g. coughing, sneezing, showering, flushing toilets, emissions from cooling towers, farming, household dusting and spraying agricultural insecticides). For most bacteria this causes few problems for man; however, some bacteria can be transmitted in aerosols to cause disease. Yersinia pestis, the causative agent of plague, is one such pathogen, and this has serious implications in the event of an outbreak. The mechanisms behind the physiological response to aerosolisation are uncharacterised. The focus of this research is to develop a suite of techniques to enable a better understanding of this phenomenon for Y. pestis.

Particle size has been demonstrated to influence bacterial survival in organisms such as Pseudomonas syringae (Lighthart & Shaffer, 1997). Two different aerosol generation devices (Collison nebuliser and flow-focussing aerosol generator) were used to generate 1 and 12-micrometer particle aerosols of Y. pestis that were captured onto microthreads. These captured aerosol particles were assessed over time for viability at 50% relative humidity and ambient temperature.

Techniques for enumeration of Y. pestis cells sampled from aerosols have been developed based on PCR to determine the total number of captured cells and those with compromised membrane integrity, alongside conventional assessment of viability by colony formation.

The data indicated that over a short period of 15 min, the viability of Y. pestis measured by the formation of colonies on plating media was maintained in both 1 and 12-micrometer aerosol particles. However, after 30 min there was a significant reduction in viability within 1-micrometer particles that was not observed in the larger particles. The reduction in viability was not linked to loss of membrane integrity as irrespective of particle size, a significant reduction in membrane integrity was observed by 5 min.

Ref: Lighthart & Shaffer (1997) Aerosol Sci Tech, 27, 439-446

8HA.22

Comparison of Face Mask Seal using Different Facial Materials on an Idealized Infant Replica. NICHOLAS CARRIGY, Connor O'Reilly, James Schmitt, Warren Finlay, *University of Alberta*

A face mask is commonly attached to a valved holding chamber (VHC) to allow for the delivery of pharmaceutical aerosols from a pressurized meter dose inhaler (pMDI) to a small child or infant who is too young to reliably breathe through a mouthpiece. Leakage can occur between the face mask and the child’s face if insufficient force is applied to the VHC by the parent; however, if too much force is applied the child may become uncooperative, preventing drug delivery. It is difficult to quantify the seal provided by the face mask using in-vivo tests. Instead, it is common to use a single replica of a child’s face to compare the seal provided in-vitro for different face mask designs. An idealized infant nasal airway and face designed to mimic the average nasal airway deposition in infants has recently been developed for in-vitro testing of pMDIs (Javaheri et al., J. Aerosol Sci. 2012, in press). However, the material used to replicate the idealized infant face has not been previously explored.

This study provides a comparison of face mask seal when different materials are used to replicate the idealized infant face. The five materials compared in this study are acrylic, metal, silicone, polycarbonate with a thin layer of silicone, and polycarbonate with a thin layer of Hitohada gel. The seal was measured as a function of applied force for commercial Aerochamber, Philips Respironics, Pocket Chamber, and Vortex VHCs with the commercial face masks available for each VHC. Experimental results were obtained by flowing pure nitrogen through the VHC and measuring total ambient air leakage into the idealized infant nasal airway with an oxygen sensor. The amount of force applied to the VHC was varied using an adjustable flat plate and measured using a load cell. This study provides a quantitative comparison of the face mask seal for five material representations of an idealized infant face.

8HA.23

Modeling Deposition of Cerium-Containing Diesel Particles Inside a Wind Tunnel. ZHEMING TONG, Thomas Peters, Robert Willis, Kathleen Fahey, Havala Pye, Max Zhang, *Cornell University, Ithaca, NY, USA*

The cerium-based fuel additive shows promise in PM emission reductions, but it also raises the concern of near-road cerium exposure. This presentation describes our modeling study of deposition of cerium-containing diesel particles inside a well-characterized wind tunnel using the Comprehensive Turbulent Aerosol Dynamics and Gas Chemistry (CTAG) model. The data was collected from an experiment conducted at University of Iowa and USEPA. The turbulent flow field is resolved by Large-Eddy Simulation (LES) model, and we apply several dry deposition models to compare the modeling results against particle deposition analyzed from TEM grids. This study helps examine our capability in capturing the dynamics of cerium-containing particles in the atmosphere.

8HA.24

How Deposition Uniformity Affects FTIR Analysis of Filter Samples. ART MILLER, Pamela Drake, Ryan LeBouf, Nate Murphy, Emanuele Cauda, *NIOSH*

Miners face a variety of respiratory hazards, including exposure to silica-bearing coal dust which can lead to silicosis, a potentially fatal lung disease. The current method for measuring airborne silica is to collect a filter sample of coal dust, send it to a laboratory for analysis and wait for a report, which may take weeks. The mining workplace is dynamic, transitioning among different geological strata with potentially varied silica levels, and more timely data on silica levels could help reduce exposures. To address this, NIOSH is investigating field portable end-of-shift (EOS) methods for measuring silica on filter samples of coal dust. Since many field portable methods entail partial, localized analyses on the filters, spatial uniformity of dust deposition can affect the accuracy and repeatability of the EOS methods. This study was designed to assess the influence of deposition uniformity on the accuracy of a portable Fourier transform-infrared method used for measuring silica on coal dust samples. Using laboratory-generated silica and coal dusts and three different types of sampling trains, multiple sets of filter samples were generated at five different dust loadings. Silica was measured by FTIR at nine locations across the face of each filter and the data analyzed by a multiple regression analysis technique using SAS software. This entailed comparing various models for predicting total silica mass on the filters using different numbers of “analysis shots”. Results show that the predictive accuracy of the various models increases with the number of shots used for the analysis, and ranges from about 4% to 10% depending on the number of points analyzed and the type of sampling train used (which was shown to affect the uniformity of deposition on the filter). Data indicate that single shot analyses of coal dust samples collected onto PVC filters in 3-piece cassettes, yield predictivity of silica mass with error of less than +/- 10% for a wide range of filter loadings. The RSD of that simplified approach is approximately 8% which makes it a simple, accurate method for EOS measurement of airborne silica in mines.

8HA.25

On Dithiothreitol (DTT) as a Measure of Oxidative Potential for Ambient Particles: Evidence for the Importance of Soluble Transition Metals. JESSICA CHARRIER, Cort Anastasio, *University of California, Davis*

The rate of consumption of dithiothreitol (DTT) is increasingly used to measure the oxidative potential of particulate matter (PM), which has been linked to the adverse health effects of PM. While several quinones are known to be very reactive in the DTT assay, it is unclear what other chemical species might contribute to the loss of DTT in PM extracts. To address this question, we quantify the rate of DTT loss from individual redox-active species that are common in ambient particulate matter. While past research has indicated that the DTT assay is not sensitive to metals, our results show that seven out of the ten transition metals tested do oxidize DTT, as do three out of the five quinones tested. While metals are less efficient at oxidizing DTT compared to the most reactive quinones, concentrations of soluble transition metals in fine particulate matter are generally much higher than those of quinones. The net result is that metals appear to dominate the DTT response for typical ambient PM2.5 samples. Using typical fine particle concentrations of soluble metals and quinones, and our measured DTT responses for these species, we find that approximately 80 % of DTT loss is from transition metals (especially copper and manganese), while quinones and other organic species likely account for around 20 %. We find a similar result for a small set of fine particle samples collected from the San Joaquin Valley of California.

8HA.26

Estimating Health Effects of Air Pollutants in Pittsburgh from 2001-2002 Using Autoregressive Moving Average (ARMA) Time Series Structural Equation Models (SEMs). RICHARD BILONICK, Daniel Connell, Evelyn Talbott, Judith Rager, Lynne Pavlic Marshall, *University of Pittsburgh*

Statistical modeling has been used extensively to estimate the effects of air pollutants on human health. Single-pollutant models have commonly been used where only one pollutant of interest at a time is modeled (usually adjusting for weather and for day-of-week, seasonal and other trends), even though it has been known since Fisher's work in the 1920s that this approach tends to introduce bias because it does not account for other pollutants with significant effects. More recently, multi-pollutant models have been used to overcome this limitation, in spite of problems with collinearity. Most importantly, however, neither the single-pollutant nor the multi-pollutant approach accounts for the typically significant amount of measurement error in air pollution measurements, which further biases model coefficients in unpredictable ways. Simply including additional pollutants in regression models or even time series models (regression models with autoregressive and/or moving-average terms) is unlikely to provide a clear understanding of which pollutants are most important. Rather, we propose the use of structural equation models (SEMs) to appropriately account for the statistical complexities associated with estimating the health effects of multiple air pollutants. SEMs provide a comprehensive and rich set of tools for producing models that can capture complex interrelationships among explanatory factors and their relationships with the response (structure) and simultaneously account for autocorrelated measurement error, autoregressive (lagged and cross-lagged) effects, and irregularly timed and/or missing measurements. Additionally, SEMs which include observed explanatory variables as indicators of latent explanatory factors can avoid problems with multicollinearity. The results of using SEMs to estimate health effects of air pollutants, including chemical constituents of PM2.5, in Pittsburgh, Pennsylvania, during 2001-2002 will be presented using data from the Pittsburgh Aerosol Research and Inhalation Epidemiology Study (PARIES).

8HA.27

Oxidative Stress and the Acceleration of Atherosclerosis in Susceptible Mice After Exposure to Semi-Volatile Components of Ultrafine Particulate Matter. ANDREW KEEBAUGH, Payam Pakbin, Loyda Mendez, Zhi Ning, Glenn Gookin, Constantinos Sioutas, Michael Kleinman, *University of California, Irvine*

Exposure to ultrafine particulate matter (UF-PM) has been associated with adverse cardiovascular health effects. UF-PM contains semi-volatile organics (SVOCs) that are bound to particles but can partition to the vapor phase after emission. SVOCs contain species such as polycyclic aromatic hydrocarbons and quinones that can induce oxidative stress and may be responsible for the exacerbation of cardiovascular disease by UF-PM. Therefore, we hypothesized that the removal of SVOCs from an aerosol should decrease the ability of the particle to cause oxidative damage and consequently the acceleration of atherosclerotic plaque formation. ApoE -/- mice, which are prone to developing atherosclerosis, were exposed to UF concentrated ambient particles (CAPs), CAPs with the SVOC components removed, or SVOC components without the particle core. A control group was exposed to purified, filtered air. Particles were concentrated using a VACES, and SVOCs were separated from the particle core using a thermal denuder. The exposures took place 5 hours/day, 4 days/week for 8 weeks in downtown Los Angeles, 100m downwind of a major freeway. Plaque formation in the aortic arch and total and LDL cholesterol in the serum were measured to evaluate the progression of atherosclerosis. Serum concentrations of lipid peroxidation, protein carbonyl content, and glutathione were assessed to determine systemic oxidative stress. Aortic plaque formation in mice exposed to unmodified CAPs was higher than in those exposed to CAPs with no SVOCs. Similarly, higher levels of lipid peroxidation were measured in mice exposed to unmodified CAPs and SVOC components of CAPs compared to those exposed to CAPs without SVOCs. The corresponding trends in plaque formation and lipid peroxidation support the notion that exposure to SVOCs may contribute to the acceleration of atherosclerosis via an oxidative stress pathway.

8HA.28

Generation of Reactive Oxygen Species from Source-Oriented, Ambient Submicron Particulate Matter in a Cell-free Surrogate Lung Fluid Solution.

NICOLE RICHARDS, Jessica Charrier, Keith Bein, Anthony Wexler, Cort Anastasio, *UC Davis*

Exposure to air pollution particulate matter (PM) is correlated to adverse health effects, but the mechanisms for this effect are unclear. One proposed pathway for PM-mediated health effects is the generation of reactive oxygen species (ROS) such as superoxide radicals, hydrogen peroxide and hydroxyl radical, which can cause oxidative stress. While past studies have quantified ROS production from PM, there are no studies that correlate ROS measurements from different particle sources. To help address this issue, we collected six different source-oriented particle mixtures (e.g., cooking, vehicular, residential heating, and biomass emissions), segregated into quasi-ultrafine (≤ 170 nm) and submicron (170 – 1000 nm) size fractions, in Fresno, California during summer 2008 and winter 2009. Hydroxyl radical and hydrogen peroxide formation were quantified by HPLC from the source-oriented particles in a cell-free surrogate lung fluid containing four antioxidants (ascorbate, citrate, glutathione, and uric acid). The oxidative potential of the particles was also measured by the dithiothreitol (DTT) method. Preliminary results show that different source-oriented PM samples have different rates of hydroxyl radical formation and DTT consumption. In these studies we found, on average, no correlation between particle size and either OH formation or oxidative potential.

8HA.29

Quantification of Leakages in Respirators using Computational Fluid Dynamics.

SUVAJYOTI GUHA, Matthew Myers, Prasanna Hariharan, *Food and Drug Administration*

Masks and respirators constitute an important component of strategies for protection against hazardous bioaerosols. In order to optimally prepare for any event involving release of bioaerosols, it is advantageous to have techniques available that can quantify the reduction in risk associated with the use of a new barrier design, or with an existing barrier in the presence of a new hazard. We have begun development of a technique that utilizes computed tomography (CT) scans to identify gaps between masks and facial profiles, and computational fluid dynamics (CFD) to characterize the particle transmission through the gaps. Multiple facial profiles will be obtained for different ethnicities, for both adults and children. This poster focuses on the validation stages of the technique, where respirators were attached to flat plates with known gap profiles. CT images of the gap profiles were obtained, and a segmentation program was employed to create finite-volume meshes from the imaged gap volumes. Finite-volume CFD computations of particle transport in and around the gaps are being performed, using a “coefficient of restitution model” to treat interaction of the aerosol with the plate and respirator. The CFD code will be validated experimentally for the flat plate model using a collision type aerosol generator for producing polydispersed NaCl aerosols and a laser aerosol spectrometer for characterizing these leakages in the 100 – 1000 nm size range. In the future, both the CFD and experimental techniques will be extended to human manikins.

8IM.1

Refinement of a Particle Trap Laser Desorption Mass Spectrometer (PT-LDMS) as a Field-Deployable Aerosol Composition Analyzer. NAOKI TAKEDA, Takuma Miyakawa, Masahiko Takei, Noritomo Hirayama, Nobuyuki Takegawa, *Fuji Electric, Co., Ltd*

A particle trap laser desorption mass spectrometer (PT-LDMS) has been developed for online particle measurements of sulfate, nitrate, and organic carbon. The first prototype of the PT-LDMS, as given by Takegawa et al. (Aerosol Sci. Tech., 2012), has been used in the laboratory to demonstrate the proof of concept. Here we present the second prototype, which is aimed to be a compact, field deployable instrument (total size of 800 mm (W) x 700 mm (D) x 800 mm (H) with two 300 l/s turbo molecular pumps (TMPs), one 80 l/s TMP, and 90 l/min backup scroll pump.)

Aerosol particles collected on the particle trap are vaporized by the CO2 laser. The evolved gas is confined within a cell and introduced into the QMS. The quartz cell used in the first prototype has been replaced with a gold-coated aluminum one for easier machining and maintenance. The measurement cycle, which consists of particle collection, inlet valve closing, laser desorption, and data acquisition, can be fully automated. The nominal collection time of 7 min and analysis and buffer time of 3 min yields the time resolution of 10 min. Evaluation of the instrument performance during ambient measurements and intercomparison with other instruments will be discussed in the presentation.

8IM.2

Development of Aerosol Particle Trapping System with Signal from OPC for Particle Visualization. CHIHO KITAYAMA, Tomomi Fujioka, Takafumi Seto, Yoshio Otani, Tetsuo Endo, *Kanazawa University*

Visualization of airborne particles is a direct method to analyze the dynamic behavior of aerosol particles and it may be used to obtain the size distribution of particles, the electric charge distribution, etc. When the concentration of aerosol is high, many particles are present in a measurement volume so that we may observe the dynamic behavior. However, when the aerosol concentration is low, the probability of particle existence in the measurement volume is extremely low. In order to capture particles in a measurement volume when sampling aerosol from the ambient air of extremely low particle concentration, we developed a new particle trap system which was activated by the signals from an optical particle counter (OPC). The system consisted of an OPC, a transfer tube (inner diameter: 4.4 mm, length: 0.75 m), solenoid valves, and a visualization cell. When particles were detected by OPC, the solenoid valves at the inlet and outlet of the visualization cell were automatically closed after a certain delay time to trap aerosol particles.

The trap efficiency of system (E) is given by the product of detection efficiency of OPC (E1), the penetration through the transfer tube (E2) and the detection efficiency of visualization cell (E3). These efficiencies were individually measured using monodisperse PSL particles with diameters from 0.5 to 2.0 micro-meter. We found that E1 was nearly 100% and E2 higher than 97% for all particle sizes measured. The maximum visualization efficiency (E3) was about 40% for 2.0 micro-meter PSL particles at the delay time for closing valves of 0.6 s.

The present visualization device is a powerful tool to trap particles which are “suddenly” generated from equipment in a clean room, and we may apply various analyzing techniques to the trapped particles for determining the size, the electric charge, and even the chemical composition.

8IM.3

Use of Inertial-Filter as Sampling Inlet of CPC for Measuring Nanoparticles. CHIHO KITAYAMA, Takebayashi Masato, Takafumi Seto, Yoshio Otani, Masami Furuuchi, Takuji Ikeda, *Kanazawa University*

There is an increasing demand for measuring airborne nanoparticles in real time. Condensation particle counters (CPC) are the instruments which can measure the real-time nanoparticle concentration, however, they cannot distinguish the particle sizes. Therefore we need a sampling inlet of CPC for nanoparticles, i.e., a classifier for Dp<100 nm. Impactors are commonly used as a low-pass filter but they must be operated at a reduced pressure to attain 100 nm cutoff size, which makes it difficult to use the impactors with CPC. Recently we have developed Inertial Filter (IF) which can classify nanoparticles with a fibrous filter at a low pressure drop. In the present work, IF made of TEM grids was applied to CPC as a PM0.1 sampling inlet and the collection performance of IF was evaluated. As a result, a decrease in the collection efficiency was observed for particles larger than 100 nm due to the bounce-off of particles at a high impaction velocity (about 30 m/s), and the collection efficiency was largely influenced by the orientation of TEM grids in each layer. Coating of TEM grids with Oleic cid suppressed the bounce-off of particles, and the layering of TEM grids with a minimal overlapped area led to the maximum collection efficiency. Taking these special cautions into account, IF was found to achieve 100 nm cutoff size in aerodynamic diameter even for the sampling flow rate of 1 L/min. The applications of IF for real-time monitoring of sub-100 nm aerosol is also discussed.

8IM.4

Development of a Triggering-LIBS for Determination of Elemental Composition of Single Particles in Real Time. Kihong Park, HEESUNG LEE, Jihyun Kwak, *Gwangju Institute of Science and Technology*

The Laser Induced Breakdown Spectroscopy (LIBS) with an aerosol focusing system has been developed to measure elemental composition of atmospheric particles in a rapid manner. The LIBS uses a powerful laser and generates a microplasma to excite particles samples at the atmospheric pressure, resulting in specific emission lights depending on the elemental constituents of the sample when the excited state goes back to ground state. The emitted emission lines are then sent into a broadband spectrometer (LIBS2000+, Ocean Optics Inc., USA), and the LIBS spectra are analyzed for identification of elements and their quantification. The LIBS was successfully applied to determine a time-resolved behavior of heavy metals during Asian Dust or local pollution event in our previous studies (Park et al., 2009; Park et al., 2011). Although the previous studies provided useful insight into temporal characteristics of particles (~1hour average data after collection of particles on to substrate), a single particle detection was not achieved due to low hitting efficiency of particles by the free-firing laser. In this study, we employed a continuous wave laser (642nm, 35mW, Excelsior Laser, Spectra Physics Inc., USA) to find the exact time for a single particle to arrive at the laser focal point and to trigger the second Nd:YAG laser (1064nm, 155mJ/pulse, Surelite II-10, Continuum Inc., USA) to produce micro-plasma, leading to enhance the hitting of particles by the second laser. Various particles of size and composition were produced in the laboratory to evaluate the triggering-LIBS system. Preliminary data show that the particle hitting efficiency of the trigger-LIBS was significantly improved compared to the free-firing LIBS system.

8IM.5

Characteristics of Nano-Particle Deposition in an Air-Liquid System. KARI KUUSPALO, Ari Leskinen, Heidi Niskanen, Pasi, I Jalava, Tiina Torvela, Stefanie Kasurinen, Maija-Riitta Hirvonen, Kari Lehtinen, Jorma Jokiniemi, *University of Eastern Finland, Kuopio, Finland*

The Air Liquid system manufactured by Vitrocell Systems GmbH represents a promising way to realistically investigate the toxicity of airborne particles from different sources. The corner stone of any aerosol toxicity investigation is the dose quantification. For larger particles a quartz crystal microbalance positioned in an exposure chamber is an adequate way, but for nano-sized particles the sensitivity of microbalance can be insufficient and more detailed analysis is needed.

A tube furnace system was used to produce single mode median size of 20 nm polydisperse Ag/Ag2O-particles to investigate the particle deposition and behavior in the Vitrocell system.

The produced aerosol number size distribution was monitored online at the entrance of Vitrocell sampling system with Scanning Mobility Particle Sizer (SMPS). Diffusional losses in the Vitrocell sampling inlets were calculated and verified by means of Transmission Electron Microscopy (TEM). Deposition and the size distribution at the target area were also investigated with TEM.

In order to quantify which particles deposit to the cells and which not we have developed a particle deposition model into the commercial CFD code CFX. With the model, in addition to obtaining the detailed flow patterns in the Vitrocell, we obtain the deposition efficiency as a function of particle size.

8IM.6

Performance Evaluation of a Recently Developed Aerosol Chemical Speciation Monitor (ACSM). NEEL KOTRA, Vishal Verma, Jiumeng Liu, Sri Hapsari Budisulistiorini, Wendy Marth, Jason Surratt, Eric Edgerton, Karsten Baumann, Eladio Knipping, Stephanie Shaw, Nga Lee Ng, Rodney Weber, *Georgia Institute of Technology*

Both epidemiological and toxicological studies have found the associations between ambient particulate matter (PM) and adverse health outcomes. Recent studies have also linked PM toxicological characteristics to their chemical composition, such as organic and inorganic species. Since most of these studies rely on the statistical associations between PM constituents (or their sources) with the health effects; an accurate measurement of the ambient levels of these components is of crucial importance for establishing the appropriate cause-effect relationships.

The Aerosol Chemical Speciation Monitor (ACSM) is a recently developed instrument for measuring the atmospheric PM1.0 composition [non-refractory organic and inorganic ions such as sulfate, ammonium, nitrate, and organic matter (OM)]. The data collected from this instrument has also been used in the source apportionment studies by applying advanced analysis techniques (e.g. positive matrix factorization; PMF); however very limited studies have been conducted to compare its results with the other established methods of measurements. This study provides an intercomparison of the performance of a newly purchased ACSM (Aerodyne Research Inc.) with other online methods, such as Ion-chromatography (IC) coupled with a Particle-Into-Liquid-Sampler (PILS), thermal-optical OC EC analyzer (Sunset Labs), thermal sulfate (Thermo Scientific Sulfate Particulate Analyzer), and a denuder difference method for nitrate. Measurements were made at two sites in Atlanta and during three different seasons (Fall, Winter/Spring, and Summer) in preparation for use of the ACSM in a larger EPA-supported field campaign (SCAPE). Overall, there was a good correlation among measurements ($R2 > 0.80$) from all instruments with variability in the ratios of ACSM's measurements with respect to other instruments. For example, OM/OC ratios varied from 1.6 in Fall to 2.5 in Winter. For inorganic ions, ACSM was lower for both sulfate (>10 %) and ammonium levels (>5 %), but higher for the nitrate levels (>20 %). These comparison results are important from the perspective of validating ACSM data, and their application in the source apportionment and health related studies. The sources of this variability in the PM component levels from different measurement techniques will be further explored and presented.

8IM.7

Development and Validation of an Isokinetic Calibration System for Cross Correlation of Differing Aerosol Measurement Methodologies.

WENDY MERKLEY, Michael Wojcik, Randy Martin, Kori Moore, *Utah State University*

A multi-port calibration fixture for the cross calibration of aerosol point sensors has been developed. The system was designed for comparative calibrations of instruments using differing measurement methodologies such as optical particle counters, aerodynamic impactors, etc. Four isokinetic sampling ports are attached to a laminar flow plenum such that all four sampling ports sample identical aerosol concentrations under identical flow conditions. Correlation and correction factors are applied to each instrument, thus a standard methodology can be applied to inter-compare and calibrate aerosol sensing instrumentation and/or to characterize the microphysical properties of a test aerosol. The performance of this fixture has been demonstrated with a TSI 3321 APS, a GRIMM 1.109 and a MetOne OPC.

8IM.8

Thermal-Optical Scripts for Carbon Aerosol Analysis (TOSCAA): Software Tools for Processing and Analyzing Data from Thermal-Optical Analysis.

JOSEPH CONNY, *National Institute of Standards and Technology*

Software has been developed to process and analyze output from thermal-optical transmission analysis for elemental carbon in atmospheric aerosols. Written in Matlab[1], a series of scripts calculate several output variables derived from the instrument's[2,1] flame ionization detector (FID) signals and laser signals, in addition to overall concentrations of organic carbon (OC) and elemental carbon in a sample.

Data analysis capabilities include determinations of carbon mass for 1) Individual valley-to-valley FID peaks and for the duration of each heating step; 2) types of method-defined OC including a) volatile OC (OC evolved prior to pyrolysis in helium), b) labile OC (OC evolved during pyrolysis in helium), and c) pyrolysis OC (carbon evolved in the O_2-He phase prior to split point). Also calculated are the apparent specific absorption cross sections ($m^2\ g^{-1}$) for pyrolyzed OC and for native black carbon as determined by the method. Included are uncertainties for individual analyses and summary statistics for multiple replicates and samples.

The scripts also provide options for processing the instrument's raw data, including:
-- Manual (or automatic) adjustment of the FID baseline;
-- Options for smoothing the laser signal using the Savitzky-Golay polynomial filter;
-- Adjustment of the time point for the initial laser response used for determining the split point;
-- Corrections of the laser signal for the temperature hysteresis between the helium and O_2-He phases;
-- Correction of the laser signal for differences in the filter-induced absorption enhancement effect.

[1] Commercial products identified here specify the means by which analyses are commonly conducted. Such identification is not intended to imply recommendation or endorsement by NIST nor is it intended that the identified products are necessarily the best available for the purpose.

[2] Thermal-optical transmission analysis is typically performed with the Sunset Lab EC-OC Aerosol Analyzer.

8IM.9

A Two-Stage Versatile Aerosol Concentration Enrichment System (VACES) for Very High Concentration of Ultrafine, PM2.5 and Coarse PM. DONGBIN WANG, Winnie Kam, Kalam Cheung, Payam Pakbin, Constantinos Sioutas, *University of Southern California*

A two-stage aerosol concentration enrichment system was developed to provide highly concentrated aerosols at a low flow rates, for applications in areas such as toxicity studies of particulate matter (PM) as well as for increasing the signal-to noise ratio in on-line particle sampling instruments. The current system is a modification of the Versatile Aerosol Concentration Enrichment System (VACES) (Kim et al. 2001) and operates by placing a second-stage miniature virtual impactor (VI) after the first-stage VIs to generate an aerosol that is sequentially enriched through each stage. With a total inlet flow of 200 LPM and a final minor flow of 1.5 LPM, the theoretical enrichment factor is approximately 130.

Laboratory evaluations were conducted using various types of polydisperse aerosols to simulate the ambient PM (ammonium sulfate, ammonium nitrate, adipic acid and glutaric acid) and monodisperse polystyrene latex (PSL) particles for 100, 300, 400 nano-meter and 1 micro-meter. System configuration was tested by adjusting the intermediate flow, which is the inlet flow rate of the second-stage VI or minor flow of the first-stage VIs, of which we determined 15 LPM to be optimal. The number and mass concentration in different particle size ranges were compared using a Scanning Mobility Particle Sizer (SMPS) before and after enrichment to determine size distribution. Overall, results indicate that the aerosol is consistently enriched by factors of 100-120 (thus at an efficiency of 75-85% of the ideal value) based on both PM mass and number concentration, and without substantially altering the particle size distribution. Efficiency curves to determine the 50% cutpoint of the second-stage VI were also performed. Continuous field tests using urban ambient PM also show consistent enrichment (by roughly 110-120) for number and mass concentration, black carbon and EC/OC.

8IM.10

Field and Laboratory Evaluation of a Sequential Time Resolved Aerosol Composition Measurement Instrument. ARSINEH HECOBIAN, Arantzazu Eiguren-Fernandez, Amy P. Sullivan, Gregory Lewis, Susanne Hering, Charles Henry, Jeffrey L. Collett,*Colorado State University*

The presence of continuous data sets on chemical composition of aerosols is essential in presenting a complete picture of their spatial and temporal distributions. Such data are necessary in studying effects of aerosols on human health, visibility degradation, and other issues. A simple, compact, robust and low maintenance system for the time resolved measurement of ambient aerosol chemical composition is needed to facilitate the collection of data for use in such studies. To this end, Aerosol Dynamics Inc. developed a system where a condensation growth tube was used to collect ambient PM 2.5 aerosols. The dried particles are deposited into specialized well plates which are subsequently detached from the system, placed in an automated sampler where ion chromatography is used to measure various anion (fluoride, chloride, nitrate, phosphate and nitrate) or cation (sodium, potassium, magnesium and calcium) components of the collected aerosols. A newly improved prototype of this instrument was evaluated in this study. Various plate materials were assessed for use with this sampler. The aerosol collection efficiency, possible interferences from ambient gaseous compounds, associated uncertainties and limits of detection of this system were measured in the laboratory. Additionally, ambient measurements of the anion component of the aerosols were performed where the new instrument was compared with data from a particle into liquid sampler coupled with an ion chromatograph (PILS-IC) in laboratory and field settings. The data from the system evaluation analysis and measurements are presented here.

8IM.11

The Age Old Question: Continuous or 24-hr Integrated Measurements. Oliver Rattigan, H. Dirk Felton, Kevin Civerolo, JAMES SCHWAB, *New York State Dept. of Environmental Conservation*

PM2.5 chemical species measurements are routinely performed using 24-hr integrated methods. The measurements provide a reliable database for determining long term trends which can be used to assess the impact of emission controls e.g. SOX and NOX on fine particle concentrations downwind of sources. Since the 24-hr samples are collected on a 1 in 3 or 1 in 6 day basis due to the high cost of filter analysis, the data is best suited for annual and seasonal trends. In addition single pollution episodes and sub-daily events can be missed. In recent years commercial instruments have been developed that can measure most of the major particle species, SO4, NO3 as well as organic and elemental carbon (and black carbon) on an hourly or sub-hourly basis. The higher temporal information is used in the interpretation of varying pollutant patterns with changing emissions and meteorological conditions. High frequency wind and species data can aid in the identification of individual sources or a localized widespread source. The temporally resolved data can also help identify high concentration periods that are likely to have the greatest impact on health. The limitation of the continuous based methods is that their response factor relative to 24-hr integrated methods can differ from unity and may vary with location or season making mass closure analysis difficult. In this poster we provide examples where 24-hr integrated data is useful and examples where continuous measurements are beneficial.

8IM.12

Method Development for Determination of Trace Concentrations of Aldehydes and Carboxylic Acids in Particulate Matter.JANA ROUSOVA, Manikyala R. Chintapalli, Anastasia Lindahl, Jana Stavova, Alena Kubatova, *University of North Dakota*

Carboxylic acids and aldehydes are present in ambient particulate matter originating from both primary and secondary organic emissions. Within secondary atmospheric reactions aldehydes readily oxidize to acids as well as participate in reactions with acids leading to formation of polymers. The activity of these reactive species in atmospheric processes demonstrates a need for their accurate determination. A common approach addressing both carbonyl and carboxylic functional groups employs O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) in sequence with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA). In this approach PFBHA is usually dissolved in water, which requires labor evaporation of particulate matter extract prior to derivatization, and labor intensive extraction of derivatized species. Therefore, in this work we have adopted a PFBHA/BSTFA protocol using PFBHA dissolved in methanol followed by gas chromatographic mass spectrometric analysis. A broad range of species with various functionalities (~35) was studied, including long chain monocarboxylic acids, dicarboxylic acids, aromatic acids, ketoacids and hydroxyacids. Unfortunately, both methyl and trimethylsilyl esters were observed upon initial derivatization with PFBHA/BSTFA rendering difficult species' identification. We have resolved this issue by adjusting the PFBHA derivatization method, a complete methylation was achieved for majority of acids with exception of aromatic acids. The derivatization of aromatic acids and species with hydroxy groups was then completed with BSTFA. The advantage of the proposed protocol is the initial methylation of carboxylic acids (in contrast to trimethylsilylation) and thus easier MS interpretation without initial interference from numerous hydroxy groups.

8IM.13

The Potential of Bio-nanoparticles as Standard Reference Materials for Mobility Calibration. MINGDONG LI, Suvajyoti Guha, George Mulholland, Michael Zachariah, *University of Maryland, College Park*

Nanotoxicology studies, nanobiotechnology research and aerosol technology studies are often restricted by a lack of accurate physical and chemical characterizations of the nanoparticles under study. One such attribute is accurate determination of the particle size. Standard reference materials with accurate and precise size characterization play a key role for attaining comparability of results among laboratories. Commonly used reference materials are PSL nanoparticles and gold nanospheres. However, we have found that some stable bio-nanoparticles such as some viruses, are more monodispersed, and highly concentrated than some current standard reference particles. These highly-duplicated bio-nanoparticles have the potential to be new standard reference materials.

8IM.14

Generation of Aerosol Particles of Controlled Mixed Composition. VASANTHI SIVAPRAKASAM, John Tucker, Jay Eversole,*Naval Research Laboratory*

In arenas where aerosol particles need to be delivered onto surfaces of sensors as in explosive detection research, bigger aerosol particle generation is preferred so as to maximize deposition and avoid the exitence of aerosol with the air flow. When the concentration of analytes need to be kept low it is not feasible to scale up the aerosol size. One method to overcome this predicament is to increase the particle size by adding an inert component to the particle. This would permit a continuously adjustable range of analyte mass delivered by each particle and the particle size can be controlled by the amount of inert material added. We proposed to use PSL, glass or PMMA bead as the inert material and homogenous material like ovalbumin, NaCl and Kaolin as the analyte for feasiblilty test purposes.

We were successfully able to produce aerosols composed of dye-doped Pmma and ovalbumin using 2 types of generators from Sonitech and Microfab. The particle generator from Microfab is capable of producing particle on demand to greater than 3000 particles/sec. By measuring the fluorescence spectra of the particles on-the-fly we were able to establish that the particles were composed of the two materials at expected concentrations. While holding the concentration of the inert material constant, we were able to vary the concentration of the analyte to produce varying size particles.

8IM.15

Performance Analysis of a High-Flow Dual-Channel Differential Mobility Analyzer (HD-DMA). ISHARA HUNGAMA MUDALIGE, Meilu He, Praney Dubey, Suresh Dhaniyala, *Clarkson University*

For size distribution measurements over a broad diameter range and with a high sample flow rate, a new high-flow dual channel differential mobility analyzer (HD-DMA) instrument design was recently designed. This electrical-mobility classification instrument has two sample ports and operates at relatively high flow rates (sheath flow ~100-300 lpm and sample flow ~ 20 lpm) while maintaining a low Reynolds number (~500) in the classification region. The reduced particle residence time in the classifier associated with the high sheath flow, enables fast scan operation with this instrument (Dubey and Dhaniyala, 2008). Classical performance characteristics of the HD-DMA, e.g., classification accuracy, precision, and particle penetration efficiency were previously established and the HD-DMA has been deployed for both airborne measurement campaigns and ground experiments. While the instrument's performance matches theoretical predictions for classification diameters and the resolutions are only ~ 75% of theoretical expectation. This presentation will highlight our recent efforts to further characterize the instrument performance, particularly to understand particle penetrations as a function of aerosol to sheath flow ratios and to accurately determine residence time of particles in the HD-DMA and their relation to fast-scan smearing artifacts. Inversion errors associated with incorrect assessment of residence time will be demonstrated to highlight its importance in fast scan measurements.

8IM.16

Comparison of Two PM Inlets for Improved Airborne lead Sampling. QUENTIN MALLOY, Andrew Dart, Jonathan Thornburg, Robert Vanderpool, April Corbett, *RTI International*

The High Volume Total Suspended Particulate (TSP) sampler, currently deployed by the US EPA, has long been recognized as a hindrance to accurate and precise assessment of ambient exposure for the Pb NAAQS. Long-standing limitations of this method include variations in size-selective performance (cutpoint and slope) as a function of wind-speed and direction, variable sampler dimensions and flow rates, poor precision, particle collection during non-sampling periods, and the filter's lack of suitability for conducting multi-element analysis and/or using other analytical techniques (e.g., XRF) The goal of this research is to determine size selective performance of candidate Total Suspended Particulate (TSP) samplers as a function of particle size and wind speed.

A low volume TSP (LVTSP) and an EPA dichotomous sampler (EPA TSP) with the internal fractionation stages removed were challenged at wind speeds of 2, 8 and 24 km/hr with 5, 10, 15 and 20 micrometer diameter particles. An Isokinetic sampler was utilized as the reference sampler. At 24 km/hr, the LVTSP consistently displayed lower efficiency than the EPA TSP sampler when compared to the reference inlet with average efficiencies of 21.7% as compared to 69.1% across all particle sizes tested. This pattern remained at wind speeds of 8 and 2 km/hr as well. It is worth noting however, the EPA TSP inlet several times reported efficiencies over 100%.

8IM.17

An Intercomparison of Airborne Aerosol Inlet Performances During ICE-T (2011) campaign. Arash Moharreri, Lucas Craig, David C. Rogers, SURESH DHANIYALA, *Clarkson University*

There are several different designs of aerosol inlets being used by researchers for aerosol sampling from aircraft platforms. While each inlet design is intended to provide a suitable sample for its corresponding instrument, knowledge of their relative efficiency in sampling particles must be known prior to any successful intercomparison of their results. As a simple measure of the relative performance of the different instruments, the total particle concentration (or CN) from different inlets can be compared under different flight and atmospheric conditions. Since most aerosol inlets have cut-sizes greater than 1 micron, and the total particle number concentrations are often dominated by sub-micron particles, the CN intercomparison provides a first measure of inlet measurement consistency. Such an intercomparison is particularly critical in determining the relative performance of inlets in cloud systems. The high speed impaction of ice particles and liquid droplets on the surfaces of the aircraft probes/inlets results in the generation of artifact particles that contaminate aerosol samples to extents that differ with inlet designs. During the ICE-T campaign (2011), three aerosol inlet designs were installed on the NSF/NCAR C-130 aircraft by Clarkson University and NCAR/RAF: BASE (Blunt-body Aerosol Sampler), HiCAS (High-speed Cross-flow Aerosol Sampler), and two SMAIs (Sub-Micron Aerosol Sampler – one operated by Clarkson and the other one by RAF). Analysis of total CN data from the inlets, suggests that the BASE samples are the least contaminated by artifact particles when sampling in cold clouds. The BASE performance, however, demonstrates a tractable dependence on phase, size and habit of cloud particles present. In warm clouds, the SMAI operated by Clarkson team showed the best performance in terms of avoiding the sampling artifacts associated with the droplet splashing phenomenon. Complete details of the different inlet designs and their measurements and relative performance will be discussed.

8IM.18

Aerosol Growth Rate Calculations from HTDMA Data: Sensitivity to Operating Conditions and Quality of Inversion Algorithm. RAGHAV RAMAN, Meilu He, Suresh Dhaniyala, *Clarkson University*

The hygroscopic tandem differential mobility analyzer (HTDMA) is a popular technique to measure changes in size of airborne particles when exposed to high humidity. Growth rate calculations from HTDMA measurements can be used to obtain equivalent bulk particle compositions and help differentiate a sample's constituents in an external mixture. The determination of growth rates from HTDMA measurements is strongly dependent on the accuracy and precision of aerosol classification with the two DMAs in the system, the humidity control throughout the system, and errors in the inversion of TDMA data. To understand the uncertainty in growth rate calculations as a function of operating conditions, a numerical modeling study is conducted. In this study a wide variety of aerosol size distributions and mixtures are considered and non-idealities in the operation of DMAs and the growth chamber are accounted for. The TDMA data is inverted considering different particle charging scenarios and inversion algorithms. The numerical modeling results help illustrate the sensitivity of particle growth factor calculation to operating conditions and choice of inversion algorithms. Detailed results from the modeling study will be presented and implications for HTDMA operation and data analysis will be discussed.

8IM.20

Physico-chemical Assessment of Biodiesel Vehicle Fuel Exhaust Emissions and the Effect of New Emission Control Devices: The EMITTED Study. NAOMI ZIMMERMAN, Krystal J. Godri, Terry Jung, Cheol-Heon Jeong, Josephine Cooper, James S. Wallace, Greg J. Evans, *SOCAAR, University of Toronto*

Diesel emissions from vehicles may be controlled using tailipipe fitted technologies including diesel oxidation catalysts (DOCs) and diesel particulate filters (DPFs). Emission control technologies primarily target regulated pollutants (e.g. particulate matter, PM; NOx); however, reaction products of other emitted, and potentially toxic, species are poorly characterized, in particular for new diesel fuel types. The EMITTED study comprehensively characterised the physical and chemical properties of particulate and gaseous biodiesel exhaust with the objective of assessing contrasting emission characteristics with respect to adverse biological responses to elucidate toxicologically relevant emission parameters.

An off-road direct injection diesel engine (Cummins B3.9, 1997) was operated under modes 2 and 9 of the ISO8178 emission test cycle. Emissions were generated using a 20/80 blend of biodiesel, either soy (NEXOL BD99.9) or animal-based (Rothsay), and a commercially available ultra-low sulphur diesel fuel. Measurements were taken upstream and downstream of the separate DOC and DPF units to isolate their individual effect on resultant physico-chemical particulate properties.

Exhaust emissions were characterised along three sampling lines: 1) real-time measurement of gaseous regulated (NOx, CO2, THC, O2, CO2) and unregulated (CH2O, N2O, SO2, NH3) pollutants with a MKS MultiGas 2030-HS; 2) collection of a liquid impinged PM solution for measurement of toxicologically relevant organic (polycyclic aromatic hydrocarbons, quinones) and metal species; and 3) dilution in a rotary disk thermodiluter (TSI 379020A) for real-time determination of particle size distribution from 5.6 to 560 nm (TSI EEPS 3090 and TSI FMPS), black carbon mass concentration (DMT PASS-3, Magee AE-21), and non-refractory particle chemical composition (Aerodyne ACSM). The latter particle sampling line was additionally operated with a thermodenuder (Dekati) to assess the contribution of volatile components to exhaust measurements.

This ongoing study will support the development of improved emission control systems, and identify toxicologically relevant parameters for future emissions regulation.

8IM.21

The USEPA Coarse PM Pilot Speciation Study. HILARY MINOR, Jay Turner, Steven Brown, Paul Roberts, Joann Rice, *Sonoma Technology, Inc.*

The U.S. Environmental Protection Agency is continuing to explore the development of a speciation monitoring program for ambient coarse particulate matter (PM_c) with multiple objectives, including the collection of data for health studies and source apportionment. Limited PM_c speciation monitoring has been conducted in the past, and most such monitoring has mimicked the conventional $PM_{2.5}$ speciation network field sampling and analytical techniques. These $PM_{2.5}$ measurement techniques may not be optimal for PM_c monitoring. Therefore, a pilot study was conducted from May 2010 to May 2011 at two sites to inform the development of PM_c sampling and analysis protocols. 24-hour integrated samples were collected nominally every third day at the 43rd Street site in Phoenix (PHX) and the 13%^(th) Street & Tudor Avenue site in East St. Louis (ESL). The measurement platform included: four Thermo 2025 series sequential samplers at each site – a $PM_{2.5}$ FRM, a PM_{10c} FRM and two dichotomous samplers (dichots); a MOUDI cascade impactor; and a Thermo 1405DF FDMS TEOM. Filter sandwiches of either Nylon-behind-Teflon or quartz-behind-quartz were used in the FRM and dichot samplers with routine analysis for gravimetric mass, elements by XRF, ions by IC, and OC/EC by TOR.

This poster will summarize key findings, including comparisons between the dichots and FRM by difference for gravimetric mass and individual species, dichot collocated precision, and mass balance closure. Results will also be presented for additional analyses, including ICP-MS, carbonate, organic speciation, and biological markers. In particular, the ICP-MS data are used to assess self absorption-induced biases in the XRF measurement of light elements. Finally, preliminary results will be presented for a follow-up study conducted in spring 2012 at Research Triangle Park evaluating changes that were made to the dichot by Thermo to obtain FEM designation.

8IM.22

Influence of Electrode and Carrier Gas Characteristics on the Measurement of Elemental Concentration of Aerosols Using Spark Plasma Spectroscopy. Prasoon Diwakar, PRAMOD KULKARNI, *Centers for Disease Control and Prevention, NIOSH*

We have recently reported on the development of an aerosol preconcentration method that allows near-real-time measurement of elemental concentration of aerosols using spark plasma spectroscopy (J. Anal. At. Spectrom., DOI:10.1039/C2JA30025G) at absolute mass detection limits in the range of 11 pg-5 ng. The method involves collection of aerosol on a tip of 500 µm tungsten electrode, followed by ablation and atomization by a pulsed spark plasma and detection of emission spectra. This study further probes the effect of electrode size (100, 250, 500 µm) and material (W, Pt, Rh), and the type of carrier gas (He, N, Ar) on the sensitivity and detection limits of our method. Results suggest that the smaller diameter electrodes result in a greater analyte signal enhancement; the 100 µm electrode gave an enhancement of a factor of 2 over 250 µm electrode. Carrier gas perhaps had the strongest influence on the signal. For a 100 µm electrode, the absolute analyte signal intensity increased by a factor of 2.5, 4, and 10, compared to that in air, when the carrier gas was He, N, and Ar respectively. Ar resulted in maximum enhancement in signal intensity (factor of 10) resulting in improved sensitivity of the technique; however also resulted in higher background intensity. No significant effect on signal intensity was observed for different electrode materials. Detection limits in sub-picogram levels can be achieved for many elements by employing 100 µm electrode in Ar carrier gas. Measurements of electron density and excitation temperature are presented and atomic emission enhancement mechanisms are discussed.

8IM.23

Corona-assisted Microwave Plasma Spectroscopy for Spectrochemical Analysis of Aerosols. PRAMOD KULKARNI, Philip Efthimion, *Centers for Disease Control and Prevention, NIOSH*

A new approach employing microwave-induced plasma assisted by localized non-thermal dc corona has been developed for near-real-time elemental analysis of aerosols. The technique involves preconcentration of aerosols for a predetermined period of time on the tip of a microelectrode located at the center of a reentrant-type microwave cavity, followed by introduction of pulsed microwaves (2.45 GHz, 3 kW). The presence of the electrode in the cavity concentrates the electromagnetic field on its tip, subsequently leading to formation of microwave-induced plasma, which ablates and atomizes the particulate matter deposited on the microelectrode tip. The resulting atomic emissions are recorded using a broadband optical spectrometer for element identification and quantification. To improve the reproducibility of the microwave plasma, a stable dc corona is introduced on the tip of the microelectrode which provides additional seed electrons for effective coupling of microwaves. This drastically improves repeatability and stability of the plasma. Lifetime of the microwave plasma was in the range of 5-10 ms, which is orders of magnitude larger than that for laser-induced or sparks plasmas of comparable power density, and leads to significantly higher signal intensities. The system was calibrated using mobility-classified aerosols of various analytes. Sensitivity and limit of detection of the method will be presented and implications for near-real-time analysis of aerosol will be discussed.

8IM.24

Testing of a Battery Powered Data-Logging TSI Water-Based Ultrafine CPC for Mobile Outdoor Use. ASHISH SINGH, Robert Bullard, Charles Stanier, *University of Iowa*

An Ultrafine Water-based Condensation Particle Counter (UWCPC-3786, TSI) was modified for battery operation and use of a data logger and global positioning system (GPS). These modifications allow the use of CPC as outdoor mobile particle counter. The major modifications will be presented in detail, including the selection of batteries, battery housing, wiring, and charging procedures for 12 volt DC operation. Additionally, integration of the portable data logger (Campbell Sci. CR 850) for data collection and GPS will be presented. CR (Campbell recorder) basic programming language was used for communication with the CPC using PC 400 version 1.4 through the RS-232 port. The total hours of operation of CPC under battery power achieved (including the initial warm up period) ranges from 1-1.3 hrs. Battery configuration was two 5 cell packs connected in parallel; individual nickel metal hydride cell (NiMH) was rated at 1.2 V and 2.5 Ah.

For data quality assurance, parallel runs between the modified UWCPC-3786 and UWCPC -3785 with mono-disperse aerosols were conducted. The testing also included mobile sampling at different traffic density areas in Iowa City.

8IM.25

Negative-ion Electrospray as an Ion Source for Chemical Ionization Mass Spectrometry of Atmospheric Gaseous Inorganic/organic Acids and Clusters. JUN ZHAO, Coty Jen, Modi Chen, Michael J. Lawler, Peter McMurry, James N. Smith,*University of Minnesota*

Electrospray ionization has been widely employed as an ionization technique in mass spectrometry for chemical analysis of organic compounds, especially biological macromolecules. Another ionization method, ionizing radiation, which provides a stable source of reagent ions, has typically been employed for chemical ionization mass spectrometry of trace atmospheric compounds. Hazards associated with the use of radioactive sources and difficulties with obtaining permits to transport equipment and to operate in the field provide obstacles to this approach. In this work, we present an alternative chemical ionization source that utilizes negative-ion electrospray of acetic acid or nitric acid solutions to produce primary acetate or nitrate cluster ions. A high resolution differential mobility analyzer (HRDMA) coupled to a sensitive electrometer was employed to classify the ions generated from electrospray of the above solutions. A series of inorganic (e.g., sulfuric acid and nitric acid) and organic acids (e.g., formic acid and malonic acid) were tested to investigate the effects of the solvents and multiple charging on the efficiency of chemical ionization. Oxidation products from ozonolysis of monoterpenes in chamber and flowtube experiments were measured with this ionization technique. The advantages and disadvantages of electrospray ion sources will be also discussed.

8IM.26

State-of-Art Toolbox for High Resolution De-convolution of Ion-Cluster Signal from Time-of-Flight Mass Spectrometry Data. HEIKKI JUNNINEN, Gustaf Lönn, Mikael Ehn, Siegfried Schobesberger, Tuukka Petäjä, Douglas Worsnop, Markku Kulmala,*University of Helsinki*

Recent developments in atmospheric measurement techniques that include a time-of-flight mass spectrometry (TOFMS) as a mean for separation and detection are increasing in number. Many of the application share the same mass spectrometer that is customizable for a specific needs and has been proven to be robust enough even for a field measurements. The TOFMS has the resolution power of 3000 to 6000 Th/Th, has mass accuracy less than 20 microTh/Th, and is built by Tofwerk AG.

Examples of application that are commercially available or built by research groups are; atmospheric pressure interface TOFMS (APiTOF - for measuring ambient ions), atmospheric pressure chemical ionization (NO3-CI-APiTOF - for sulphuric acid detection with nitrate ionization; H-CI-APiTOF – proton transfer for amine and ammonia detection), reduced pressure chemical ionization (Ac-CI-APiTOF – acetic acid ionization for detection of weak acidic molecules; PTR-TOF – proton transfer for VOC detection), aerosol instruments (TD-CIMS, thermal desorption aerosol collection of 10-30nm particles, laser-AMS – for laser desorption of 10-30nm particles, MOVI-CIMS – simultaneous sampling of aerosol and gaseous sample).

Common for the all techniques listed above is the same mass spectrometer and the same data format and thus, the same data analysis requirements and needs. Work presented here provides common tools for initial steps of data analysis of time of flight mass spectrometry data. Each sampling and ionization technique has a specific post-processing and calibrations but the raw data acquired by the mass spectrometer is the same for all.

Toolbox presented here features all the essential steps required for high resolution data analysis, including custom time averaging and filtering of raw data, robust mass calibration, defining instrument parameters, unit mass resolution stick calculations and high resolution peak fitting. The later includes custom peak shape and isotope locking. In the presentation these steps will be explained in detail and real world examples will be used to illustrate the process.

8IM.27

Drift Tube Ion Mobility Spectrometry of Sub-10 nm Nanoparticles. DEREK OBERREIT, Peter McMurry, Christopher Hogan Jr.,*University of Minnesota*

A new drift tube type Ion Mobility Spectrometer (DT-IMS) designed specifically for aerosol particle measurements from ambient environments is presented. DT-IMS devices allow for determination of the electrical mobility of a charged particle through measurement of the time necessary for a particle to travel a fixed distance through a tube in the presence of an electrostatic gradient. These instruments have traditionally been limited to measurements of ionized molecules and small (~1 nm) charged clusters. Previously developed devices are not able to sample charged aerosol particles from the ambient because of the high electric fields present at the beginning of the drift region. An additional limitation of existing DT-IMS devices is the low sensitivity of the Faraday Cup Electrometers at concentrations found in typical aerosols. Conversely, DT-IMS devices have the advantages of mobility invariant high resolving power (>R~20), low drift gas flow rates compared to DMA sheath gas flowrates and shorter measurement times as compared to most scanning differential mobility analyses.

The modifications to traditional DT-IMS devices required for application ambient aerosol measurement include a novel gateless sample introduction scheme, and the ability to couple to an aspirating Condensation Particle Counter (CPC), which is able to detect single particles. The gateless sample introduction uses a combination of a controlled flow path and stepped voltage at the start of a measurement to effectively select a 'packet' of aerosol. Additional aerosol is not able to enter the sample region after the start of a measurement due to the presence of an electrostatic field. The coupling to a CPC requires a controlled flow that splits to provide the drift gas and the gas aspirated by the CPC. A prototype device was built and tested. The device has a linear relationship between drift time and mobility and a resolving power greater than ~10. Measurements of proteins show good peak separation and compare well to DMA measurements.

8IM.28

Comparing Two Laser Ablation Time-of-Flight Aerosol Mass Spectrometers. SOEREN ZORN, Klaus-Peter Hinz, Tabitha Schwinger, Philip Croteau, Alois Fendt, Bernhard Spengler, Douglas Worsnop, John Jayne, Achim Trimborn, *AeroMegt GmbH*

Mass spectrometry has become a very powerful tool for the analysis of the atmospheric aerosol. Modern on-line instruments offer not only a very high time resolution with sampling intervals down to seconds and essentially real-time analysis of the chemical and physical parameters of aerosol particles but can also be deployed with little effort at very remote locations.

Currently two types of aerosol mass spectrometers either based on thermal desorption electron ionization or laser desorption ionization are commonly used.

Most aerosol mass spectrometers using thermal desorption electron ionization are based on a common instrument platform and because of this, results from these instruments can generally be easily compared.

For laser ablation instruments the situation is more complex. Many such instruments are individual builds. Besides the differences in construction the lasers used for the ablation of particles in the individual instruments differ in wavelength as well as in pulse energy. This makes a comparison of results from various laser desorption ionization instruments more difficult. Here we present a comparison of two laser ablation instruments. A newly developed, very compact single particle mass spectrometer (LAAPTOF; AeroMegt GmbH) that is commercially available is compared to a custom built system (LAMPAS 3, University of Gießen). For the comparison of the two instruments we used a test set of aerosols comprised of several different chemicals. All test aerosols were dried prior to sampling. Additionally, spectra for each chemical makeup were recorded at different pulse energies for the ablation laser, to investigation the variability as well as the wavelength and energy dependence of the resulting ions and spectra.

The results allow not only a direct comparison of both instruments for the tested compounds but can be also applied to field measurements as well as show the best instrument configuration for intercomparison.

8IM.29

Online Chemical Characterization of Sub-micron Organic Particles Using Direct Analysis in Real Time Mass Spectrometry (DART-MS). THEODORA NAH, ManNin Chan, Stephen R. Leone, Kevin Wilson, *University of California, Berkeley*

A major fraction of atmospheric aerosols is made up of organic matter. Once airborne, organic aerosols can undergo oxidation reactions (termed "aerosol aging") with gas phase oxidants such as ozone, nitrogen oxides, and hydroxyl radicals, resulting in changes to their chemical composition. On-line aerosol mass spectrometry (AMS) is an important tool for aerosol aging studies due to its high sensitivity and ability to analyze the chemical composition of aerosol particles in real time. Although a variety of AMSs with different ionization techniques are currently being used in field and laboratory aerosol studies, they all generally involve the complete vaporization of the particle before ionization, thus yielding a mass spectrum representative of the entire particle (i.e. bulk composition). However, there may be structural and chemical inhomogeneities within the aerosol particle that may play a significant role in controlling the oxidation rate and mechanism. Chemical reactions may also occur either at the surface or in the bulk of the particle during the aerosol aging process to produce a variety of reaction products located at different regions of the particle interface.

Direct analysis in real time mass spectrometry (DART-MS) is an ambient mass spectrometric surface characterization technique that can analyze gaseous, liquid and solid polar and non-polar samples without prior sample preparation. Here, we report the real time chemical characterization of sub-micron aerosol organic particles using DART-MS. Aerosol particles are introduced between the DART ion source and the atmospheric interface inlet of a mass spectrometer where the outermost surface layers of the aerosol particles are thermally desorbed, ionized and analyzed by a mass spectrometer. Organic particles containing molecules of different chemical functionalities are detected with reduced molecular ion fragmentation, allowing for easy identification. Measurements show that the ion signal generated by DART-MS scales with total particle surface area, thus suggesting that DART-MS is able to measure the chemical composition of the particle interfacial region. DART-MS can also be used to identify products and quantify reaction rates in aerosol aging reactions. This is demonstrated by the use of DART-MS in the ozonolysis of sub-micron oleic acid aerosol particles. Together these measurements indicate that DART-MS is a promising online chemical characterization technique for aerosol studies.

8IM.30

Toward In-Situ Characterization of Aerosol Optics with a Supercontinuum Light Source Covering Most of the Solar Spectrum. Ian Arnold, HANS MOOSMULLER, Noopur Sharma, Claudio Mazzoleni, Patrick Arnott, *Desert Research Institute*

The ongoing development of a novel Photoacoustic Aerosol Light Absorption and Albedo Spectrometer (PALAAS) for real time, in situ, first principle measurement of aerosol light absorption, scattering, and single scattering albedo spectra is discussed. This instrument utilizes a novel broadband supercontinuum light source covering the solar spectral range from 400 to 2000 nm for simultaneous measurement of aerosol light absorption and scattering coefficients and aerosol single scattering albedo. Initial work has demonstrated the use of this light source in combination with multiple bandpass filters for the measurement of absorption and scattering coefficients. Currently, we are working toward the simultaneous measurement in 32 spectral bands, thereby increasing the number of bands by about one order of magnitude over state-of-the-art three-wavelength photoacoustic instruments. Simultaneous absorption and scattering measurements in these 32 bands will be enabled by using prisms to (1) spatially separate the super continuum spectrum, (2) modulate each spectral band at an individual acoustic frequency with a custom optical chopper, (3) recombine the spectrum into a laser beam, and (4) send the laser beam through a photoacoustic resonator. Measurements of the scattering coefficient with a scattering sensor in the photoacoustic instrument and the absorption coefficient with the photoacoustic instrument can be achieved for all 32 wavelength bands simultaneously by decoding modulation frequencies with fast Fourier transform (FFT) analysis. This instrument will be used for characterizing carbonaceous aerosol optics, visibility impairment, and radiative forcing by providing real time, in situ, first principle measurements of aerosol light absorption, scattering, and albedo spectra covering most of the terrestrial solar spectrum.

8IM.31

Estimating the Primary Particle Size of an Agglomerate Using APM and SMPS. MIKA IHALAINEN, Terttaliisa Lind, Jorma Jokiniemi, *Paul Scherrer Institut, Switzerland*

Evaluating the size of the primary particle in an agglomerate traditionally requires the use of the microscopy methods. Being able to measure the primary particle size online would make the analysis not only much faster but also cheaper. One possible approach to tackle the problem could be the measurement of size dependent effective density of the agglomerates and utilising it in addition to the bulk density of the agglomerate material to estimate the primary particle size.

The method to estimate the primary particle size was the following. An aerosol particle mass (APM) analyzer combined with a scanning mobility particle sizer (SMPS) was used to calculate the size dependent effective density of the agglomerates. The relation between the electrical mobility diameter and the effective density could be described with a power law. An asymptotic extrapolation was then made to see at which electrical mobility particle size the effective density would reach the bulk density of the material and, thus, revealing the primary particle size. The method assumes that the power law relation between the electrical mobility and effective density holds over the size range from the size of the primary particle to the agglomerate size and that the size distribution of the primary particles is monodisperse.

TiO2 agglomerates of different primary particle diameter were generated through chemical vapor synthesis to test the described method. Transmission electron microscopy (TEM) was used as a reference method to measure the primary particle sizes. The preliminary results show that for the primary particle sizes 37, 26, 22 and 10 nm measured with the TEM while the APM-SMPS system gave 43, 27, 23 and 5 nm, respectively. The results show that while there were variations in the primary particle size results measured with the APM-SMPS system compared to the TEM method, it still gave reasonably good estimations of the primary particle size.

8IM.32

Potential Effects of Agar Plate Volume on Bioaerosol Impactor Measurement Accuracy. JENNIFER THERKORN, Gediminas Mainelis, *Rutgers, The State University of New Jersey*

Understanding how agar volume in bioaerosol impactors influences the efficiency of microorganism collection and preservation of their viability may lead to more efficient bioaerosol sampling. Optimizing sampling efficiency of impactors can allow for more accurate estimation of bioaerosol concentrations. Therefore, this research investigated how varying plate agar volume in impactors may affect accuracy of measured bioaerosol concentrations. The BioStage Impactor (SKC Inc., Eighty Four, PA), a single-stage Andersen N6-equivalent, was used to sample bacterial aerosols generated in a laboratory test chamber while the amount of agar in the sampler varied – 20, 35, or 50mL. These bacterial aerosols included a hardy (Bacillus subtilis) and sensitive (Escherichia coli) species. Using a BioStage Impactor as a reference with constant agar volume, outdoors sampling was also performed for both bacterial and fungal bioaerosols with varying agar amounts in a second BioStage Impactor, the Sampl'air (AES-Chemunex Inc., Princeton, NJ) and the SAS Super 180 (Bioscience International, Rockville, MD) impactors. For laboratory experiments with E. coli and B. subtilis, single factor ANOVA resulted in statistically significant differences in number of colony-forming units between the 20, 35, and 50mL volumes of agar (p-value < 0.05). Post hoc Sheffe's test showed that 20mL agar volume resulted in statistically significantly fewer E. coli colony-forming units than tests done with either 35mL or 50mL of agar. Preliminary results with B. subtilis suggest an opposite trend with 50mL agar volume producing the lowest number of colony-forming units. In general, for bioaerosols in the laboratory and outdoors, trends could be seen of increasing colony-forming units as agar volume is adjusted to 35mL. This suggests there may be an optimal volume of agar for which there is both sufficient removal of biological particles from the airstream as well as increased maintenance of collected microorganism viability.

8IM.33

Bipolar Neutralization of Spherical Particles <23 nm using Radioactive, X-ray and AC Corona Methods. JACOB SWANSON, Jean de La Verpilliere, Adam M Boies, *University of Cambridge*

Many methods of particle size and concentration measurement rely on the knowledge of the distribution of charges such particles have acquired after a charging or neutralization process. Variations in neutralization techniques may lead to different charging characteristics and other parameters such as particle size, shape, composition, concentration, and ambient air properties impact the charging process.

In a typical neutralizer, particles pass through a cloud of ions and acquire a steady state distribution of charges that is slightly asymmetrical. Many techniques are available to generate these ions but this work focuses on radioactive sources (10 and 2 mCi 85Kr, 3077 TSI, Inc), X-rays (3087 Soft X-ray Charger, TSI, Inc), and corona discharge (1090 Electrical Ionizer, MSP Corp). These methods differ in the way they ionize the surrounding gas. For example, the de-facto standard, 85Kr, emits highly energetic beta particles. On the other hand, the x-ray charger generates energy x-rays (<9 keV) and the electrical ionizer uses corona discharge operated with AC voltage to generate positive and negative ions.

The objective of this work is to better quantify the impact of these neutralization techniques and aerosol composition on the neutralization process. A series of experiments were conducted using solid silver particles <23 nm. For all experiments, the four chargers were operated using a realistic aerosol flowrate of 1.5 L/min. Carrier gas composition was varied to examine the sensitivity of charging to aerosol chemistry. Carrier gases included dry nitrogen, humidified nitrogen, humidified air, humidified air with sulfur dioxide, and dry argon. For each neutralizer and carrier gas condition the ion mobility distribution, particle charged and neutral fractions, and the particle size distribution were measured. Overall, results obtained from these measurements provide further insight into the nature of particle charging for very small particles.

8IM.34

New Detection Method of Filter Leak using the Schlieren Shadow-graph Technique. SHIGERU KIMOTO, Lin Li, Joseph Peterson, David Pui, *University of Minnesota*

There are several detection methods for filter leak (e.g., scanning, fluorescence, particle image velocimetry, thermal imaging, etc). For aerosol related methods, particles passing through the leakage at the filter can be detected by a scanning probe connected to a particle counter to locate the leakage, or by Particle image velocimetry (PIV), obtaining the flow speed and direction using the scattered light from particles. In the fluorescence detection, a UV light source is used to examine the filter bags for leaks, and wherever there is a leak, the tracer powder will glow brightly under the detector lamp. However, the aerosol methods are usually time consuming and particles are loaded on the filter, which is avoided in some applications and test environment. The imaging methods, e.g. thermal imaging using infrared radiation to form an image and Schlieren shadow-graph technique, have the advantage of visibility, quick response, simplicity and prevention of particle loading.

In this study, we use the Schlieren shadow-graph technique for filter leak detection. Schlieren technique uses light from a single collimated source shining on or from behind a target object (the space downstream of the filter). Variations in refractive index caused by density gradients in the fluid distort the collimated light beam, creating a spatial variation of light intensity, which can be visualized directly. Filters with different pinhole sizes are evaluated and the detail results will be presented in the conference.

8NM.1

Fabrication of Micron Sized Porous Silicon Particles from Silicon Kerf Loss. HEE DONG JANG, Dae-Sup Kil, Hankwon Chang,*Korea Institute of Geoscience and Mineral Resources*

As the semiconductor and photovoltaic industry are going through rapid growth, a large amount of silicon sludge is generated from cutting process of silicon ingot in Korea. Recently, recovery of silicon powder from the sludge has been of great concern because the silicon sludge contains valuable resource such as high purity silicon. In the present study, we investigated the fabrication of micron sized porous silicon particles from silicon kerf loss that mainly composed of silicon carbide and silicon particles. After removing metallic impurities by acid leaching, the silicon particles higher than 99.9% in purity were recovered from the colloidal mixture of silicon and silicon carbide by applying ultrasonic wave and centrifugation. Then, porous silicon particles less than 5 micron in average diameter were prepared from colloidal solution of silicon particles by aerosol spray drying. The porous silicon particles are expected as a raw material of silicon ingot of ultra high purity.

8NM.2

Inhibition of Thermal Charging of Gold Nanoparticles by Surface Modification. CHI-TUNG CHIANG, Jeffrey Roberts, *Purdue University*

Thermal charging of gold aerosol nanoparticles (AuNPs) at high temperatures (>600 degrees C) has been known for over a decade. However, the mechanism for formation of multiply charged states is still not well-understood. In this work, the surfaces of mobility-selected AuNPs were chemically modified with organic functional groups, as a way of studying the mechanism for charging. AuNPs were generated by a home-built heating well in which gold pieces were placed in an alumina-coated tungsten wire basket. Aerosol particles were formed by flowing 1.5 lpm nitrogen gas over near-molten gold inside a resistively-heated basket. The surfaces of mobility-selected particles were modified in the aerosol state by reacting them with volatile organic compounds, including alcohols and amines. Changes in mobility diameter after surface modification were monitored by tandem differential mobility analysis (TDMA). Collected particle samples were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy. Surface-modified particle streams were swept through a tube furnace at temperatures above 600 degrees C to evaluate changes in thermal charging efficiency. These results could show that some adsorbed layers suppress particle charging. These results suggest a strategy for inhibiting thermal charging of aerosol particles at high temperatures.

8NM.3

Mass-Mobility Characterization of Flame-made ZrO2 Aerosols: the Primary Particle Diameter and Extent of Aggregation.MAX L. EGGERSDORFER, Arto Groehn, Chris Sorensen, Peter McMurry, Sotiris E. Pratsinis, *ETH Zurich*

Gas-borne nanoparticles undergoing coagulation and sintering form irregular or fractal-like structures affecting their transport, light scattering, effective surface area and density. Significant advances have been made in characterization of agglomerates (physically – bonded particles) of monodisperse particles in point contact. However, once coalescence or sintering starts between these primary particles, sinter necks are formed between them converting the agglomerates to aggregates (chemically- or sinter-bonded particles) [1].

Here, zirconia (ZrO_2) nanoparticles are generated by scalable spray combustion and their mobility diameter and mass are obtained by differential mobility analyzer (DMA) and aerosol particle mass (APM) analyzer measurements. Using these data, the density of zirconia and a power law between mobility diameter and primary particle diameter [2], the structure of fractal-like particles is determined (mass-mobility exponent, prefactor and average number and surface area mean diameter of primary particles). The primary particle diameter determined by DMA-APM measurements and this power law is in good agreement with those obtained by nitrogen adsorption and microscopic analysis. That way the effect of flame spray process parameters (e.g. precursor solution and oxygen flow rate as well as zirconium concentration) on fractal-like particle structure characteristics is investigated in detail during particle synthesis. The primary particle diameter varied between 5 and 25 nm and the mobility diameter from 30 – 400 nm depending on process conditions. Longer particle residence times at high temperatures and high precursor concentrations resulted in larger primary particles with increased degree of aggregation.

[1] Eggersdorfer, M.L., Kadau, D., Herrmann, H.J. and Pratsinis, S.E., Multiparticle sintering dynamics: from fractal-like aggregates to compact structures, Langmuir 27 (2011) 6358-6367.
[2] Eggersdorfer, M.L., Kadau, D., Herrmann, H.J. and Pratsinis, S.E., Aggregate morphology evolution by sintering: Number and diameter of primary particles, J. Aerosol Sci. 46 (2012) 7-19.

8NM.4

A Novel Method for Bacteria Inactivation Using Engineered Water Nanostructures. GEORGIOS PYRGIOTAKIS, James McDevitt, Toshiyuki Yamauchi, Yosuke Mitsuyama, Philip Demokritou, *Harvard University*

Herein, we present a nanotechnology-based, novel method for microbial disinfection that utilizes Engineered Water Nanostructures (EWNS) synthesized via electrospraying. The atmospheric water vapor is condensed on a Peltier cooled electrode and high voltage (5 kV) is applied to spray the water. During this process ROS and RNS are generated. A a high volume (up to 15 lpm) EWNS generator was constructed which also allows to vary the particle concentration levels up to 500,000 particles per cubic centimeter.

The physicochemical properties of the EWNS such particle size distribution, surface charge and chemical species were also investigated in this study. The ability of the EWNS to inactivate bacteria on both surfaces and in the air was investigated. For the surface bacteria inactivation experiments a number of vegetative bacteria (Serratia Marcenses, Staphylococus aureus) and a spore (Bacilus Subtilis) were exposed over time to EWNS and the bacteria inactivation potential was assessed. Similarly, in a chamber experiment the ability of the EWNS to inactivate airborn serratia marcenses was examined. Serratia bacteria were aerosolized using a collison nebulizer and exposed to EWNS aerosol in an environmental chamber (1000 lt). The bacteria inactivation potential in the air was assessed under different simulated environmental conditions (steady state and decay scenarios) using a culture system approach. The bio aerosol size distribution in the chamber was measured using an Andersen bio-sampler.

Our results show that the generated EWNS have unique physico-chemical properties. Their median diameter is approximately 18 nm, and have a highly charged surface (10 electrons per particle). Their charge increases the effective surface tension lowering the evaporation rate, extending their lifetime to more than 5 minutes. The EWNS also contain in their core reactive oxygen species (ROS) such as hydroxyl radicals and superoxides. The surface bacteria inactivation experiments showed that for Serratia Marcescens and staph aureus there was more than a 2-log10 and 1-log10 reduction respectively. Similarly the air inactivation experiments showed that the EWNS aerosol can reduce the presence of bacteria by 50% and accelerate the decay of the bacteria in a room environment.

8NM.5

Green Synthesis and Characterization of Silver Nanoparticle for Reference Material. GUO-DUNG CHEN, Han-Fu Weng,*Center for Measurement Standards, ITRI, Taiwan*

Application of nanomaterials has been extended from industrial application such as energy, chemical engineering, optoelectronics, machinery and etc, to consumer goods such as cosmetics, metical products, textiles and home applications. However, with widely use of these nanomaterials, these issues of environmental safety and human health are more important in the world. Especially silver nanoparticles, because of its significant antimicrobial efficacy, it has been widely used in sprays, clothing, daily necessities, household appliances and building materials. Whether these products with silver nanoparticles are poisonous or not, these issues still lack scientific evidences. Therefore, the national labor safety organization (such as the United States National Institute for Occupational Safety and Health, NIOSH) and OECD (Organization for Economic Co-operation and Development) agreed that development of reference materials was a important to environmental safety and health-related researches. For example, U.S. NIST started to developed a variety of nano reference materials and organized relative activities. In order to provide the standard materials in Taiwan, we synthesized silver nanoparticles for reference material. The silver nanoparticle was synthesized by using silver nitrate as a precursor of Ag. Silver nitrate was dissolved in starch solution together with arginine which reduced the silver ions to silver nanoparticles. Beside, we used the microwave as a heating source to obtain more uniform nanoparticles. The mean particle size of silver nanoparticles determined from image analyses of SEM micrographs was 14.1 nm. The silver concentration of the solution was measured by inductive couple plasma optical emission spectroscopy. On the other hand, because the process was bio-compatible, we also cooperated with National Health Research Institute, R.O.C. for toxicity test. The results will be presented in the future.

8NM.6

Aero-Sol-Gel Processing of Porous TiO2 Nanoparticles and Their Photovoltaic Properties in Dye-Sensitized Solar Cells.KOOK JOO MOON, Ji Young Ahn, Ji Hoon Kim, Soo H. Kim, *Pusan National University*

Porous TiO2 nanoparticles (NPs) were synthesized by an aero-sol-gel process in this approach. By varying the mass fraction of inorganic templates, the formation of porous TiO2 NPs with various specific surface areas and pore size distributions was examined. And then, the photovoltaic properties of the resulting porous TiO2 NPs were systematically investigated by applying them into the photovoltaic active layer (6 mm × 6 mm) of dye-sensitized solar cells (DSSCs). The porous TiO2 NP-based DSSCs fabricated in this study showed an improved short circuit current density and power conversion efficiency compared with solid TiO2 NP-based DSSCs due to the increase of the amount of inorganic dye (N719) adsorption in the porous TiO2 NPs. The values increased from 2.02 ± 0.11 to 8.16 ± 0.51 mA/cm2 and from 1.07 ± 0.21% to 3.88 ± 0.33%, respectively. It was also found that when the average pore size of porous TiO2 NPs is comparable to or smaller than that of dye molecules (< 2 nm), the dye molecules are not able to penetrate through the pores, and as a result, the amount of dye adsorption inside the pore structures of TiO2 is significantly decreased. Therefore, the optimized conditions in terms of both specific surface area and average pore size should be determined in order to increase the amount of dye adsorption in the porous TiO2 particles. The specially designed porous TiO2 NPs in this approach have great potential as an effective dye supporting and electron transfer medium to improve the photovoltaic properties of DSSCs.

8NM.7

Multi-jet Electrospinning with High-Throughput Using a Coaxial Grooved Nozzle and Two Fluids. INYONG PARK, Woojin Kim, Sang Soo Kim, *KAIST*

Electrospinning is a simple and versatile technique for fabricating nanofibers and fibrous mats, capable of producing continuous nanofibers with various types of surface morphology. Because of its numerous advantages, the procedure has been widely employed with variety of polymers in various applications.Nevertheless, despite its simple methodology and promising array of applications, the development of electrospinning has been hampered by extremely low throughput, which is usually only about a few milliliters per hour. It is not easy to increase the throughput, simply because the flow rate is one of the most sensitive processing parameters in electrospinning. To broaden the applications of the electrospinning technique, high throughput is one of the primary goals of many researchers. To overcome the throughput limitation, we have introduced coaxial grooved nozzles. By using a coaxial grooved nozzle and two fluids, including polyethylene oxide (PEO), we are able to achieve stable multi-jet operation and relatively high throughput. The multi-jets are initiated by the multi-jet mode of the inner fluid, and share the total flow rate of the polymer solution. We have investigated the operating conditions for various flow rate combinations of two fluids. The morphology of the resulting nanofibers is uniform without bead formation. The fibers have an average diameter of about 350 nm.

8NM.8

Improvement of Amorphous Silica Encapsulation Efficiencies on Welding Fume Particles. JUN WANG, Jianying Guan, Alex Theodore, Jessica Sharby, Chang-Yu Wu, Kathleen Paulson, Omar Es-Said, *University of Florida*

The welding process results in the formation of high concentration of nano-sized particles loaded with toxic metals such as hexavalant chromium, nickel, and manganese. Welding fume poses serious health risks to welders as it can cause respiratory and neurological ailments as well as cancer. The overall objective of this study was to develop an innovative amorphous silica encapsulation (ASE) technology to coat the metal particles as well as limit oxidation of chromium, thus reducing welding fume toxicity. Previous experiment showed a reduction of Cr(VI) concentration in welding fume over 90% by utilizing ASE technology. However, only 39% of metal particles were coated in silica film. The relatively low efficiency of silica precursor was mainly due to premature decomposition of silica precursor. A prototype insulated double shroud torch (IDST) was developed to overcome the limitation of this technology. Tetramethylsilane (TMS) vapor saturated argon flowed separately with primary shielding gas; it was then injected to the welding arc zone at the end of the IDST. Ceramic shell was employed in the DSWT to avoid the excess thermal energy transferred to the silica precursor. Silica coating efficiency (SCE) was determined by comparison of using two types of strong acid digestion methods. Experimental results showed about 76%, 63%, and 59% of particles are encapsulated inside silica shell at maximum, under high (30 Lpm), medium (25 Lpm), and low (20 Lpm) primary shielding gas flow rate, respectively. Transmission Electron Microscopy (TEM) imagery was used to visualize evidence of silica coating on metal particles. Further structure test confirmed no statistically significant difference of the mechanical properties of weld generated in baseline and by ASE technology. The success of this technique will bring great health and safety benefits to welders.

8NM.9

Synthesis of Nanostructured Metal Oxide Films by Electrospray Deposition of Nanoparticles. JUSTIN TANG, Alessandro Gomez, *Yale University*

We present here the use of the electrospray (ES) to create high surface area, metal oxide nanoparticle-based films for applications in energy conversion and energy storage. Although the particle can be synthesized directly by spray pyrolysis, the technique implemented in the present approach involves electrospraying a colloidal suspension with a conductive and volatile solvent and depositing nanoparticles onto a selected substrate in a continuous and controlled manner, after solvent evaporation. The suspension is sufficiently dilute so that one nanoparticle is present, on average, per droplet generated by the electrospray. The deposition of the nanoparticle is governed by the relative importance of the charged particle drift imposed by the external electric field and the thermal velocity due to Brownian motion. The deposition mechanics can be expressed in terms of a single parameter: the ratio of the terminal velocity to the thermal velocity. While the thermal velocity is a function of the nanoparticle size, the external field can be independently manipulated. Zinc oxide and titania films of several microns thick were synthesized by this ES route, and cross sectional SEM images revealed morphological differences between low and high speed ratio deposition conditions. We found that low-speed ratio deposits have dendritic structures and high-speed ratios have columnar structures. Ellipsometry measurements show that the films are highly porous. Importantly, the small throughput for a single electrospray can be scaled up through multiplexing. As a result, the technique can meet the deposition rates that are needed in applications. This approach to thin film synthesis provides control over thickness and morphology and does not necessitate a clean room facility.

8NM.10

Near-field Electrospray Printing of Polymer Derived Ceramics. CHENG LI, Hongxu Duan, Weiwei Yang, Johan Rodriguez, Brandon Lojewski, Linan An, Weiwei Deng, *University of Central Florida*

Ceramic MEMS sensors are potentially game-changing devices in many applications in high-temperature and corrosive environments, where the use of conventional MEMS materials such as silicon is prohibited. However, micro-fabrication of ceramic MEMS sensors remains a major technical challenge. Polymer derived ceramic (PDC) is a promising material that enables new ways to fabricate such devices. Here we report a method to directly print micro PDC patterns using near-field electrospray. We demonstrated that the highly viscous ceramic precursor liquids can be printed reliably without any clogging issues. The spray self-expansion due to Coulombic repulsion force amongst charged droplets can be suppressed by decreasing the droplet residence time in space. Further, we derived an approximate spray expansion model which predicts the line-width and the prediction is in decent agreement with the experimental results at relatively high driving fields (>1 kV/mm). We demonstrated printed PDC 1D features as narrow as 35 µm. Moreover, after pyrolysis of PDC at 1100 °C in nitrogen, amorphous alloys of silicon, carbon and nitrogen (SiCN) are obtained and the sample keeps its integrity and shows no signs of cracks. Our study shows that the maskless near-field electrospray is a promising tool to directly print micro patterns of PDC for high temperature MEMS sensor applications.

8NM.11

Comparison of Release Profiles of Drug-Loaded PLGA Polymer Particles in Well-Mixed and Encapsulated Forms. JENNIFER HEAD, Da-Ren Chen, *Washington University in St. Louis*

The release profiles of nano-sized, drug-loaded PLGA particles produced in well-mixed form and in encapsulated form by electrospray (ES) were compared to determine the optimal particle structure design for nanomedicine as well as the effect of solute diffusion during the particle formation. A single-capillary ES system was utilized to produce nanoparticles in the well-mixed form. In this case, poly(lactic-co-glycolic acid) (PLGA) 85:15 and Paclitaxel (PTX), a commercially available drug often used in cancer treatment, were both dissolved in the same solution containing 1:1 dimethyl sulfxoxide (DMSO): acetonitrile (ACN). A dual-capillary ES system with compound jets was used to produce encapsulated particles at high encapsulation efficiency. Separate solutions of 1:1 DMSO: ACN containing PLGA and PTX were fed through the outer and inner ES capillaries, respectively. The overall size of as-prepared PLGA nanoparticles and the percent PTX in final particles were held constant at 100 nm and 20%. Particles containing PTX only were also produced by single-capillary ES system as the reference.

The concentration of solutes in an evaporating sphere was modeled for the well-mixed case. As solvents evaporated during the particle formation, the solutes became more concentrated in the particle sphere. Solutes with higher diffusion coefficients (i.e., PTX) were able to travel more rapidly to the center of the particle, while slow moving ones (i.e, PLGA polymer) concentrated near the particle’s border. As a result, well mixed cases whose solutes had widely different diffusion coefficients had release profiles more similar to those produced from the encapsulated form. Tests were repeated using PLGA 50:50 as the polymer to further examine the effect of relative diffusion coefficients on release profiles. The details of this study will be presented in a poster at the AAAR conference.

8NM.12

Synthesis of Spherical Mesoporous Silica Particles by Spray Pyrolysis from Aqueous Silicic Acid. HANKWON CHANG, Jin Woo Lee, Hee Dong Jang, Dae-Sup Kil, Jeong Woo Choi, *Korea Institute of Geoscience and Mineral Resources*

We successfully prepared spherical mesoporous silica particles, of which main pore diameter was 3.8 nm, by spray pyrolysis from aqueous silicic acid. And we manipulated process variables such as precursor concentration, reaction temperature, and the addition of urea and PEG to investigate the effect of process variables on the particle diameter and pore properties such as pore diameter, total pore volume, and specific surface area. The porous particles properties were analyzed by using FE-SEM, particle size analyzer, and nitrogen absorption-desorption analysis. With an increase of the precursor concentration from 0.2 M to 0.7 M, the average particle diameter, total pore volume, and specific surface area of the porous silica particles increased from 0.56 to 0.96 um, 0.434 to 0.486 cm^3/g, 467.8 to 610.4 m^2/g, respectively. Within the temperature range (600 - 800 ^oC), there was no significant difference in the pore diameter, total pore volume, and specific surface area. In addition, the addition of urea as an expansion aid led to slight increases in particle diameter, pore diameter, and specific surface area. However, when the polyethylene glycol (PEG) as an organic template was used, the total pore volume of porous particles increased dramatically.

8NM.13

Aerosol Synthesis of Surface Modified Lipid Nanoparticles. Amol Ashok Pawar, Pranav Asthana, CHANDRA VENKATARAMAN,*Indian Institute of Technology Bombay*

Nanoparticle surface properties, by which their outer layers are made hydrophilic, can increase stability in aqueous suspension or assist escape of their detection by macrophages. Surface modification using polymers and surface active molecules can be used for this purpose. Recently, droplet-phase aerosol synthesis has been used in this group to prepare nanoparticle aerosol lipid matrices (NALM) with controlled size, structure and crystallinity. This work investigates modification of stearic acid NALM during aerosol synthesis, using surface-active molecules, through the possible route of evaporation-induced self-assembly, wherein the polar head could orient towards the interface with the non-polar tail in the lipid core. For biocompatibility, physiological molecules like 1, 2–dipalmitoyl–sn–glycero–3–phosphocholine (DPPC) and 1, 2–dipalmitoyl–sn–glycero–3–[phospho–rac–(1–glycerol)]–sodium salt (DPPG) were used. A pulse-heat aerosol reactor, developed in earlier work, was used to prepare nanoparticles from atomized precursor solutions of stearic acid, with and without DPPC or DPPG (4% w/w), dissolved in chloroform. Particle mobility distributions were measured using an SMPS. Nanoparticle suspensions were made by direct collection into a de-ionized water layer using a custom-built wet electrostatic precipitator. Suspension stability was evaluated through hydrodynamic diameter and polydispersity measurement (using dynamic light scattering) at regular intervals for one month. The structure of nanoparticles was studied using electron-imaging (FEG-TEM). Mean mobility diameter ranged 108-156 nm, with a unimodal distribution and geometric standard deviation of 1.6–1.8. Suspensions made from pure stearic acid (not surface modified) NALM exhibited immediate aggregation or settling of nanoparticles (with large and variable hydrodynamic diameter of 471 ± 81 nm and high polydispersity 0.75). Suspensions of surface modified NALM, using both DPPC and DPPG, exhibited good stability with smaller, stable hydrodynamic diameter (156 ± 8 and 134 ± 8 nm) and low polydispersity of 0.32-0.46 over 7 days. Surface modified NALM exhibited double or multilayer lamellar structures, typical of particle substructure formed during evaporative self-assembly. The poster will discuss the influence of aerosol processing conditions on nanoparticle structure and suspension behaviour.

8NM.14

To Maximize Triple-Phase Interfaces Between Fuel, Electrolyte, and Electrode of Direct Coal Fuel Cell Through CeO2 Coating. CHENGGUO LI, Donggeun Lee, *Pusan National University, Busan, South Korea*

A new type of high-temperature fuel cell directly using pulverized coal particles, which is called direct coal fuel cell (DCFC), has recently attracted scientific and industrial attention due to its excellent electrochemical efficiency and efficient use of least expensive coal. However, the fuel cell system is still in its infancy mainly because triple-phase interface between an Ni-based anode, solid fuel, and molten electrolyte where electrochemical reaction occurs is limited as compared to gaseous fuel of hydrogen. Hence, this study was devoted to find a new way to enhance the electrochemical usage of the fuel. The first trial is to use a porous Ni electrode in which coal powder are fed to maximize the physical contact between the coal and electrode. This approach was found to be five times more efficient in electrochemical performance of the system. As the triple phase contact is even more enhanced by making the fuel electrode wettable to the electrolyte of molten carbonate, the second trial was made to coat the electrode with CeO2 for this purpose. As a final result, the electrical power output reached 70mW/cm2 at a current density of 150mA/cm2 which was actually 40% increased from the case of non-coated anode.

8NM.15

Aerosol-Gel Synthesis of Pt-Based Catalysts for Hydrocarbon-Based Selective Catalytic Reduction of Nitrogen Mono-Oxide. RIYAN ZAHAF, Jae Wook Jung, Dudi Adi Firmansyah, Yongho Kim, Donggeun Lee, *Pusan National University, Busan, South Korea*

Silica-supported and alumina-supported platinum catalysts have been successfully prepared using the aerosol-gel method for hydrocarbon-based selective catalytic reduction of nitrogen mono-oxide. The Pt dots as small as 1-2 nm were well dispersed on silica and alumina spherical particles with large number of active surface. By flowing NO gas through the catalysts powder which was kept at different temperatures and measuring the composition of NO gas, steady-state catalytic de-NOx performance was tested as a function of temperature. Of particular interest is to note that the alumina-supported catalysts were more active even as low as 150 oC as compared to silica-based catalysts. The NO conversion efficiency reached 60% with wider temperature range.

8NM.16

A Cost-Effective Method of Aerosolizing Dry Powdered Nanomaterials. Andrea Tiwari, LINSEY MARR, Caleb Fields, *Virginia Tech*

The growth of nanotechnology has led to increased concerns about the toxicity of aerosolized nanomaterials. Producing aerosolized nanomaterials in an environmentally relevant form for inhalation toxicology studies can be a challenge. Wet methods such as spray-drying can alter particle chemistry, and commercially available dry powder dispersers cannot easily generate sub-100 nm aerosols.

This work demonstrates the production of nanoscale aerosols from dry powdered nanomaterials using an inexpensive vacuum generator (Tang et al, 187:27-36, Powder Technology) to disperse engineered materials into a chamber. Tested nanomaterials include C_{60} fullerenes and TiO_2 (original particle size 30-50 nm). The resulting aerosol size distributions were measured using a scanning mobility particle sizer (SMPS) and aerodynamic particle sizer (APS).

Results show that this system may be used to easily disperse dry nanostructured materials into aerosols which have a size distribution peaking near or below 100 nm. Aerosol mass concentrations achieved using this system range from 0.3 – 5 x 10^3 micrograms m^-3. The number and mass concentration output of the system can be controlled by loading different amounts of the nanomaterial into the disperser. This control is afforded by a linear relationship between loaded nanomaterial mass and particle mass output.

This aerosol production system offers a simple and inexpensive alternative to commercially available dispersion instruments. Since spray-drying and other ‘wet’ techniques require creating a liquid suspension that may alter particle chemistry, this approach using dry particles may be preferable in some cases for generating sub-100 nm aerosols from nanomaterials for inhalation toxicology and aerosol chemistry research.

8RA.1

Studies of the Optical Properties of Mineral Dust Aerosol from the IR to the Visible. JENNIFER ALEXANDER, Olga Laskina, Brian Meland, Vicki Grassian, Mark Young, Paul Kleiber, *University of Iowa*

Atmospheric dust plays a key role in the Earth’s radiation balance, affecting climate forcing by direct and indirect means. Accurately treating the radiative transfer effects of dust requires knowledge of aerosol concentration, composition, size, and shape distributions. While much of this information can be obtained from satellite or ground-based remote sensing measurements, the retrieval algorithms depend on precise models of the aerosol optical properties. Unfortunately, accurate modeling of dust optical properties is complicated because atmospheric dust particles are typically irregular in shape and can be an inhomogeneous mixture of different minerals.

In this work, infrared extinction and visible phase functions and polarization profiles are measured for complex authentic dust samples including Saharan sand and Iowa loess. Particle size distributions are measured simultaneously along with the optical properties. These complex dust mixtures are modeled as external mixtures of mineral dust components. Experimental data are compared with T-Matrix theory simulations using a priori particle shape models for each mineral component. The success of this approach is highlighted for these complex dust mixtures.

8RA.3

Measurement of Free Tropospheric Aerosols in the North Atlantic at the Pico Mountain Observatory. KATJA DZEPINA, Sumit Kumar, Claudio Mazzoleni, Paulo Fialho, Mike Dziobak, Jacques Hueber, Detlev Helmig, Louisa Kramer, Seth Olsen, Lynn Mazzoleni, *Michigan Technological University*

The Pico Mountain Observatory is located at 2225 m amsl on an inactive volcano at Pico Island in the Azores archipelago in the North Atlantic ~3900 km east and downwind of North America (38°28’15’’N; 28°24’14’’W). The unique location of the Observatory enables sampling of free tropospheric air transported over long, intercontinental distances and is rarely affected by local emissions. The Observatory is affected mainly by North American outflow after its trans-Atlantic transport. Therefore, its location is ideal for observations of long-range transported pollutants emitted from anthropogenic and biogenic continental sources.

The composition of continental pollution outflow is altered during transport by mixing, chemical reactions, phase changes, and removal processes. Thus, the properties of aerosol and trace gases in downwind regions are impacted by the outflow of pollutants, their chemical transformation, and sinks. In previous work, the sampled air-mass measurements (including CO, O_3, NO_x, NO_y, NMHC, black carbon and aerosol optical size) and the simulations of their dispersion indicated outflow of North American tropospheric ozone and its precursors. Although the measurements have been crucial in explaining the evolution of North American gaseous pollution, little is known regarding the nature of the aged aerosol. New work is currently underway at the Observatory to provide chemical characterization of the intercepted free tropospheric aerosols.

Here, we show the preliminary results of the free tropospheric aerosol composition and its physical properties. Samples were collected using high-volume filter samplers with quartz filters and analyzed for organic and elemental carbon (OC and EC, respectively). We compare the observed OC and EC values to the collocated measurements of gas- and particle-phase species, meteorological parameters and to the values found in current literature. We highlight the future work in which we will select filter samples based on the arrival of highly polluted air masses from anthropological or biomass burning emissions for further detailed analysis.

8RA.4

Source Identification and Long-term Trend Analysis of Finnish Arctic Aerosols. JAMES R. LAING, Philip K. Hopke, Liaquat Husain, Vincent A. Dutkiewicz, Jussi Paatero, Tanveer Ahmed, *Clarkson University*

Arctic Haze has been a focus of study since the early 1970, but there are relatively few long-term datasets of their chemical composition. Week-long historical filter samples collected at Kevo, Finland from 1964-2010 have been analyzed for various chemical species. Major ions and methane sulfonate (MSA) have been analyzed by ion chromatography (IC), trace elements by inductively coupled plasma - mass spectrometry (ICP-MS), and BC by light transmission. The 47-year complete data set will be analyzed by Positive Matrix Factorization (PMF). The receptor modeling results will be connected with back trajectory data in a Potential Source Contribution Function (PSCF) analysis to determine possible source areas. The combination of PMF and PSCF will identify source profiles and the geographic areas of those sources. Sources of wood smoke, oil and coal burning, non-ferrous metal smelting, biogenic sulfate, and crustal elements will be identified. Trend analysis on the sources produced by PMF will be performed to evaluate the evolution of sources over time. Global inventories of anthropogenic emissions indicate a dramatic decrease in the early 1990’s in the Soviet Union [Bond 2007; Smith 2011]. The Kevo site is heavily impacted by the Kola Peninsula industrial area. It is expected that elemental markers of industrial processes there will decrease starting in the early 1990s. Of particular interest are the factors for forest fires and biogenic sulfate. Siberian forest fires are a major source of Arctic BC during the spring/summer [Generoso 2007]. It has been predicted that climate change has increased forest fires in central Canada and Russia [Stocks 1998]. This prediction will be assessed and source areas of forest fires will be determined. Sea surface temperatures in the North Atlantic have increased since 1970 [Thompson 2010]. Whether the biogenic sulfate factor is correlated with increased temperatures will be examined and source locations will be determined.

8RA.5

Aerodynamic Chracteristics of Fugitive Dusts by the Types of Animal Feed Stuffs Duing Gravitational Settle Down. Hak-Joon Kim, Bangwoo Han, YONG-JIN KIM, *Korea Institute of Machinery and Materials*

During gravitational settle down of the five types of animal feed stuff (Wheat Bran Pellets, Palm Kernel Expellers, Corn Gluten Feeds, Soy Been Meals, Copras), which are the crucial sources to generate fugitive dusts near the port of In-cheon, Korea, the aerodynamic characteristics of the feed stuffs were analyzed. 1.0 g of each feed stuff powder was dispersed in the closed chamber, 30 cubic meters, and the changes in the concentration of the airborne particle in the chamber based on particle volume and number were monitored using two optical particle counters and a SMPS for micro-meter and nano-meter particles, respectively. The experimental results show that the decay constants of the five types of dusts by gravitational settling were linearly proportional to the square of the size of the airborne dusts. In addition, the decay constant of 0.3 µm particles by the gravitational settle was seven times smaller than that of 5.5 µm particles for WBP, and fifteen times for PKE and CGF, respectively. In particular, the decay of the SBM was fastest, and those of COP and WBP, CGF, and PKE were followed, and this order of the decay constants by the types was dependent of the density of the stuffs. These results indicate that when they aerosolized during load and unload of the feed stuffs, the aerodynamic properties of the animal feed stuffs were dependent on the density and size of the dusts.

8RA.6

Aerosol Emissions by Bitter-Salty Lakes in the Altai Territory in the Summer of 2011. ALEXANDR SAFATOV, Galina Buryak, Sergei Olkin, Irina Reznikova, Yurii Marchenko, Boris Desyatkov, Natalya Lapteva, Irina Andreeva, Alexander Kozlov, Sergei Malyshkin, Igor Sutorihin, Vladimir Bukatyi, Svetlana Litvinenko, Boris Smolyakov, Marina Shinkorenko, *FBRI SRC VB Vector*

Salty lakes are unique ecological systems. Present work deals with estimation of total aerosol emission from the surfaces of two such lakes of the Altai Territory.

A sampling network was situated in each lake's region: one sampling site was windward and four ones were leeward. Each sampling site contained three samplers with fibrous filters and one impinger. Leeward onshore site contained a DAS and a APS also. The collected aerosol and brine samples were studied for the ionic composition, total protein concentration, culturable microorganisms number and their diversity.

The measured concentration values for each substance were used to determine the fluxes of this substance from the land and water surfaces using a previously developed mathematical model.

Preliminary estimates show that aerosol emission by a unit of water reservoirs surfaces considerably exceeds the emission by a unit of land surface in the region of measurements. Consequently, it is the lakes that mainly contribute to air pollution in the vicinity of these lakes.

8RA.7

Assimilation of TES Ammonia and Ground-based Aerosol Observations during CalNEX to Refine Emissions Estimates.

SHANNON CAPPS, Daven Henze, Armistead Russell, Athanasios Nenes, *Georgia Institute of Technology*

Regions of high ammonia (NH_3) emissions can challenge the capability of chemical transport models (CTMs) to represent the atmospheric state, especially aerosol concentrations, accurately. Uncertainties in the input of reactive nitrogen through fertilizers as well as the dependence of vegetative and soil NH_3 emissions on surrounding concentrations complicate model refinement. Satellite-based observations of atmospheric ammonia and ground-site measurements of inorganic aerosol species provide a constraint for the modeled concentrations. A robust inverse modeling system will assimilate these data to refine estimates of inorganic aerosol precursor emissions.

Here, the GEOS-Chem adjoint framework, equipped with ANISORROPIA, ingests two disparate types of observations to refine emissions estimates, which are evaluated with a unique dataset from CalNEX. To represent the distinct regional sources in California, in particular, the GEOS-Chem adjoint is nested from the coarser 2 degree latitudinal by 2.5 degree longitudinal grid sizes with global coverage to 0.5 degrees by 0.666 degrees over the continental US. The assimilation window encompasses the early summer months of 2010. TES NH_3 special observations provide a constraint on the highly variable tropospheric ammonia concentrations, especially over the Central Valley. The complementary aspect of the aerosol-gas partitioning puzzle is constrained by ground-based IMPROVE site measurements, which are more frequent than TES observations. Refined estimates of emissions of inorganic aerosol precursors are evaluated by comparing optimized results with CalNEX AMS and NH_3 measurements.

8RA.8

Determination of Seasonal and Height Resolved Number Concentration Patterns in a Pollution Impacted Rural Continental Location.

ROBERT BULLARD, Charles Stanier, Patrick Sheridan, John Ogren, *University of Iowa*

Aerosols play an important role in Earth's radiation balance and their climate forcing effects represent the largest uncertainties in the Intergovernmental Panel on Climate Change's 2007 fourth assessment report. The nucleation, with subsequent growth of nuclei into liquid or solid phase particles is the main source of ultrafine aerosol particles in the atmosphere. While data on nucleation is limited to specialized field campaigns which are limited both temporally and spatially, data on atmospheric particle number concentration is much more widespread. Our current goal is to use five years (2006 – 2010) of highly time resolved particle number concentration data (NOAA Global Monitoring Division of the Earth System Research Laboratory) in conjunction with vertical flight concentration data (NOAA Airborne Aerosol Observatory) near Bondville, IL to better understand season, diurnal, and vertical variation in aerosol number concentration. Preliminary analysis shows peaks in condensation nuclei greater than 10 nm during the spring months (May, April) and during the fall months (September, October). The diurnal pattern of aerosol number has a midday peak which is enhanced during the months of highest number concentration. Particle number peaks coincide with months and times of day of low aerosol mass and surface area. Average vertical profiles show a nearly monotonic decrease with altitude in all months, and vary in magnitude similar to the ground-based measurements. Individual vertical profiles show evidence of plumes of enhanced number concentration, and periods when the entire boundary layer is enhanced by high particle number concentration. These results, while not directly indicating nucleation, will assist field researchers and modelers by providing the seasonal intensity patterns of particle number increases on the ground and aloft.

8RA.9

Characterizing the Influence of Transport Variability on Aerosol Concentrations at Mauna Loa Observatory.

LAUREN POTTER, Sonia Kreidenweis, Molly Morman, Barry Huebert, Steven Howell, John Zhuang, *Colorado State University*

Located in the remote Pacific Ocean at an elevation of nearly 4 kilometers above sea level, Mauna Loa Observatory (MLO) is an ideal and unique measurement site for ground-based, free tropospheric observations. This study makes use of a unique, 20-year data set of aerosol ionic composition, obtained by the University of Hawaii at Manoa. Collections of daily filter samples were made during nighttime downslope (free-tropospheric) transport conditions, from 1989 to 2009, and were analyzed for the following species: HNO3(g), and aerosol-phase concentrations of NO_3^-, SO_4^{2-}, MSA, Cl^-, Oxalate, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}. Understanding the factors involved in seasonal and interannual variations in aerosol speciation and concentrations at this site are complicated by the relatively short lifetimes of aerosols, compared with many greenhouse gases that have also been sampled over long time periods at MLO. Our study applies a combination of back trajectories and climate indices to interpret the relative roles of large-scale transport variability and variability in aerosol primary and secondary emissions, on the overall observed aerosol variability.

We find that aerosol concentrations at MLO were highly influenced by variations in transport efficiency in this portion of the central Pacific, which is highly dependent on synoptic variations due to the El-Niño Southern Oscillation. The degree of Asian continental influence at MLO during late winter/early spring was shown to be strongly related to such circulation characteristics, similar to observations for greenhouse gases. We further find a trend in springtime sulfate aerosol concentrations at MLO of 6%/year over the time period studied, significant at the 95% confidence level. This trend reflects, at least in part, estimated increasing trends in Asian anthropogenic emissions over the same time period, that are superimposed on the variability in transport efficiency.

8RA.10

Application of an Ultrafine V-TDMA to Atmospheric Aerosols in Eastern Iowa.

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

Volatility of freshly nucleated particle provides important information to understand the balance of volatile, semivolatile, and nonvolatile particle components, as well as the mixing state of these components.

The design, construction, testing, and field application of a Volatility Tandem Differential Mobility Analyzer system (V-TDMA) will be presented. The system is designed to study the volatility of ambient aerosols, including those recently created from new particle formation and growth. Our V-TDMA has two nano-DMAs (Nano-DMA, TSI model 3085) in tandem, and a thermodenuder for thermal treatment of sub-30 nm aerosols. The V-TDMA system was tested in laboratory using mono-disperse ammonium sulfate, sodium chloride, and secondary organic aerosol components (e.g., pinic acid, pinonic acid, and adipic acid) to understand system performance and benchmark behavior against published volatility data. Performance was tested as a function of size, concentration, residence time, Reynolds number, chemical composition (pure component vs. mixture), and thermodenuder design parameters such as dimension of heating and denuder, choice of denuder type (activated charcoal and without activated charcoal), and whether the denuding section was cooled. Details regarding these different aspects of thermodenuder design will be presented. Field testing was conducted in eastern Iowa at V-TDMA temperatures ranging from 25 to 300 C to characterize volatile and non-volatile components and mixing state of ultra-fine aerosol.

8RA.11

Two Years of Measurements of Atmospheric Aerosols at a Remote Mountain Site in NE of Spain. ANNA RIPOLL, Jorge Pey, Andrés Alastuey, María-Cruz Minguillón, Xavier Querol, *IDAEA-CSIC*

This work summarizes the results of the tropospheric aerosols physico-chemical properties and its time variation interpretation at a remote background site Montsec (MSC, NE of Spain, 42 degrees 3’ N; 0 degrees 44’ W) from 2010 to 2011. The MSC is located at 1570 m amsl in the Pre-Pyrenees mountain range, isolated from industrial/urban agglomerations, and influenced by the Mediterranean characteristics, European episodes and Atlantic advections.

The time variability of aerosol parameters was investigated as a function of the meteorology and the origin of the air masses, determined based on HYSPLIT back-trajectories and BSC/DREAM8b, SKIRON and NAAPS models. Mean concentrations of PM_10, $PM_2.5$, PM_1, measured by a Grimm Optical Particle Counter were 12, 9, and 6 micro-gram m^{-3}, respectively. Mean black carbon (BC) concentration, measured by a Multi Angle Absorption Photometer, MAAP, was 0.2 micro-gram m^{-3}. These concentrations fall in the typical range of continental background sites. However, mean particle number (N) concentration, measured by a CPC3776 TSI, was 3588 particles cm^{-3}, similar to concentrations measured in regional background and suburban areas. These relatively high levels of N are mainly related to the intense and recurrent photochemical nucleation episodes, identified to happen at midday with southwest prevailing wind conditions.

PM_10 and PM_1 24h samples were collected on quartz fibre filters at a ratio of 1 sample out of 4 days by sequential high-volume samplers, for subsequent determination of concentrations of major PM components (Al, Ca, Fe, K, Mg, Na, NO_3^-, NH_4^+, SO_4^{2-}, Cl^-, OC and EC) and trace elements (V, Ni, Ti, Cu, Zn, As, among others).

8RA.12

Characterization of Tropospheric Aerosols in a Remote Mountain Site in NE of Spain with an Aerosol Chemical Speciation Monitor. ANNA RIPOLL, María-Cruz Minguillón, Jorge Pey, Marco Pandolfi, Andrés Alastuey, Xavier Querol, Jose-Luis Jimenez, Douglas Day, *IDAEA-CSIC*

An Aerodyne Aerosol Chemical Speciation Monitor (ACSM) was deployed at the Montsec (MSC, NE of Spain, 42 degrees 3’ N; 0 degrees 44’ W) remote background site, to characterize tropospheric aerosols composition, source origin and atmospheric processes. The ACSM measures the mass and the chemical composition of non-refractory submicron particulate matter in real-time, so concentrations of organics, sulfate, nitrate, ammonium and chloride were measured in situ at a time resolution of 1 hour. These non refractory components were also offline determined in PM_1 24-h samples collected on quartz fiber filters with a sequential high-volume sampler. The refractory material in the aerosol was characterized with measurements of black carbon (BC) by using a Multi Angle Absorption Photometer (MAAP) one minute time resolution and of dust and metals using offline analyses.

This study shows the preliminary results of ACSM data and comparisons to other aerosol mass concentration estimation instruments. The ACSM + BC mass concentration shows good agreement with estimated mass from a Grimm Optical Particle Counter and a TSI SMPS size distribution of submicron particles. The ACSM + BC mass concentration is also well-correlated with submicron scattering measurements from a nephelometer (Aurora 3000, ECOTECH Pty) at three wavelengths, with mass scattering efficiencies consistent with the literature for each wavelength. Comparisons of the results from the filter measurements and the ACSM species concentrations will also be presented. Back-trajectory analyses and Positive Matrix Factorization (PMF) results from the ACSM organic spectra and the filter data will be used to characterize the contributions of different sources and processes.

8RA.13

Characterization of Bioaerosols Isolated from Atacama Desert, Chile. GUISELLA ESCALANTE, Carla León, Victor Campos, Roberto Urrutia, María Angélica Mondaca, *Universidad de Concepción, Chile*

Many processes associated with global change such as desertification and changes in the land use, are promoting an increase of dust in the atmosphere, that has been particularly marked in recent decades. In Chile, swirling dust are produced more frequently in desert areas where the surfaces are strongly heated by the sun. In the Atacama desert, in Huara's area (I region), Chile has come to have simultaneously, more than 70 swirling.

The objective was to isolate and characterize microbiological and molecularly bioaerosols from Atacama desert. The bioaerosols were obtained in Huara, (latitude 19º59'26,5"S and longitude 69º44 and 24,52W) using theTactical air sampler to collect small particles. the filters were analyzed using scanning electron microscopy (SEM), the total bacteria count was obtained by the epifluorescence technique. Culturable bacteria isolation was performed on R2A agar. The bacterial community was characterized by analysis of 16rDNA by DGGE and phylogenetic analysis of the sequences. The SEM of filter samples revealed the presence of bacterial cells with different morphological characteristics. The total count of bacteria in the filters by epifluorescence was approximately 10^9cels/ml. After incubation of the filters in R2A agar was found that 46% of microorganism found were Gram positive and 54% were Gram negative. Preliminary results show the presence of culturable and nonculturable bacteria in the air samples of Atacama desert. These results may provide a baseline for future research and are the first samples obtained in Atacama desert, Chile.

8RA.14

Development of a Process-Based Model for the Estimation of Beef Cattle Ammonia Emissions. ALYSSA MOORE, Peter Adams, *Carnegie Mellon University*

Ammonia is an important air pollutant because it is an irritant and a precursor to the formation of fine particulate matter in the atmosphere. The livestock industry emits between 70-90% of ammonia emissions in the United States, and the largest emitters are dairy and beef cattle, swine and poultry. Beef cattle contribute more than 25% of livestock ammonia emissions, so it is important to better understand and estimate ammonia losses from beef cattle excrement to improve manure management and reduce impacts of livestock production on air quality. Practices used in the production of beef cattle vary regionally and depend on meteorological conditions. Measurements can help us estimate emissions for a specific set of practices and meteorology, but not all practices and meteorology can be measured, so a model that describes how emissions occur throughout the manure management process, also called a process-based model, will be used to estimate ammonia emissions from beef cattle. Using the model framework developed by Pinder, et al. (2004) for dairy cows and based on the governing equations of Hutchings, et al. (1996), we can tune the model to predict ammonia emissions from single beef farms. Preliminary results for several test farms indicate that beef emissions are somewhat lower than those from dairy cows, especially from those raised on pasture. Emissions also depend strongly on the ammonia concentration of the excrement as well as its pH and increase with increased temperature and wind speed and decrease with precipitation. Further work will tune model to reported beef emission factors. After validating the farm emission model, we will use this data to build up a national inventory for beef cattle ammonia emissions.

8RA.15

Free Tropospheric Aerosol Measurements at the Pico Mountain Observatory, Azores (2225m asl). CLAUDIO MAZZOLENI, Lynn Mazzoleni, Paulo Fialho, Sumit Kumar, Katja Dzepina, Mike Dziobak, Louisa Kramer, Seth Olsen, Robert Owen, Detlev Helmig, Jacques Hueber, Swarup China, *Michigan Technological University*

The Pico Mountain Observatory is located in the summit caldera of Pico Mountain, an inactive volcano on Pico Island in the Azores, Portugal (38.47°N, 28.40°W, Altitude 2225m asl). Due to the elevation and steep terrain, local sources have been shown to have a negligible influence at the observatory. The value of the station stems from the fact that this is the only permanent mountaintop monitoring station in the North Atlantic which is typically located above the marine boundary layer (average MBL heights are below 1200 m and rarely exceed 1300 m) and often receives air characteristic of the lower free troposphere. The Azores are often impacted by polluted outflows from the North American continent making it an ideal site for studying long range transport. The station was installed in 2001 with a focus on gaseous species (e.g.; ozone, carbon monoxide and nitrogen oxides) with continuous measurements during the summer seasons. Black carbon (BC) measurements have been carried out at the station since the beginning and continue now using a seven-wavelength Aethalometer. In the summer of 2012, new aerosol instrumentation and samplers were installed at the station. The new equipment includes a three wavelength nephelometer which measure aerosol scattering and backscattering fraction, a set of four high volume samplers for the collection and chemical analysis of aerosol, a sequential sampler to collect aerosols on membranes for electron microscopy analysis, and an optical particle counter. Ancillary measurements include non-methane hydrocarbons, meteorological parameters, carbon monoxide and ozone.

In this poster we will discuss some of the analysis of the decadal BC mass data as well as some preliminary analysis of the new aerosol data with a focus on aerosol optical properties and morphology of long range transported aerosols, relevant to climate science.

8SA.1

Improving Particulate Matter Source Apportionment: A Hybrid Approach Utilizing Chemical Transport and Receptor Models with Geostatistical Methods. CESUNICA IVEY, Heather Holmes, Yongtao Hu, Armistead Russell, James Mulholland,*Georgia Institute of Technology*

An integral part of air quality management is knowledge of the impact of pollutant sources on ambient concentrations of particulate matter. Further, there is a growing desire to directly use source impacts in health studies [1, 2]. However, source impacts cannot be directly measured. Traditionally, observed concentrations have been utilized in source apportionment methods such as receptor-oriented modeling (RM). Several challenges are presented by this method, leading to the development of a novel hybrid approach that is used to determine source impacts by combining the capabilities of RM and chemical transport modeling (CTM). The hybrid method calculates an adjustment factor (R) for estimated impact of each source at each monitor location using observations and results of CTM sensitivity analysis [3]. R is a scaling factor applied to the original CTM source impacts and is obtained using a chemical mass balance approach that incorporates measurement, modeling and emission uncertainties. Previously, R was calculated only at monitoring locations [3]. That approach is extended to produce an R value for every grid cell in the CTM domain for source impact adjustments at locations beyond observation locations. The interpolation can also be done in time. In this study, kriging is the primary method to spatially interpolate R values calculated using data from Speciation Trends Network (STN) locations. An urban-rural analysis is completed using data from the SEARCH monitoring network [4] to determine the performance of the hybrid and kriging methods. Results are evaluated by comparing observed values to reconstructed species concentrations, which are derived using R values. Typically, the STN data are limited temporally, as the monitoring networks report data one in every three or six days, so temporal interpolation is assessed as well. Data from additional monitoring sites with daily observations are used to assess the performance of temporally interpolated R values.

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8SA.2

Status of Air Quality: Experience in Bangladesh. BILKIS ARA BEGUM, Philip K. Hopke, Andreas Markwitz, *Atomic Energy Centre*

In Dhaka, Bangladesh particular matter (PM) among the measured criteria pollutants, is most harmful to the public and the environment. From For the last couple of years, the Government is trying to control PM emission originating from anthropogenic sources. It has been found that 30-50% of the PM10 mass in Dhaka is fine particulate matter with aerodynamic diameter less than 2.5 µm. These fine particles are mainly of anthropogenic origin and come predominately from transport related sources. However, during wintertime, local air pollution is enhanced by transboundary air pollution which results in an increase in PM concentrations significantly above the Bangladesh National Ambient Air Quality Standard (BNAAQS). It has been found that black carbon amounted to approximately 50% of the total fine PM mass before adoption of control policies. The Government has taken several steps to reduce PM and BC for the last few years. As a positive result of the legislation, PM emissions and BC concentrations did not increased linearly compared to the contributions from combustion sources such as motor vehicles, diesel power generators or brick kilns. Positive matrix factorisation modeling was performed on fine PM data set starting from January 2007 to February 2009. A key result of the analysis is that motor vehicles contributed less BC compared to the brick kiln industry. This is a good achievement of the Government policy interventions. Black carbon is often transported over long distances, mixing with other aerosols along the way. Transboundary transport of air pollution in the South Asian region has been an issue of increasing importance over the past several decades. Long-range transport of anthropogenic pollution is contrasted with that of pollution produced by natural processes such as dust storms or natural forest fires.

Keywords: Particulate matter, black carbon, transboundary transport

8SA.3

Identifying Key Sources of Ambient PM1 During Foggy and Clear Winter Days and Nights at Kanpur (India). TARUN GUPTA, Anil Mandaria, *IIT Kanpur*

The key goal of this study was to determine the major sources of PM1 (particles having aerodynamic diameter < 1.0 µm) within and near Kanpur, in the Indo-Gangetic Plain (IGP). Day time and night time, 10 h long each, filter-based aerosol samples were collected for 4 months throughout the winter season. After calculating the PM1 mass concentrations, Teflon filter papers were analyzed for seventeen elements – As (Arsenic), Ca (Calcium), Cd (Cadmium), Co (Cobalt), Cr (Chromium), Cu (Copper), Fe (Iron), K (Potassium), Mg (Magnesium), Mn (Manganese), Na (Sodium), Ni (Nickel), Pb (Lead), Se (Selenium), Ti (Titanium), V (Vanadium), Zn (Zinc), 4 anions – F- (Fluorine), Cl- (Chlorine), NO3- (Nitrate), SO42- (Sulfate) and one cation – NH4+ (Ammonium) using ICP-OES and IC, respectively. The mean PM1 mass concentrations were 114 ± 71 microgram per cubic meter. Positive Matrix Factorization (PMF) was employed to apportion the sources for submicron particles and understand the variation in the source strength. PMF apportioned the PM1 mass into eight factors, including incinerator/waste burning/biomass burning, coal combustion, crustal material, fugitive dust, secondary aerosol, composite vehicle, iron/steel production and metallurgical industries and heavy oil combustion.

8SA.4

Chemical Source Profiles for Airborne Crustal Material Over a Region in Central India. RAMYA SUNDER RAMAN, Rohit Sirvaiya, Masood Ayub Kaloo, *Indian Institute of Science Education and Research, Bhopal*

Recently, source apportionment of ambient aerosol over locations in India utilizing receptor modeling techniques have been performed by various investigators. Source apportionment studies that use the Chemical Mass Balance (CMB) model are compelled to utilize the USEPA 'fingerprints', which are often inappropriate for aerosol measured over locations in India. Thus, the current study is aimed at generating source profiles for crustal material over a region in Central India. A novelty of this study is the characterization of light attenuation along with chemical species abundances in source profiles. This inclusion will help assess whether or not the differences in light attenuating species between sources can help enhance source-resolution by receptor models.

Aerosols from various crustal sources at different locations in and around Bhopal were collected using standard methods. The aerosol from each location for each source category (e.g., paved and unpaved road dust, agricultural tilling, construction, demolition, storage piles) was then sieved and re-suspended in a chamber (fabricated based on the UC Davis re-suspension chamber design). A composite aerosol for each source type (e.g., paved road dust) was obtained by compositing the aerosol collected from different locations. Once composite samples representative of different crustal sources were obtained, dried and sieved, they were resuspended to permit sampling them on to filter substrates. The resuspended aerosol was collected using a MiniVol® sampler. Both PM_10 and $PM_2.5$ inlets were used to permit the sampling of crustal material in both size fractions. Subsequent to the collection of samples on to filter substrates (Teflon and Quartz Fiber), the filters were subjected to chemical analyses including organic and elemental carbon (OC/EC), inorganic anions/cations, and trace element concentrations. Teflon filters were also used to quantify the light attenuated at two different wavelengths (870 nm and 320 nm) using an optical transmissometer (Magee Scientific, OT21).

The source profiles (chemical species and light attenuation) for PM_10 and $PM_2.5$ aerosols from different locations and source categories, and profiles for aerosol samples composited by source type from different locations will be discussed. Variability within source profiles from the same source category and size bin will also be outlined.

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8SA.5

Verification of Fire Weather Forecasts Using PM2.5 Sensitivity Analysis. SIVARAMAN BALACHANDRAN, Karsten Baumann, Jorge Pachon, James Mulholland, Armistead Russell, *Georgia Institute of Technology*

Using records from a six year period of prescribed burning (PB) activity from Camp Lejeune, NC and ambient PM2.5 from neighboring Jacksonville, NC, we employed a principal components regression (PCR) technique to verify the validity and relative importance of weather forecast parameters used by land managers in determining optimum conditions to conduct PB. The PCR results help identify sensitivities of local PM2.5 burden to the different meteorological parameters relative to PB.

The approach involves running principal components analysis (PCA) on data sets containing daily average PM2.5 mass concentration, fire activity and two types of meteorological data: i) observed meteorological conditions with A.M.-reported meteorological forecast (PC-AM) and ii) observed meteorological conditions with P.M.-reported meteorological forecast (PC-PM). Both of these data sets contained 635 days of observed and modeled meteorological parameters. The first seven principal component scores explaining over 80% of the PM2.5 variance, were regressed against measured PM2.5 for a subset of days with simultaneous occurrence of PB activity. The importance of lag on sensitivities was examined by regressing principal component scores from day n against PM2.5 from days n (lag 0), n+1 (lag 1), and n+2 (lag 2).

This analysis shows that PB can have significant impact at lag 0 but this impact is not seen at greater lags; at lags 1 and 2, meteorology drives PM2.5 levels with PB smoldering emissions seemingly having negligible effect. For both PCA-AM and PCA-PM, at lag 0, i) PB contributes approximately 3 µg m-3 per 1000 acres burned, and ii) the same NWS forecast parameters characterizing atmospheric stability; e.g. Haines index, ventilation rate, wind speed and mixing height have similar importance in keeping ambient PM2.5 levels low. Thus, foresters can plan PB conduct the day before and still meet the objective of minimal impact on local PM2.5 pollution.

8SA.6

Characterization of Re-suspended Soil Dust Samples from Sources Common in the Desert Southwest United States.ANDREA CLEMENTS, Matthew Fraser, Nabin Upadhyay, Pierre Herckes, Paul A. Solomon, *Arizona state University*

The performance and accuracy of many atmospheric source apportionment models is sensitive to representative and accurate source characterization. When it comes to a soil source signature, some source appointment studies rely on chemical source profiles for soil that were generated from samples outside the study area, many do not try to differentiate between soil type or land-use, and occasionally source profiles are not size specific. As a result, the use of profiles in the source-apportionment studies can have serious drawbacks due to representativeness issues. This might lead to an under- or over-estimate of the soil dust contribution to atmospheric particulate matter (PM).

During a recent atmospheric particulate matter characterization and source apportionment study conducted in Pinal County, Arizona, numerous samples were collected from regional dust sources including paved and unpaved roads, agricultural soils, native (undisturbed desert), and material from within a cattle feed lot. Samples were collected during several seasons. Each sample was re-suspended in the laboratory followed by collection of PM10 and PM2.5 to obtain a more accurate representation of aerosol re-entrainment by particle size. Samples were chemically characterized for bulk organic and elemental carbon content as well as for more specific markers including water-soluble ions, elements, and organic species including alkanes, organic acids, polycyclic aromatic hydrocarbons, and saccharides.

Results from this work show uniform composition of most crustal elements between PM10 and PM2.5 samples. Comparison with upper continental crust, a common surrogate for crustal material, shows several important compositional variations. As one example, arsenic is elevated in all samples consistent with water and soil samples from the desert southwest. Comparison with local native desert samples elucidates marker species that can be used to differentiate between different land use types.

8SA.7

Sources of Ultrafine Particles in the Atmosphere over the Eastern United States. LAURA POSNER, Spyros Pandis, *Carnegie Mellon University*

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

Source contribution simulations were completed by zeroing out the emitted particles smaller than 150 nm, for only one source per simulation, but maintaining larger particles and the corresponding surface and mass concentrations. Contributions of boundary conditions, initial conditions, and nucleation were also quantified in separate sensitivity tests. The source contributions of gasoline, on- and off-road diesel, natural gas, wood, biomass, dust, and other emissions to particle number in the Eastern United States were quantified for a typical summertime period. For Pittsburgh, PA, approximately 51% of the total number of particles is due to nucleation, while 29% comes from traffic emissions, 2% from power plants, and 18% from other sources, such as long-range transport. The results are consistent with observation-based estimates of the sources of ultrafine particles in Pittsburgh, though the contributions of the various sources and processes are highly variable in space and time.

8SA.8

Source Apportionment of Particles in London Paddington Station. UVEN CHONG, Jacob Swanson, Adam M Boies, *University of Cambridge*

Enclosed transit stations with diesel-powered trains are a health risk because of the close proximity of particle emissions to passengers and workers. Diesel train emissions are regulated directly by EU emissions standards and indirectly by the sulphur content of gas oil. To evaluate the impact of diesel engine exhaust within a train station relative to other emission sources, particulate matter (PM) measurements were taken at London Paddington Station. The purpose of this study is to measure the air quality (particle number and mass) within Paddington and determine the sources of particle emissions. We determine the relative contribution of PM from various sources by measuring particles in different locations and analyzing their chemical and size characteristics.

An initial station survey was conducted using a P-TRAK 8525 and OPS 3330 (TSI, Inc.) to measure the airborne particle number concentration below 0.1 micro-meters and between 0.3-10 micro-meters, respectively. Elevated levels of PM were observed during departing and arriving train activity, with departing engine acceleration causing higher levels of PM than braking from arriving trains. Measurements near food vendors also showed elevated levels of particles, indicating that cooking may be a large contributor to airborne particulates within the station.

A subsequent measurement campaign was conducted to apportion the sources of PM. PM mass concentration measurements were taken continuously at 6 locations using a TSI AM510 monitor and a portable ELF Pump with a filter. A CPC and a DMS50 (Cambustion, Inc.) were rotated between three locations. Measurements were taken with and without a catalytic stripper to determine the EC/OC ratios. Filtered PM samples were used to determine the chemical composition of particles. The results of these measurements demonstrate the relative contribution of engine and cooking particle production and provide information for policy decisions to improve air quality in Paddington by targeting the appropriate sources.

8SA.9

Positive Matrix Factorization of PM2.5 -- Uncertainty and Bias Assessment of Factor Contribution. MINGJIE XIE, Joshua Hemann, Steven Dutton, Jana Milford, Shelly Miller, Michael Hannigan, *University of Colorado at Boulder*

The Denver Aerosol Source and Health (DASH) study aims to identify and quantify the sources of ambient PM2.5 that are detrimental to human health given short-term exposure. A 2.8-year series of daily PM2.5 compositional data from Denver, CO, including concentrations of sulfate, nitrate, bulk elemental (EC) and organic carbon (OC), and 51 organic molecular markers (OMMs), was analyzed using positive matrix factorization (PMF). A novel method has been developed by Hemann et al. (2009) to estimate the uncertainty and bias related to factor contributions at the daily time scale. A stationary bootstrap technique is used to create replicate datasets, and then analyzed with PMF for each. Neural networks are trained to align the factor profiles from each PMF bootstrap solution to that of the original solution based upon the observed data (known as the base case). A PMF bootstrap solution is recorded only when each factor of that solution could be uniquely matched to a base case factor. The measurement days resampled in each recorded solution are tracked to examine the bias and uncertainty in contribution of each factor on each day. This method was applied to the 2.8-year series of PM2.5 characterization; results will be presented with an emphasis on improving the understanding of uncertainty, bias and robustness of PMF solutions for long time series.

9AC.1

Effects of Thermal Decomposition and Ion Fragmentation on Elemental Ratios and Chemical Compositions Measured with High Resolution Aerosol Mass Spectrometry. MANJULA CANAGARATNA, Paola Massoli, Leah Williams, Sean Kessler, Edward Fortner, John Jayne, Kevin Wilson, Jesse Kroll, Douglas Worsnop, *Aerodyne Research, Inc.*

Aerosol mass spectrometry has been widely used to characterize aerosol chemical composition in both laboratory and ambient environments. In thermal vaporization based aerosol mass spectrometers particulate material is first heated and the resulting gas is ionized and detected. Thus, the mass spectra obtained from these instruments reflect both thermal decomposition and ion fragmentation. Oxidized organic aerosol (OOA) species, which are known to account for a significant fraction of the organic aerosol mass measured in most ambient environments, are expected to undergo significant thermal decomposition and ion fragmentation.

In this study we use several commercially available oxidized organic molecules to evaluate the Aerodyne aerosol mass spectrometer's (AMS's) response to different types of OOA. A distinguishing feature of ambient OOA mass spectra measured with the AMS is a peak at m/z 44 (CO_2^+), which is broadly known to result from thermal decomposition and/or ion fragmentation of carboxylic acid containing moieties. Thus high resolution AMS spectra of several types of organic acid species (polyacids, keto and hydroxy acids and aromatic acids) as well as other mixed oxygen-containing functionalities are measured as part of this work. Thermal decomposition effects in AMS spectra were examined with oven temperatures ranging from 200 C to typical operating temperatures of 600 C. Ion fragmentation effects were further examined by comparing AMS spectra from conventional electron impact ionization (70 eV) with AMS spectra obtained using softer photoionization from vacuum ultra-violet light (8.5 eV-12.5 eV). Taken together, these measurements provide insight into how thermal decomposition and ion fragmentation processes affect the elemental ratios and chemical functionality information that is extracted from high resolution AMS spectra of OOA. The temperature dependent decomposition behavior of oxidized organic species is also of broader interest to other aerosol measurement techniques that utilize thermal methods to volatilize particulate material.

9AC.2

MOVI-CIMS Measurements of Organic Aerosol Generated by a Potential Aerosol Mass (PAM) Reactor. PUNEET CHHABRA, Andrew Lambe, Timothy Onasch, Manjula Canagaratna, John Jayne, Scott Herndon, Douglas Worsnop, Paul Davidovits,*Aerodyne Research, Inc.*

We present semi-continuous measurements from a micro-orifice volatilization impactor (MOVI) inlet coupled to a chemical ionization mass spectrometer (CIMS). This instrument is capable of generating high resolution time-of-flight mass spectra of gas and particle-phase organic compounds, as well as thermograms of particle-phase organics desorbed from the MOVI inlet. Here, acetate reagent ions were used in the HRToF-CIMS to facilitate the selective measurement of organic acids with minimal fragmentation. The MOVI-CIMS was used to characterize the chemical composition of laboratory secondary organic aerosol (SOA) generated in a Potential Aerosol Mass (PAM) flow reactor. Mass spectra were characterized following exposure of biogenic and anthropogenic SOA precursors to OH radicals over timescales of approximately 1 to 10 days of equivalent atmospheric oxidation at an average OH concentration of $2*10^6$ molec cm^{-3}. Positive matrix factorization of the CIMS mass spectra was used to identify gas- and particle-phase oxidation products that correspond to different generations of oxidation in the PAM reactor. These results should aid in the interpretation of ambient HRToF-CIMS measurements. Lastly, comparisons to parallel HR-ToF-AMS measurements are made to relate the CIMS results to the total secondary organic aerosol composition produced in these experiments.

9AC.3

A Source of Oxygenated Organic Aerosol and Oligomers from Primary Emitted Gases. JOHN LIGGIO, Shao-Meng Li, Alexander Vlasenko, *Environment Canada*

Recent evidence suggests that oligomer and high molecular weight (MW) species formed as a result of heterogeneous chemistry mechanisms may play an important role in SOA formation. Such a pathway is usually considered a result of the oxidation of precursors on the time scale of hours. Therefore, the degree of oxygenation in measured OM has been used as a metric to infer source types, and high OM oxygenation as represented by the atomic O:C ratio has been linked to varying degrees of aerosol aging and SOA formation, while conversely, POA is associated with a very low O:C.

In the present study the potential for primary hydrocarbon-like gases to partition and react on short timescales with inorganic seed particles is investigated by exposing ambient air influenced by vehicle emissions, to sulfuric acid particles in a smog chamber. The results demonstrate that the mixture and concentration of organic species in the ambient air is sufficient for a large organic uptake to particles to occur in less than 2 minutes. The resultant particulate organic mass spectra from the experiments were highly correlated to those of experiments exposing gasoline engine exhaust to neutral particles, and concurrent with measured decreases in unsaturated hydrocarbons from the gas-phase. The initially added organics were considerably more oxygenated than that reported for primary organic aerosol, while the presence of numerous m/z fragments greater than 300 amu suggested that oligomer formation also occurred. Oligomerization was enhanced at high acidity but otherwise unaffected by subsequent particle neutralization. These results potentially represent a new source of oxygenated POA and high molecular weight species to the atmosphere will be indistinguishable from POA mass. The results also suggest that a fraction of measured oxygenated OA, which correlate with secondary sulphate, may be of a primary source, formed prior to any gas-phase oxidation.

9AC.4

Oligomer-like Aerosol Formation from the Reactions of Secondary and Tertiary Amines with Hydroxyl and Nitrate Radicals. DEREK PRICE, Xiaochen Tang, David R. Cocker III, Kathleen Purvis-Roberts, Philip Silva, *University of California, Riverside*

Emissions of aliphatic amines are common near agricultural facilities such as animal feed lots. Determining the reactions of these amines with common atmospheric radicals is important to understanding both daytime and nighttime atmospheric chemistry. A series of smog chamber experiments were conducted in which aliphatic tertiary and secondary amines were reacted with either hydroxyl radical (OH) or nitrate radical (NO_3) in both dry and humid conditions. Chemical composition of the aerosol products was obtained with a High Resolution Time of Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and a Particle Into Liquid Sampler Time of Flight Mass Spectrometer (PILS-ToF-MS). A number of mass spectra showed highly oxidized fragments at much higher mass than the amine precursor. It is proposed that these larger compounds were formed through peroxy radical reactions with hydrogen rearrangement. Another reaction pathway observed was the formation of amine salts. While previous studies have focused on the production of amine salts, this study looks at the importance of peroxy radical reactions to the formation of secondary organic aerosol.

9AC.5

Particle Size-Dependent Incorporation of Dimethylamine into Ammonium Sulfate and Nitrate Nanoparticles. BRYAN R. BZDEK, Andrew Horan, M. Ross Pennington, Murray Johnston, *University of Delaware*

It is now established that amines can displace ammonia on the surface of 1-2 nm diameter sulfuric acid-ammonia clusters with near unit efficiency. Exposure of amines to macroscopic ammonium sulfate-coated surfaces has been shown to result in uptake coefficients on the order of 10^-2 to 10^-3. In addition, amines have been shown to slowly displace ammonia in 15-35 micrometer diameter ammonium sulfate particles. While there is now a large body of knowledge concerning amine-ammonia chemistry, reaction rates vary significantly with the type of sample, and the reactivity of amines with ultrafine ammonium salt particles has not been studied. In this work, size-selected ammonium sulfate particles in the 10-30 nm diameter range were sent through a flow tube reactor and exposed to dimethylamine vapor. At the outlet of the flow tube, particle elemental composition was measured quantitatively by the Nano Aerosol Mass Spectrometer. The amount of ammonia displaced by dimethylamine was monitored by the elemental carbon to nitrogen (C/N) ratio. By changing the length of the flow tube, kinetics for the displacement reaction were experimentally determined. Preliminary results indicate that amine incorporation into the particle bulk is highly suppressed, but becomes more favorable as the particle size increases. These observations suggest that increased particulate water content (and a less significant Kelvin effect) as particle size increases may play a key role in modulating the reaction kinetics. The kinetics are consistent with previous work showing ammonium ions on the surface of 1-2 nm diameter clusters exchange quickly with dimethylamine, while those in the cluster “core” exchange slowly if at all.

9AP.1

Agglomerate and Spherical Nanoparticle Penetration Through Nuclepore Filters: Models and Experiment. SHENG-CHIEH CHEN, Jing Wang, Heinz Fissan, David Pui, *University of Minnesota*

Nanotechnology is being developed rapidly in the past decade leading to a potential increase of engineered nanosized and submicron particles release to atmosphere as well as in workplaces. To better understand the toxicity of these small particles, Cyrs et al. (2010) conducted nuclepore filter collection with a further electron microscopy analysis to measure particle number and surface area concentrations which have been shown to associate closely with adverse health effects. The existing models such as Spurny et al. (1969) and Manton (1978) were usually used to predict the particle penetration and then provided the information for selecting a nuclepore filter with an appropriate pore size to minimize the pressure drop. In these models, particle size was one of important parameters of penetration when they were always assumed to be spherical particles. However some of these released particles are in the shape of chain-like agglomerates. For example, particles are released from welding process, CNT manufacturing, nanopodwer manufacturing and so on. Besides, penetration characteristic of agglomerates across filters is different from those of spheres with the same mobility diameter due to the difference of dynamics. To understand the difference of filtration penetration between spherical particles and agglomerates, penetrations of silver spheres and loose agglomerates, soot agglomerates, spherical PSL and cubic NaCl through Nuclepore filter were studied experimentally. The data were compared with the existing models for spheres firstly for validating the models. Then a modified fractal dimension prediction model was developed and used to predict particle effective length with different fractal agglomerates for calculating their penetrations. Good agreement between the data and model was found for various filtration operation conditions in terms of face velocity, pore diameter, particle density and particle fractals.

9AP.2

Variation in Aerosol Nucleation and Growth in Coal-Fired Power-Plant Plumes due to Background Aerosol, Meteorology and Emissions: Sensitivity Analysis and Parameterization. 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 remains 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 is thus limited by the resultant uncertainties in aerosol size distributions. In this presentation, we focus on sub-grid sulfate aerosol processes within coal-fired power-plant plumes: the sub-grid oxidation of SO_2 with condensation of H_2SO_4 onto newly-formed and preexisting particles.

Based on the results of the System for Atmospheric Modelling (SAM), a Large-Eddy Simulation/Cloud-Resolving Model (LES/CRM) with online TwO Moment Aerosol Sectional (TOMAS) microphysics, we develop a computationally efficient, but physically based, parameterization that predicts the characteristics of aerosol formed within coal-fired power-plant plumes based on parameters commonly available in global and regional-scale models. Given large-scale mean meteorological parameters, emissions from the power plant, mean background condensation sink, and the distance from the source, the parameterization will predict the fraction of the emitted SO_2 that is oxidized to H_2SO_4, the fraction of that H_2SO_4 that forms new particles instead of condensing onto preexisting particles, the median diameter of the newly-formed particles, and the number of newly-formed particles per kilogram SO_2 emitted.

We perform a sensitivity analysis of these characteristics of the aerosol size distribution to the meteorological parameters, the condensation sink, and the emissions. In general, new-particle formation and growth is greatly reduced during polluted conditions due to the large preexisting aerosol surface area for H_2SO_4 condensation and particle coagulation. The new-particle formation and growth rates are also a strong function of the amount of sunlight and NO_x since both control OH concentrations. Decreases in NO_x emissions without simultaneous decreases in SO_2 emissions increase new-particle formation and growth due to increased oxidation of SO_2.

The parameterization described here should allow for more accurate predictions of aerosol size distributions and a greater confidence in the effects of aerosols in climate and health studies.

9AP.3

A Study on Mixing Structure of Atmospheric Ultrafine Particles by Using the Thermo-Denuder HTDMA System. Kihong Park, JAE-SEOK KIM, *School of Environmental Science and Engineering, Gwangju Ins*

A hygroscopicity tandem differential mobility analyzer (HTDMA) system with a thermo-denuder (heated tube and charcoal absorber) system was applied to determine mixing structure of the size-selected ultrafine particles at urban Gwangju in Korea. Number concentration of particles of 20-600 nm was continuously measured with a scanning mobility particle sizer (SMPS). When formation of ultrafine particles was observed (e.g., photochemical and combustion events), the tandem system was triggered to measure the mixing structure of the size-selected ultrafine particles. The size-selected ultrafine particles by the first DMA were introduced into the thermo-denuder system to remove volatile species with varying temperature (20-250 oC), and the remaining particles (i.e., core particles) were exposed to increased RH to determine the hygroscopicity of the remaining particles. It was found that a distinct difference of the hygroscopicity of the remaining particles was observed between photochemical and combustion events. In the combustion event, non-volatile core was identified (i.e., no more size change with increasing the thermo-denuder temperature up to 250 oC), and the hygroscopicity of particles decreased after removing volatile species, suggesting that the core particles mainly consist of non-hygroscopic black carbon species and that the volatile species included hygroscopic species. In the photochemical event, after removing volatile species, the hygroscopicity of the remaining particles was not changed and the non-volatile core was not observed (i.e., particles were completely evaporated at 200 oC).

9AP.4

Reconciling Surface-Based Aerosol Retrievals with In-situ Aircraft Measurements in the Baltimore-Washington Area during DISCOVER-AQ. SUZANNE CRUMEYROLLE, Luke Ziemba, Andreas Beyersdorf, Lee Thornhill, Edward Winstead, Gao Chen, Joel Schafer, Brent Holben, Richard Moore, Bruce Anderson, *NASA Langley Research Center*

Satellite measurements of aerosol and trace gas species represent an important tool in expanding the global observational dataset. These measurements are often challenged near urban areas by complex spatial and vertical structures arising from the combination of intense local emissions sources and long-range pollution transport. In-situ aircraft observations provide a detailed picture of vertical aerosol structure, and are thus essential for bridging the gap between satellite observations and ground based sensors.

We present detailed measurements of aerosol optical, chemical, and microphysical properties measured aboard the NASA P-3B aircraft in the Baltimore-Washington area during the July 2011 DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) mission. Over two-hundred aircraft spiral ascents and descents were performed in the vicinity of six ground sites equipped with Aerosol Robotic Network (AERONET) sun photometers. The payload of the P-3B included a comprehensive suite of aerosol instrumentation including humidified and dry TSI 3-wavelength integrating nephelometers, a 3-wavelength Radiance Research Particle Soot Absorption Photometer (PSAP), a custom scanning mobility particle sizer (SMPS), a Droplet Measurement Technologies Ultrahigh Sensitivity Aerosol Spectrometer (UHSAS), and a TSI Aerodynamic Particle Sizer (APS). Column-integrated AERONET retrievals of aerosol single scattering albedo, Angstrom exponent and size distributions varied from those observed by the P-3B, which suggests contribution of local sources. A persistent coarse aerosol mode was retrieved from the ground, which was not observed onboard the P-3B, the implications of this disagreement for both AERONET and satellite retrievals will be discussed.

9AP.5

Validation of the Particle-Resolved Aerosol Model PartMC With Data from Chamber Experiments. JIAN TIAN, Nicole Riemer, Benjamin T. Brem, Tami Bond, Mark Rood, Martin Schnaiter, Karl-Heinz Naumann, *University of Illinois at Urbana-Champaign*

The stochastic particle-resolved aerosol model PartMC is a recently developed aerosol model that explicitly resolves and tracks the size and composition of individual particles as they undergo transformations by coagulation and condensation in the atmosphere. This approach spreads the initial aerosol size distribution over a finite number of Monte Carlo particles and allows them to evolve using the appropriate probabilities for coagulation and other processes.

We adapted PartMC for this study from the original Lagrangian parcel model to be able to represent the aerosol evolution in an aerosol chamber, with the intention to use the model as a tool to interpret and guide chamber experiments in the future. For this purpose we added chamber-specific processes such as wall losses due to diffusion and sedimentation, and dilution effects due to sampling using the approach by Naumann (2003).

We then validated the model by comparing with data from two different aerosol chambers. First was the AIDA chamber at the Karlsruhe Institute of Technology, Germany, from which we used a multi-hour data set of coagulating fractal soot particles. For this purpose the model was also extended with a treatment of fractal-like agglomerates. Second was the mixing chamber at the Department of Civil and Environmental Engineering at the University of Illinois, where we obtained several data sets of coagulation experiments using ammonium sulfate particles and succinic acid particles. We present validation results for both the particle number concentration and aerosol size distributions in the two chambers.

9CA.1

Soot Aggregate Restructuring: Effect of Surface Chemistry and Water Condensation. XIAOFEI MA, Christopher Zangmeister, George Mulholland, Michael Zachariah, *University of Maryland-College Park*

A collapsed soot structure is observed in laboratory prepared fresh soot particles upon exposure to high humidity environment followed by rapid water evaporation. The fresh soot was generated in a Santoro style ethylene diffusion burner, and the condensation of water on soot particles was realized in a temperature-controlled ADI water growth tube. The structure transformation of soot particles under different humidity conditions was monitored using a Differential Mobility Analyzer – Aerosol Particle Mass Analyzer (DMA-APM) and Tandem Differential Mobility Analyzer (TDMA) methods. The primary measured properties were mass-mobility scaling exponent, particle mass and mobility size before and after processing. A critical saturation ratio was observed above which the structure of soot start to collapse. The morphological change was visualized by taking electron microscopic images. The effect of soot surface properties on the soot structure change was investigated by measuring the critical saturation ratio for different surface-modified soot. XPS analysis found the critical saturation ratio was related to the soot oxygenation extent. A mechanism based on water droplet formation and capillary force on soot primary particles was proposed to explain the soot structure collapse process.

9CA.2

Soot Aggregate Restructuring Due to Coatings of Oleic Acid and Dioctyl Sebacate. Rouzbeh Ghazi, JASON OLFERT,*University of Alberta*

It is generally accepted that aerosols can affect climate and Earth's temperature by the scattering and absorption of sunlight. A large positive component of this radiative forcing from aerosols is due to soot that is released from the burning of fossil fuel and biomass. Freshly emitted soot particles are typically hydrophobic and fractal and mostly externally mixed with non-refractory compounds. Once emitted into the atmosphere, soot particles undergo several aging processes, and non-refractory compounds will condense on them. Soot particles in the atmosphere have different amounts of coating, and the morphology and optical properties of soot can change depend on coating thickness.

In this study, the effect of coating thickness on the morphology of soot particles is investigated by using oleic acid and dioctyl sebacate coatings. A wide range of coating thicknesses was used, with up to 12 times as much coating as the mass of the soot. It is shown that as the coating mass increases the degree of collapsing increases, but after the mass coating fraction becomes more than five, the change in diameter of the black carbon core is not significant. A model is presented to predict the change in mobility diameter after coating/denuding process. The change of effective density of soot particles in coating/denuding processes is reported. As the coating mass increases the effective density drastically increases and after that it slightly decreases. After denuding the coated particles the effective density increases due to particle collapsing. Condensing coating material on the soot causes the shape factor to drastically decrease to one and become constant for a mass coating ratio of five. After a coating/denuding process the shape factor decreases compared to fresh particle. Upon coating, the mass-mobility exponent increases from 2.14 to 3.02 (for highest mass coating fraction) and after denuding decreases to 2.38.

9CA.3

Characterization of Black Carbon Aging Processes with a Size-Dependent Timescale. LAURA FIERCE, Nicole Riemer, Tami Bond, *University of Illinois at Urbana-Champaign*

The microphysical properties of particles containing black carbon (BC) are altered soon after emission by condensation, coagulation, and photochemical reactions, collectively termed "aging". The adequate representation of these processes in models is a key challenge in determining the optical properties, chemical reactivity, and cloud condensation nuclei (CCN) activity of aged particles. The simplest representation classifies fresh BC as hydrophobic and aged BC as hydrophilic, assuming that hydrophobic BC is converted to hydrophilic BC using a fixed first-order timescale. Estimates of BC's lifetime are sensitive to the assumed aging timescale, so constraining this value is essential in determining BC's burden and climate forcing.

In this work, we present a method for explicitly calculating a size-dependent aging timescale using the particle-resolved model PartMC-MOSAIC. We define aging as the rate at which particles transition from CCN-inactive to CCN-active at a specified supersaturation threshold. The aging timescale is a function of the wet diameter of BC-containing particles $D_{wet,BC}$, the supersaturation threshold S, and the time of day t.

We determined size-dependent aging timescales for combustion-generated particles under about 300 scenarios, exploring a range of environmental parameters and pollution characteristics. The value of the timescale varied from minutes to weeks, depending on the size of the fresh BC-containing particles and the local plume dynamics. The condensation aging timescale was shortest (~10 minutes at S=0.3%) for the largest ($D_{wet,BC}$>100 nm) fresh particles and decreased with the secondary aerosol mass production rate per wet aerosol surface area (from ~1 week to ~1 hour for $D_{wet,BC}$≈100 nm at S=0.3%). The coagulation aging timescale was shortest (~1 hour at S=0.3%) for the smallest ($D_{wet,BC}$<20 nm) fresh particles and decreased with the total number concentration of large (D_{wet}>200 nm) particles. Therefore, both condensation and coagulation play important roles in aging, and their relative impact depends on the particle size range.

9CA.4

Diurnal Variations and the Effect of Atmospheric Transport on Black Carbon Mixing State: Observations from the 2010 Carbonaceous Aerosols and Radiative Effects Study (CARES). R. SUBRAMANIAN, Arthur Sedlacek, Rahul Zaveri, *RTI International*

Direct radiative forcing by BC-containing aerosols (BCA) is affected by the relative fraction of non-BC material and the particle morphology – collectively referred to as "mixing state". In June 2010, as part of the CARES field campaign, DMT single particle soot photometers (SP2) were deployed at two ground sites. T0 was located inside the Sacramento, CA urban area, while T1 was 40 km away in Cool, CA. The SP2 provides BC mass per particle, as well as information on the mixing state at the single-particle-level for a narrow range of aerosol sizes. The SP2s deployed at CARES reported mixing state information for BCA larger than ~170 nm. The incandescent lag time, defined as the time gap between the scattering signal peak and the incandescent peak for a given particle, is used as a coating indicator. An incandescent lag time of 1.5 microseconds divides thinly-coated and thickly-coated BCA, with larger values indicating thickly-coated BC cores. Meteorological conditions favored transport from T0 to T1 over certain periods, including June 23. On this day at T0, 10.5±2.1% of the morning rush-hour (7 AM – 10 AM) BCA was thickly-coated, compared to 16.9±2.0% in the afternoon (2 PM to 6 PM). However, no such variability was observed at T1, where 17.0±1.9% of the BC cores sampled from 7 AM to 7 PM were thickly-coated. The mixing state of BC at T0 was influenced by local sources as well as by a build-up of aged aerosols in the region over June 22-28, when the thickly-coated BCA number fraction reached almost 30%. Preliminary results using Gao et al. (2007)'s Leading-Edge Optimization technique indicate that at T0, BC cores smaller than 100 nm mass-equivalent diameter are thickly-coated, with a coating thickness between 60-120 nm; little coating is observed for BC cores larger than 200 nm.

9CA.5

Black Carbon Optical Properties Measured in Pasadena, Los Angeles During CalNex. Jonathan Taylor, JAMES ALLAN, Michael Flynn, Patrick Hayes, Jose-Luis Jimenez, Barry Lefer, Hugh Coe, *University of Manchester*

In climate models, black carbon absorption is commonly modelled using Mie theory, assuming a concentric sphere core-shell configuration. The resultant modelled absorption is sensitive to the physical size and complex refractive index of the particles. As nonrefractory species condense to form a thicker coating, the amount of light absorbed per unit mass of black carbon is increased, analogous to a lensing effect focusing light onto the core.

This effect has been studied in detail theoretically and observed in numerous laboratory studies. Many ambient measurements of mass absorption cross-section (MAC) are available, though most used filter-based methods, which are subject to artefacts when nonrefractory material is present. Core-shell measurements are available using the single-particle soot photometer (SP2), but the SP2's scattering measurements are sensitive to assumed refractive indices. We discuss the ambiguity in determination of the core refractive index, the sensitivity to calibration material, and the effect this has on calculated optical properties.

We present results from the CalNex study, which took place in Pasadena, Los Angeles in summer 2010, to provide a real-world assessment of the validity of models and parameters used to represent black carbon optical properties. An SP2 was deployed alongside a 3-wavelength photoacoustic soot spectrometer (PASS) measuring absorption. Combining both measurements yields the MAC in high time-resolution, free from filter-based artefacts. We compare measured MAC to that calculated from SP2 core-shell measurements using Mie theory under a range of different atmospheric conditions, to quantitatively constrain the applicability of the core-shell model in an urban environment.

9HA.1

Effects of Ambient Air Pollution on Daily Morbidity in a Developing Mega City. HAIDER A KHWAJA, Daniel Malashock, Zafar Fatmi, Azhar Siddique, Zafar Aminov, David Carpenter, *Wadsworth Center, University at Albany*

Particulate air pollution is an important public health issue. Population-based studies have documented health risks resulting from short-term exposure to particulate matter. This study investigated the short-term effects of PM2.5, black carbon (BC), and Delta-C in ambient air on hospital admissions and emergency room (ER) visits among residents living in one of the largest cities in the developing world, Karachi, Pakistan. Daily records of hospitalizations and ER visits for cardiovascular diseases (CVD) at three major hospitals serving the city were collected. The 24 h concentrations of PM2.5 were collected at two commercial/residential and industrial/residential sites. BC and DC measurements were obtained from PM2.5 filters using an optical transmissometer. Single- and multi-pollutant lagged generalized linear time-series models were utilized to analyze daily counts of hospital, meteorological, and pollutant data. PM2.5 , BC, and DC concentrations in the city ranged 27 - 279 µg/m3, 1 - 32 µg/m3 , and 0 - 9 µg/m3, respectively. Analysis showed the evidence of positive associations of fine particle air pollution, meteorological factors, and seasonal parameters with ER visits and hospital admissions due to CVD in Karachi. Statistically strongest relationships were observed for all patients (RR = 1.499, 95% CI = 1.240 – 1.812 for Korangi; RR = 1.778, 95% CI = 1.349 – 2.345 for Tibet Center) and hospital admissions (RR = 1.613, 95% CI = 1.274 – 2.043 for Korangi; RR = 2.036, 95% CI = 1.424 – 2.911 for Tibet Center) for PM2.5 concentrations (151 – 200 µg/m3). Higher effect estimates per 1 µg/m3 for BC and DC compared with PM2.5 were observed. When PM2.5 was modeled with an additional indicator, estimates generally increased and became more robust. Results suggest BC and DC were associated with CVD health effects that were not reflected quantitatively when modeled with PM2.5. This study provides scientific evidence on the magnitude of health effects associated with air pollution in urban centers of large developing nations, evaluate BC and DC as additional indicators for evaluating health impacts associated with ambient air pollution, and finally, to provide scientists and policy makers with vital information for policy planning.

9HA.2

Characterization of Ambient Air Pollution Measurement Error in a Time-Series Health Study using a Geostatistical Simulation Approach. GRETCHEN GOLDMAN, James Mulholland, Armistead Russell, Katherine Gass, Matthew Strickland, Paige Tolbert, *Georgia Institute of Technology*

In recent years, geostatistical modeling has been used to inform air pollution health studies. In this study, distributions of daily ambient concentrations were modeled over space and time for 12 air pollutants and used to assess the impact of measurement error in a time-series study of emergency department visits for cardiovascular disease. Simulated pollutant fields were produced for a 6-year time period over the 20-county metropolitan Atlanta area using the Stanford Geostatistical Modeling Software (SGeMS). The simulations incorporate the temporal and spatial autocorrelation structure of ambient pollutants, as well as season and day-of-week temporal and spatial trends. Simulated monitor data were then generated by adding measurement error representative of instrument imprecision to the simulated concentrations at the locations of actual monitors. From the simulated monitor data, four exposure metrics were calculated: central monitor and unweighted, population-weighted, and area-weighted averages. For these metrics, the amount and type of error relative to the simulated pollutant fields are characterized and the impact of error on an epidemiologic time-series analysis is predicted. The amount of error, as indicated by a lack of spatial autocorrelation, is greater for primary pollutants than for secondary pollutants and is only moderately reduced by averaging across monitors; larger error amount results in reduced statistical power in the epidemiologic analysis. The type of error, as indicated by the correlations of error with the monitor data and with the true ambient, varies with exposure metric, with error in the central monitor metric more of the classical type (i.e. independent of the monitor data) and error in the spatial average metrics more of the Berkson type (i.e. independent of the true ambient). Error type affects the bias in the health risk estimate, with bias toward the null and away from the null depending on the exposure metric; population-weighting yielded the least bias.

9HA.3

Toxicological Effects of Fresh and Aged Particulate Matter Emissions from a Wood Stove in Two Different Combustion Conditions. PASI, I JALAVA, Oskari Uski, Joakim Pagels, Erik, Z Nordin, Axel Eriksson, Christoffer Boman, Robin Nyström, Jorma Jokiniemi, Maija-Riitta Hirvonen, *University of Eastern Finland, Kuopio, Finland*

We studied the toxicological effects including inflammation, cytotoxicity and genotoxicity in mouse macrophage cells, which are the primary defense cell type in the airways against the particulate exposure. RAW264.7 macrophages were exposed for 24 hrs to four doses (15, 50, 150 and 300 micrograms in milliliter) of the particles from four different biomass combustion aerosols. Emissions from "nominal" and "poor" combustion conditions in a wood stove firing birch logs were used, either fresh or aged with ozone in a chamber of 17 cubic meters in volume. The production of cytokines (TNF alpha, MIP-2), and cytotoxicity (MTT, PI-exclusion, apoptosis and cell cycle) was analyzed thereafter. Genotoxic properties of the particulate samples were investigated with the Comet assay.

Exposure to particulate samples caused marked cytotoxicity, particles from poor combustion being significantly more cytotoxic than those from nominal conditions. In both cases aging of the aerosol increased their cytotoxicity. In addition, the emissions from poor combustion conditions increased the inflammatory response in the cells when compared to nominal conditions. Aging increased the inflammatory potential of particulate sample from nominal condition, but decreased that of poor combustion sample. All the samples induced similar genotoxic responses, but aging increased substantially the response by poor combustion sample. Genotoxicity of the largest dose of poor combustion particles could not be analyzed due to large cytotoxicity.

Accordingly, both combustion conditions and atmospheric transformation processes may affect the toxicological properties of the emitted particles from small-scale wood combustion, which may have significant role in the harmfulness of the ambient particulate matter.

9HA.4

Investigation of Air and Soil Pollution Control and Health Effects of the Population in Mitrovica. AFRIM SYLA, Rizah Hajdini,*University of Prishtina, Kosovo*

The problem of air pollution in the surroundings of Trepça mine appeared as early as 1930 when English company "TREPÇA MINES Ltd". Historic and ongoing mining activities from the Trepca group of mines have contributed to an environmental level of heavy metal and acid mine drainage pollution of the areas in close proximity to the Stari Trg with lead in particular having a well documented impact on human health, particularly in the vicinity of Mitrovica. Where the water, soil and food produced in the area have high levels of lead reported. The past and present mining activities are principally impacting on the residential areas through heavy metals being transported either through the air as dust from tailings. Showing that the mine complex at Stari Trg, including Zarkov Potok, contribute to the heavy metal contamination of Mitrovica and the surroundings through air and water pollution, though it forms only one part of such pollution caused by the poorly controlled activities of the whole industrial and mining complex in the area.

Nowhere is this impact as evident as in analysis of blood lead levels in children closest to the point sources of pollution which have been at extremely dangerous levels. The situation is so serious that the United States Center for Disease Control (CDC) was involved in emergency chelation therapy to reduce blood lead level in the most severely impacted children. The World Health Organisation (WHO) and national public health institutes have also been heavily involved in seeking to minimize the problem.

In general the information presented points to the lead dust sources (through food and transported surface dust) contributing to the worst aspects of lead, arsenic and cadmium load in the community and water pollution currently is secondary in importance. With the Zarkov Potok tailings dam perched above the town of Mitrovica with the dry tailings beaches forming an elevated mound on top of the tailings dam wall, it represented a clear point source of such airborne heavy metal contamination and was therefore selected for cleanup in this project programme. The Zarkov Potok tailings area indicate it blows directly into the village area when a southerly wind is blowing, leading to contamination of arable land and water resources from airborne dust as well as to adverse health effects of the population.

9HA.5

Traffic Related Emissions and the Risk of Pulmonary Impairment Among Traffic Wardens in Two Selected Local Councils in South Western Nigeria. GODSON ANA, John Olamijulo, *University of Ibadan*

This comparative cross-sectional study was designed to characterize traffic related air pollutants and compare lung function status of 122 traffic wardens (TW) with 125 regular police officers (RP) who served as controls and all selected from two Local councils in Ibadan. Levels of sulphur dioxide (SO2), nitrogen dioxide (NO2), and carbon (II) oxide (CO) emissions were determined using calibrated gas meters viz SO2 model Z-1300 , NO2 metre model Z-1400 and CO model CO10. Respirable Suspended Particulate Matter (PM10) was measured using personal respirable dust sampler model APM 801 and values were compared with Nigeria Guideline limits(NGL). Measurements were carried out in the morning (6am-8am), afternoon (12pm-2pm) and in the evening (4pm-6pm) for a period of 12 weeeks. A calibrated spirometer was used to determine the Forced Expiratory Volume in 1 second (FEV1) of consenting (124) TW and RP. Data were analyzed using descriptive statistics,T-test and Chi-square statistic.Mean Gas Emission Values (GEV) were CO (66.2 ± 31.5ppm), SO2 (2.1 ± 0.6ppm), NO2 (0.2 ± 0.2ppm) and PM10 (28.1 ± 11.5 µg/m3). These values exceeded NGL for CO (10ppm), SO2 (0.01ppm) and NO2 (0.06ppm) respectively The maximum GEV were obtained in the evening (4pm-6pm). Mean PM10 was lower than the NGL of 250µg/m3. There was a significant difference between the observed FEV1 in litres among TW (2.2 ± 0.7) and RP (3.4 ± 0.5).Vehicular emissions at sampling points exceeded the standard for work environment and the burden of respiratory impairment was higher among traffic wardens. The use of nose mask, routine environmental monitoring and health audit is therefore advocated.

9IM.1

Droplet Growth Kinetics from Scanning Flow CCN Analysis Data Using an Instrument Model. Tomi Raatikainen, Terry Lathem, Jack Lin, Richard Moore, ATHANASIOS NENES, *Georgia Institute of Technology*

Cloud droplet activation, and especially subsequent droplet growth, are kinetically limited by the transport of water vapor; first to the droplet surface, and then to the bulk solution. Typical inorganic salts dissociate rapidly and have a negligible effect on the vapor-liquid interface, thus droplet growth depends mainly on bulk hygroscopicity and ambient water vapor concentration. Organics species however may further slow down water vapor condensation by forming compressed surface films or exhibiting slow dissolution kinetics (promoted perhaps by glassy or highly viscous organic states). These effects are often described by an effective water vapor uptake coefficient. The information about ambient water vapor uptake coefficients is highly limited, but it has been suggested that kinetic limitations may exist in dry and cool environments.

Measurements of the water vapor uptake coefficient can be inferred from Cloud Condensation Nuclei (CCN) counters that also measure the size of activated droplets; however, the technique has proven to be challenging and requires a fully coupled instrument model. The size of activated droplets is not only dependent upon the water vapor uptake coefficient, but also the instrument operation conditions, which include column temperature, particle hygroscopicity and size distribution, and water vapor depletion effects. The influence of each of these parameters on droplet size must be carefully understood with a CCN droplet growth model in order to accurately infer the water uptake coefficient. We have developed and tested a droplet growth model for the Droplet Measurement Technologies CCN counter operated in constant flow mode (Raatikainen et al., ACPD, 2012). The model is being updated to include growth kinetics for Scanning Flow CCN Analysis (SFCA) (Moore and Nenes, Aerosol Sci. Technol., 2009), where supersaturations are scanned rapidly by changing flow rates. The updated model can also be used to predict instrument and supersaturation responses to changes in operation parameters.

9IM.2

Accurate Determination of Aerosol Activity Coefficients at Relative Humidities up to 99% Using the Hygroscopicity Tandem Differential Mobility Analyzer Technique. SARAH SUDA, Markus Petters, Timothy Wright, *North Carolina State University*

Aerosol water content plays an important role in aqueous phase reactions, in controlling visibility, and in cloud formation processes. The total amount of water bound in the particle phase depends on the aerosol hygroscopicity and the ambient relative humidity (RH). One way to quantify aerosol water uptake is to measure hygroscopic growth using the Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) technique, which uses two differential mobility analyzers (DMAs) to determine particle size before and after humidification at a known RH. However, the HTDMA technique becomes less reliable at RH > 90% due to the difficulty of controlling temperature and RH inside the second DMA. For this study we have designed and implemented a new HTDMA system with improved temperature and RH control. Temperature stability in the second DMA was achieved to ±0.02 degree C tolerance by implementing active control using four thermoelectric heat exchangers and PID control loops. The DMA size resolution was increased by operating high-flow DMA columns at a sheath-to-aerosol flow ratio of 30:1. This improved size resolution allowed for improving the accuracy of the RH sensors by interspersing ammonium sulfate reference scans at high frequency. We present growth factor data for pure compounds at RH up to 99% and compare the data to theoretical values and to available bulk water activity data. With this HTDMA instrument and method, the osmotic coefficients of spherical, non-volatile aerosols of known composition between 30 and 500 nm in diameter can be determined within ±20%. We expect that data from this instrument will lead to an improvement of aerosol water content models by contributing to the understanding of aerosol water uptake at high RH.

9IM.3

A Novel Compact Aerosol Mass Spectrometer - the ToF-ACSM: Instrument Performance and First Field Deployment. Roman Fröhlich, MICHAEL CUBISON, Jay Slowik, Andre Prévôt, Urs Baltensperger, Urs Rohner, Marc Gonin, Joel Kimmel, Douglas Worsnop, John Jayne, *Tofwerk AG*

The Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne, 2000) provides quantitative, highly time-resolved mass spectra of non-refractory, submicron particles. These data have been widely used to quantify inorganic species and organic material, segregate primary and secondary aerosol, and identify certain primary sources. The Aerosol Chemical Speciation Monitor (ACSM) (Ng, 2011) is a low-cost version of the AMS designed for long-term operation and stability. Its small size also makes it well-suited for integration into existing monitoring stations, or other locations where space is limited. However, the quadrupole-based ACSM (hereafter denoted ``Q-ACSM'') is much less sensitive than the standard AMS, constraining both detection limits and achievable temporal resolution. Here we present the testing and initial deployment of a new Time-of-Flight ACSM (ToF-ACSM).

The new Tofwerk E-ToF mass spectrometer employed in the ToF-ACSM yields a higher mass spectrometer duty cycle and improved sensitivity with respect to the Quad. Preliminary results indicate a hardware dependent improvement of the detection limits compared to the Q-ACSM of a factor of 4-18 (organics). This means that the detection limits lie between that of the W- and V-mode HR-ToF-AMS. With a resolving power of 300-500 mTh/Th, isobaric mass peaks are easily resolved, and even the mass excess of ions is discernible.

We will report instrument performance, including detection limits, short- and long-term stability and maintenance requirements. An intercomparison of the ToF-ACSM with Q-ACSM and a high resolution (HR-) ToF-AMS will be presented. Furthermore we will present first ToF-ACSM field data from deployment at the high-altitude Jungfraujoch station, which resides in the free troposphere for most of the year (Baltensperger, 1997). The low aerosol concentrations at this site provide an ideal test case for the ACSM. Finally we will demonstrate the application of the positive matrix factorization (PMF) (Ulbrich, 2009) source appointment method to the ToF-ACSM data.

9IM.4

First Field Application of a Thermal Desorption Resonance-Enhanced Multiphoton-Ionisation Single Particle Time-of-Flight Mass Spectrometer for On-line Measurements of Particle Bound Polycyclic Aromatic Hydrocarbons and Source Identification. MARKUS OSTER, Michael Elsasser, Jürgen Schnelle-Kreis, Ralf Zimmermann, *Helmholtz Zentrum München*

Laser based mass spectrometry is an important tool for the on-line detection of individual single aerosol particles. The detection of organic molecules, that are often responsible for adverse health effects, is often complicated due to a high degree of fragmentation in single particle laser mass spectrometry. Therefore, an analytical tool that uses soft ionisation techniques would be desirable.

The results of a first field application of a single particle laser mass spectrometry setup combining single particle (SP) analysis with soft ionisation during a measurement campaign are presented. This setup consists of a differentially pumped inlet system to generate a particle beam, a sizing unit for laser velocimetry of individual particles, an ion source and a reflectron time-of-flight mass spectrometer (TOFMS) for ion production and detection. The ion source consists of a heated metal surface (T=550 degrees C) for thermal desorption (TD) of particle bound components and a KrF-excimer laser (lambda=248 nm) for resonance-enhanced multiphoton-ionisation (REMPI) that is triggered according to the particle velocity to selectively ionise polycyclic aromatic hydrocarbons (PAH). The two-step desorption/ionisation allows the detection of organic molecules with reduced fragmentation.

The TD-REMPI-SP-TOFMS setup was successfully tested for the first time in the field during a measurement campaign in Augsburg, Germany in winter 2010 with the aim to analyse the impact of wood combustion on ambient aerosol with an urban background. About 360.000 particle events were detected with this setup during the campaign. Data analysis of the acquired mass spectra showed, that PAH could be found on 15.7 % of the observed particles. 2.1 % of the spectra showed besides peaks typical for PAH a peak at m/z=234, that is dedicated to retene, a marker for coniferous wood combustion. It could be shown, that there are differences in the time series, diurnal variation of occurrence and size distributions of PAH-containing and PAH-free particles, that indicate that mainly agglomerated and re-suspended particles were detected.

9IM.5

Laser Ablation Aerosol Mass Spectrometry for Molecular Analysis of Biological Materials. LIZABETH ALEXANDER, Matthew Newburn, Douglas Day, Jose-Luis Jimenez, Manjula Canagaratna, Douglas Worsnop, Vanessa Bailey, *Pacific Northwest National Laboratory*

We report on fundamental studies in the development of a laser ablation micro-sampling system coupled with aerosol mass spectrometry (LA-AMS) for micron scale characterization of microbial and other biogeochemical samples. This work extends existing laser ablation techniques, originally developed for geological and other refractory inorganic samples, to biological and other organic sample matrices. Geological analyses by laser ablation typically involve elemental and isotopic detection by ICP-MS/AES. Research in this field over the last decade established that laser ablation of refractory samples using UV wavelengths with pulse lengths below 10 ns results in the production of particles whose composition is representative of the solid material which are therefore suitable for elemental analysis with ICP-MS/AES.

Results are presented which demonstrate that laser ablation of biological and organic sample matrices by nanosecond UV commercial laser ablation systems at 193 And 266 nm (Photon Machines Analyte G2 and Cetac LSX-500) results in the production of particulates which preserve molecular information representative of the solid sample. We have characterized particle size distributions using both an SMPS and a high resolution time-of-flight aerosol mass spectrometer (Aerodyne HR-ToF-AMS) and observed a mass-weighted peak from 100 to 200 nm, an ideal size range for quantitative transport from the ablation cell to the AMS. The HR-ToF-AMS was also used to demonstrate that molecular information from complex biological and organic samples is preserved and can be used to characterize a given sample matrix using the detailed suite of statistical methods and software developed for the characterization of atmospheric aerosols. Initial data is presented using this new LA-AMS method to generate chemical images of biological samples including soil aggregates and actively growing fungi at resolutions down to 5 microns. These data also provide insights into the mechanism of particle formation by laser ablation in biological sample matrices.

9SA.1

Chemical Characterization of Ice-Nucleating Bacteria by Aerosol Mass Spectrometry. ROBERT WOLF, Jay Slowik, Johannes Schneider, Caroline Oehm, Ottmar Möhler, Andre Prévôt, Urs Baltensperger, *Paul Scherrer Institute*

Bacteria are omnipresent in the atmosphere. They have an impact on climate as efficient heterogeneous ice nuclei and they can pose a risk to human health. However, their contribution to ambient aerosol is still uncertain since quantitative online measurement techniques for the detection of airborne microorganisms are lacking. A better knowledge of the chemical composition of pure bacteria is necessary before they can be distinguished from other sources that contribute to total aerosol in ambient air. We present results of the analysis of selected ice-nucleation active bacteria by means of aerosol mass spectrometry. Different Pseudomonas species sampled from cloud and glacier-melt water were introduced into the AIDA chamber facility in Karlsruhe, Germany. An Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) equipped with a PM2.5 aerodynamic lens was used to determine the size and the chemical composition of the bacteria. The heater of the AMS was operated at 600°C and 730°C to investigate the influence of a delayed vaporization at the heater surface. At increased heater temperature the resulting size distributions show a bimodal structure in which the larger mode can be attributed to bacterial cells. The smaller mode at about 200-400 nm vacuum aerodynamic diameter can be assigned to both residual particles from the Agar nutrition medium and bacteria fragments. We demonstrate that the mass spectral signatures of the bacteria can be separated from those of the residual particles by principal component analysis. High-resolution mass spectra of the different Pseudomonas species and some nitrogen-containing marker peaks which could be used in the future to estimate the contribution of these bacteria to ambient aerosol will be presented.

9SA.2

Real-time Continuous Characterization and Quantification of Isoprene Epoxydiol (IEPOX)-Derived Secondary Organic Aerosol in Downtown Atlanta, Georgia Using the Aerodyne Aerosol Chemical Speciation Monitor (ACSM). SRI HAPSARI BUDISULISTIORINI, Manjula Canagaratna, Philip Croteau, Wendy Marth, Karsten Baumann, Eric Edgerton, Stephanie Shaw, Eladio Knipping, John Jansen, Roger Tanner, Douglas Worsnop, John Jayne, Jason Surratt, *University of North Carolina at Chapel Hill*

Real-time continuous measurements of the chemical composition of PM_1 were made using an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) during the summer and fall seasons of 2011 at Jefferson Street, Atlanta, Georgia, one of the research sites of the Southeastern Aerosol Research and Characterization (SEARCH) network.

The organic mass spectra measured by the ACSM were analyzed with positive matrix factorization (PMF), yielding three conventional factors: hydrocarbon-like organic aerosol (HOA), semi-volatile oxygenated organic aerosol (SV-OOA), and low-volatility oxygenated organic aerosol (LV-OOA). In addition to these conventional factors, in the summer PMF analysis we found an additional OOA factor that contributed on average to 32.2% to the total organic aerosol loading.

The time series of this additional factor is not correlated to anthropogenic pollutant tracers (i.e., NOx, NOy, EC, and CO) but shows a moderate correlation to SO_4, temperature, aerosol acidity and odd oxygen. These correlations suggest that the factor has a low-volatility and a temperature dependence that is consistent with that of biogenic VOC emissions. Comparison of this factor's ACSM mass spectrum with that from an aerosol mass spectrometer (AMS) previously collected by our laboratory suggests that isoprene epoxydiol (IEPOX)-derived SOA may be the source of this additional factor.

In order to further investigate the source of this factor, we chemically analyzed low-volume PM_2.5 filter samples collected from the same site by GC/MS for IEPOX-derived SOA tracers. A strong correlation ($r = 0.90$) was found between the additional factor and the sum of the IEPOX-SOA tracers, while the other factors were weakly or uncorrelated to the sum of the IEPOX-SOA tracers.

Results from our filter analyses constitute strong evidence that the additional OOA factor is attributable to IEPOX-derived SOA in the Atlanta metropolitan area. This finding illustrates the important contribution of isoprene oxidation to biogenic SOA in the Southeastern United States.

9SA.3

Characterizing Carbonaceous Materials Emitted from Animal Feeding Operations. STEVEN TRABUE, Kenwood Scoggin, Laura McConnell, Ronaldo Maghirang, Alam Hasson, Segun Ogunjemiyo, *USDA-ARS*

Studies on emission of coarse particles from animal feeding operation show that are dominated by carbonaceous materials and they are thought to be a major source for the transport of odorous material. However, few studies have characterized/quantified carbonaceous material. In this study, TSP, PM10 and PM2.5 from several different animal feeding operations (AFOs) were analyzed for VOC profiles at control, source and downwind locations (50-400 m). The types of operations monitored included both cattle and dairy feedlots, and swine operations. Sample were analyzed by thermal desorption GC-MS (TD-GC/MS) technique. The VOC compounds assoicated with PM from AFO were oxgenated and dominated by n-alkanoic acids with C16 and C18 as the most abundant compounds. Other compound classes included alcohols, carbonyls, ketones, phenols, and several multi-functional group compounds. The VOC profiles for each PM size fraction were similar for each production/animal facility. The types of production facility did influcence the VOC profile for PM. We will discuss differences between various AFO as well as the change in VOC profile of samples taken at source and downwind locations.

9SA.4

Source Apportionment of EC and OC in Beijing: Comparison between 14C Measurement and Chemical Transport Model.YU MORINO, Toshimasa Ohara, Shuichi Hasegawa, Akihiro Fushimi, Miyuki Kondo, Masao Uchida, Kiyoshi Tanabe, Kazuyo Yamaji, Bin Zhao, Jiayu Xu, Jiming Hao, *National Institute for Environmental Studies*

For the source apportionment of carbonaceous aerosols, combined analysis using radiocarbon (14C) measurement and chemical transport model (CTM) is effective (Morino et al., EST, 2010). Concentrations of fine-mode aerosols, including elemental carbon (EC), organic carbon (OC) and 14C, were observed with a time resolution of 6 hours near the urban center of Beijing in June 2010. We evaluated the model performance of CTM (CMAQ v4.6, Byun and Schere, AMR, 2006) on simulation of EC and OC. The CTM well reproduced the diurnal variation of ozone and EC, while it largely underestimated OC concentration. From sector-based tag simulation, we directly compared observed and simulated TC (=EC+OC) from fossil and nonfossil sources. Fossil-TC was well reproduced by the CTM during nighttime and largely underestimated during daytime. By contrast, nonfossil-TC concentration was underestimated both during daytime and nighttime. This result suggests that the CTM largely underestimated fossil-secondary-OC (SOC) during daytime assuming EC to primary-OC (POC) ratio from fossil sources to be correct. Underestimation of nonfossil-TC suggests that the CTM underestimated POC from biomass burning or cooking and/or biogenic SOC. Further studies on their validation and model improvement are necessary. The CTM indicated that contributions from nonfossil sources were 20% and 60% to EC and POC, suggesting that biomass burning and domestic burning had important contributions to POC in Beijing. Emissions outside Beijing contributed by 25% and 50% to EC and POC.

9SA.5

Off-Line Organic Aerosol Analyses of Filter Samples Using Aerosol Mass Spectrometry. IMAD EL HADDAD, Kaspar Dällenbach, Peter Zotter, Jay Slowik, Urs Baltensperger, Andre Prévôt, *Paul Scherrer Institute*

Field deployments of the Aerodyne Aerosol Mass Spectrometer (AMS) in the last years have advanced the real-time measurement of particle matter. Positive matrix factorization techniques applied on organic aerosol (OA) spectra demonstrate that these contain sufficient information to differentiate several OA sources. These sources include primary emissions from traffic, biomass burning and cooking and oxygenated OA interpreted to be mostly secondary. However, the high cost of the AMS and the complexity of its deployment in certain environments greatly limit the spatial coverage of AMS measurements and make the collection of long-term, continuous datasets not easily achievable. These limitations motivated us to explore the application of laboratory AMS measurements on aerosol filter samples. Such samples are relatively easy and inexpensive to collect and store, and are already routinely collected at many air quality stations worldwide. The approach consists of water or organic solvent extraction of the particulate matter from quartz filters and subsequent atomization of resulting solutions into the AMS. Using only water, we found typically an extraction efficiency of about 70%.

The obtained mass spectra from the off-line analyses were compared to average mass spectra taken from on-line mass spectrometer measurements. We found very similar mass spectra, with correlation coefficients (R2) higher than 0.97. These comparisons were done for both summer and winter samples. Both online and offline methods show for instance higher contributions from m/z related to biomass burning organic aerosol (e.g. m/z 60, 73) and hydrocarbon-like organic aerosol (e.g. m/z55, 57, 69) for the winter sample and higher contributions from OOA-related m/z ratios (e.g. m/z 43, 44) for the summer samples. Further, we will present the first application of this method on filter samples collected at different stations in Switzerland with different exposure characteristics. Source apportionment results using these data will be discussed.

10AC.1

Potential Aerosol Mass (PAM) Chamber Measurement in the Ambient Air for the Secondary Aerosol Formation and Oxidation Potential of Air Masses Transported from Korea and China. EUNHA KANG, William Brune, Taehyoung Lee, Joon-young Ahn, Meehye Lee, *Korea University, South Korea*

Potential Aerosol Mass (PAM) chamber measurement in the ambient air was performed in Baek-young Island, South Korea in August 2011 to study the secondary aerosol formation and oxidation potential of air masses transported from China and the Korean Peninsula. The site is situated in the northernmost island of South Korea in the yellow sea, which is only distanced 740 km from Beijing, China and 211 km from Seoul, Korea. The PAM chamber was a small flow-through photo-oxidation cylinder made with aluminum body and ultraviolet lamps in order to continuously photo-oxidize the sample air at high concentration of OH and O3. The OH exposure was similar to about 5 days of the integrated OH exposure for typical atmospheric OH concentration. The ambient air mass was photo-oxidized by passing through the PAM chamber and then the PAM-through aerosols were measured by the High Resolution-Time of Flight-Aerosol Mass Spectrometer (HR-ToF-AMS) and Scanning Mobility Particle Sizer (SMPS). The ambient aerosol was measured with same instruments alternately with PAM aerosol every 6 minutes. Both PAM aerosol and ambient aerosol were sampled through a PM1.0 cyclone.

The results cover the mass concentration and the size distribution of aerosols and major components such as sulfate, ammonium, nitrate and organics for two episodes; organic dominant and sulfate dominant episodes. Organic dominant episode showed the increase of highly oxygenated organic aerosols (OOAs) (e.g. m/z 44) and the formation of sulfates in PAM from the relatively fresh air masses, which was fast transported from the Korean Peninsula. Sulfate dominant episode was characterized to the no increase of OOAs in PAM due to the relatively aged air masses, which was slowly transported from China. The detailed size distribution of PAM and ambient aerosols will be further discussed regarding the possible mixing state of aerosols.

10AC.2

Volatility and Gas-Particle Partitioning of Organic Acids in a Ponderosa Pine Forest. LAXMINARASIMHA YATAVELLI, Harald Stark, Samantha Thompson, Joel Kimmel, Douglas Day, Pedro Campuzano-Jost, Michael Cubison, Joel A. Thornton, John Jayne, Douglas Worsnop, Jose-Luis Jimenez, *University of Colorado, Boulder, CO*

We present diurnal variations, volatility, and gas-particle partitioning of organic acids measured in a ponderosa pine forest during July and August 2011 as part of the Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H2O, Organics & Nitrogen - Rocky Mountain Biogenic Aerosol Study (BEACHON-RoMBAS; http://tinyurl.com/BEACHON-RoMBAS). Data was collected using a micro-orifice volatilization impactor chemical ionization high-resolution time-of-flight mass spectrometer (MOVI-HRToF-CIMS; Yatavelli et al., submitted, 2012) with acetate as the reagent ion. The volatility measurement is based on collection of submicron aerosol particles in the MOVI (Yatavelli and Thornton, AS&T, 2010) in parallel with gas-phase analysis, followed by temperature-programmed thermal desorption (TPTD) of the collected aerosol.

Estimation of ambient aerosol volatility is based on an empirical estimation following a method similar to that developed by Chattopadhyay and Ziemann (Anal. Chem. 2001) and Faulhaber et al. (AMT 2008) for other TPTD techniques. and calibrated using known semivolatile and low-volatility organic acid mixtures. The log of the vapor pressure of each compound is shown to be strongly related to the inverse of the desorption temperature for standards spanning 6 orders of magnitude in vapor pressure. A shift in the calibration curve when compared to other techniques is attributed to differences in time available for evaporation and physical arrangement of the particles on the aerosol collection surface. Positive Matrix Factorization (PMF) of individual TPTD spectra and of the time series of TPTD spectra reveal several components with reproducible differences of volatility and mass spectra, which are compared to the components derived from a co-located Aerodyne aerosol mass spectrometer (AMS) with volatility information using a thermal denuder (Huffman et al. AS&T 2008). The correlation of elemental composition and volatility is also explored. Particle fraction is shown to increase with compound carbon number, with qualitative behavior consistent with partitioning theory.

10AC.3

Closing the Gas Phase Organic Carbon Budget in Aircraft Engine Exhaust: Characterizing Low Volatility Organic Compounds (LVOCs). EBEN CROSS, James Hunter, Jonathan Franklin, Scott Herndon, Richard Miake-Lye, Michael Timko, Yu Zhenhong, Edward Fortner, John Jayne, Douglas Worsnop, Jesse Kroll, *MIT*

Gas phase low volatility organic compounds (LVOCs) comprise an atmospherically important, largely unmeasured class of organic species in the atmosphere. LVOCs consist of intermediate volatility organic compounds (IVOCs; i.e. C13-C20) and semi-volatile organic compounds (SVOCs; i.e. C21-C32). Atmospheric oxidation of gas phase LVOCs leads to the formation of secondary organic aerosol (SOA) which in turn has direct implications for climate and human health. The rates and the chemical properties of LVOC emissions are poorly characterized and not accurately parameterized in atmospheric chemistry models.

Here we describe results from the Alternative Aviation Fuels Experiment (AAFEX-II) obtained with a recently developed technique that measures the amount, volatility and bulk composition of LVOCs. LVOCs were measured as a function of engine power and fuel type at a sampling position 143 m downwind of the NASA DC-8 aircraft. Results show that LVOC emissions are highest during low engine power operating conditions (4-7% thrust), indicating that LVOCs comprise a significant fraction (~30%) of the total hydrocarbon emissions under engine idle/taxi operation. With increasing engine power, the volatility of the LVOC emissions shift from higher to lower volatility species. Combining LVOC emission indices with VOC and PM emissions provides a more comprehensive characterization of the organic carbon emitted by aircraft engines.

10AC.4

Atmospheric Chemistry of Sea Salt Particles Internally Mixed with Secondary Organic Material: Surprising Reactivity of NaCl with Weak Organic Acids. Alexander Laskin, BINGBING WANG, Alla Zelenyuk, Jacqueline Wilson, John Shilling, Rahul Zaveri, Jerome Fast, Alexei Tivanski, Mary Gilles, Ryan Moffet, Steven Kelly, Nigge Pascal, *Pacific Northwest National Laboratory*

Chemical imaging analysis of internally mixed NaCl and secondary organic material particles was performed using complementary techniques of electron microscopy-EDX microanalysis, synchrotron based X-ray spectro-microscopy, micro-FTIR spectroscopy, and single-particle mass spectrometry. Substantial chloride depletion and formation of organic salts were observed, along with distinctive changes in particle internal composition and morphology. We present field evidence, corroborated by laboratory experiments, indicating that chloride components in sea salt particles may effectively react with organic acids releasing HCl gas to the atmosphere, leaving behind particles depleted in chloride and enriched in the corresponding organic salts. While formation of the organic salts products is not thermodynamically favored for bulk aqueous chemistry, these reactions in aerosol are driven by high volatility and evaporation of the HCl product through large surface area of the particles. This substantial chemical reactivity of sea salt particles with organic acids has been largely overlooked in the atmospheric aerosol chemistry. Atmospheric aging, and in particular hydration-dehydration cycles of mixed sea salt/organic particles may result in formation of organic salts that will modify the acidity, hygroscopic and optical properties of aged particles.

10AC.5

Contribution of Cooking Emissions to Primary and Secondary Organic Aerosol in Urban Atmospheres. IMAD EL HADDAD, Stephen Platt, Jay Slowik, Claudia Mohr, Monica Crippa, Brice Temime-Roussel, Anaïs Detournay, Nicolas Marchand, Urs Baltensperger, Andre Prévôt, *Paul Scherrer Institute*

Recent, Positive Matrix Factorization (PMF) techniques applied to ambient aerosol mass spectrometer (AMS) data identified primary cooking emissions (COA) as one of the main sources of primary organic aerosol (POA) in major cities like London, New York and Beijing, contributing up to 30% of OA. Cooking processes can also be associated with volatile organic compounds that can act as secondary OA (SOA) precursors, explaining potentially in part the high levels of oxygenated OA (OOA) identified in urban areas. At present, the main cooking activities emitting primary OA and the secondary aerosol production potential (SAPP) of these emissions remain virtually unknown.

The approach adopted here is multi-dimensional, involving ambient measurements of COA contribution in European megacities, as well as laboratory quantification of PM and VOC emission factors from the main primary COA emitting processes and their SAPP. Primary emissions from deep-fat frying, vegetable boiling, vegetable frying and meat cooking were analysed under controlled conditions after ~100 times dilution for different oils, meats and vegetables. An AMS and a high resolution proton transfer time-of-flight mass spectrometer (PTR-ToF-MS) were used to quantify OA and VOC emissions, respectively. SOA production potential of the different emissions was quantified by introducing them into the new PSI mobile smog chamber where they were photochemically aged.

Our AMS measurements in Paris and Barcelona showed that cooking emissions constitute a predominant source of urban OA. In the case of Barcelona for example, COA contributed, on average, 17% to total OA. Laboratory measurements of primary emissions suggest that COA identified in ambient atmospheric aerosols is mostly related to fat release from frying with vegetable oils or grilling fatty-meats. In contrast, vegetable cooking was associated with significant VOC emissions. Emission factors and SAPP from all these processes and their potential contribution to ambient OA in urban areas will be discussed.

10AC.6

Real-Time Secondary Organic Aerosol Formation from Ambient Air using the Potential Aerosol Mass (PAM) – Aerosol Mass Spectrometer. JOSE-LUIS JIMENEZ, Amber Ortega, Brett Palm, Douglas Day, Pedro Campuzano-Jost, Patrick Hayes, William Brune, Rui Li, Daniel Bon, Joost de Gouw, Lisa Kaser, Thomas Karl, Juliane L. Fry, Kyle Zarzana, Steven Brown, et al.,*University of Colorado*

To directly study SOA formation in ambient air in real-time, we have deployed a Potential Aerosol Mass (PAM; Kang et al. ACP 2007) photooxidation flow reactor with rapid cycling of the light intensity. The input and output of PAM are analyzed with an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer, a Scanning Mobility Particle Sizer (SMPS), and a Proton Transfer Reaction-Mass Spectrometer (PTRMS). We have used this system to characterize SOA formation in (a) urban air during CalNex-LA-2010 in the Los Angeles area of California, (b) forest air at the USFS Manitou Forest in Colorado during BEACHON-RoMBAS-2011, and (c) biomass smoke at the USFS Fire Science Lab in Missoula, MT, during FLAME-3 in 2009. In some campaigns we used a gas-phase denuder to study heterogeneous OH processing of the pre-existing aerosol, or injected O3 or N2O5 in PAM without lights to investigate SOA formation from O3 or NO3 oxidation. In all cases PAM OH photoxidation enhances SOA at intermediate exposure but results in net loss of OA at very high exposures. SOA formation greatly exceeds that calculated from the measured precursors in urban air, but differences are much smaller in forest air. PAM oxidation also results in a similar slope in the Van Krevelen diagram to ambient oxidation, and in similar evolution in the AMS f44-f43 diagram as observed in PAM lab studies. New particle formation is often observed when using OH as an oxidant, but not when using O3 or NO3. Lab experiments are used to obtain SOA yields for the key precursors of the above campaigns under the same PAM conditions used in the field, and also to study SOA formation under conditions simulating the 2010 Gulf of Mexico oil spill.

10AP.1

Polarized Elastic Scatter Measurements from Optically Trapped Micron Sized Individual Particles. VASANTHI SIVAPRAKASAM, Jozsef Czege, Jay Eversole, *Naval Research Laboratory*

We are developing an experimental setup to measure multi-angle, multi-wavelength polarized scattering measurements of single aerosol particles on-the-fly. Our technique utilizes a novel approach that is a radical departure from conventional approaches to the measurement of polarized scattering data. We will present our experimental approach based on a super continuum light source, an array of optical fibers, an imaging spectrometer and EMCCD camera to instantaneously create a two-dimensional snapshot of scattering data as a function of both wavelength and scattering angle. All the parameters needed for the complete inversion analysis of the particles' size, shape and composition can be measured simultaneously.

To simplify the experimental approach we started our initial measurement on trapped particles instead of the end goal of flowing particles. We use a diode laser at 405 nm to optically trap the particles. We will present some of the polarized elastic scatter measurements from particles held in the trap. As the particles can be held stably for hours, we are able to change the optical configuration (polarizer and retarders) and make multiple Muller matrix indices on the same particle. We have done initial modeling for this measurement at specific angles and the comparison with experimental measurements shows good agreement. We are currently working on expanding our computation capabilities.

10AP.2

Infrared Extinction Spectra of Mineral Dust Aerosol. OLGA LASKINA, Jennifer Alexander, Mark Young, Paul Kleiber, Vicki Grassian, *University of Iowa*

Mineral dust aerosol plays an important role in the Earth's radiative budget. It affects the atmosphere by absorbing and scattering radiation. The effect of atmospheric dust on climate is studied by various remote sensing techniques. Key atmospheric properties are determined based on measurements from narrow band IR channels of satellites. It is important to take radiative effects of mineral dust aerosol into account to correctly process remote sensing data. In this study, Fourier transform infrared (FTIR) extinction spectra and aerosol size distributions have been simultaneously measured for authentic dust samples. The mineralogy of complex samples was inferred using linear combination of FTIR spectra. Spectral simulations were carried out using both Mie theory and solutions derived in the Rayleigh regime for specific particle shapes. Simulations of the extinction based on Mie theory shows that it does not accurately reproduce the peak position and band shape of the prominent IR resonance features. Moreover, it tends to considerably underestimate the integrated absorbance in important narrowband satellite channels. Errors in simulated peak position and line shape associated with Mie theory could adversely affect determination of mineral composition based on IR satellite data. Analytic solutions for various shapes derived from Rayleigh theory offer a better fit to the major band features of the spectra, therefore the accuracy of modeling atmospheric dust properties might be improved by using these analytic solutions.

10AP.3

Toward Understanding the Role of Turbulence in Enhancing Particle Deposition onto Vegetation. Eric Pardyjak, John Veranth, TIM PRICE, Sean Moran, *University of Utah*

Particulate matter deposition onto vegetation in the atmosphere is a complex process. This work considers a simplification of the real world problem by investigating the effect of isotropic turbulence on the enhancement of particle deposition to vegetative surfaces for inertial impaction dominated processes. Wind tunnel experiments using non-volatile particles depositing onto idealized plastic substrates and various types of artificial vegetation under controlled turbulence conditions were conducted and results are compared. The contribution of turbulence on deposition to plastic substrates is shown to scale with a dimensionless parameter formed from a combination of the classical Stokes number and a turbulence-based Reynolds number. This scaling helps to understand the role that the intermediate eddies and turbulent fluctuations have on deposition. A modified deposition fraction parameterization was devised to utilize this new scaling and incorporate physically significant turbulence parameters. Individual leaves of artificial vegetation were also shown to scale using a similar parameterization using an average leaf characteristic dimension. These results indicate that past impaction parameterizations substantially underestimate deposition in the presence of turbulence. These new parameterizations can be integrated within the Quick Urban and Industrial Complex (QUIC) Dispersion Modeling System to better estimate aerosol particles removed by vegetation and the resulting plume concentration in complex vegetative and urban environments.

10AP.4

Coulombic Fission of Ionic Salt Solution Droplets at Super-Rayleigh Limits. ASIT RAY, Kuo-Yen Li, *University of Kentucky*

Evaporation of neutral solvent from a charged solution droplet causes reduction in the droplet size, and an increase in the surface charge density. Ultimately, the charge density attains a critical limit where the droplet becomes unstable, and it regains stability by emitting a fraction of its charge and mass in the form of progeny droplets. The process is referred to as the Coulombic fission which has been confirmed to occur at the Rayleigh limit by numerous experiments. In this study we have examined the effects of ionic salts on Coulombic fission of evaporating microdroplets. Experiments were conducted on single charged droplets that were suspended in an electrodynamic balance. A resonance based light scattering technique was used to determine the size and the size change of a droplet at a charge instability induced fission, while the charge level and the charge loss were obtained from the dc voltages required to gravitationally balance the droplet. We have studied diethylene glycol and triethylene glycol droplets containing lithium chloride or calcium chloride at varying concentrations. The results of the present study on droplets containing ionic salts show that droplet fissions occur at significantly higher charge levels than the Rayleigh limit. The charge limit at a fission depends on the salt concentration in a droplet and increases as the concentration increases. When a droplet undergoes multiple fissions we observed that the charge level of a succeeding fission is always higher than preceding one due the concentrating effect of the salt. The observed charge limit increases linearly with the increasing concentration below the saturation point, and above the saturation value, the dependence of the charge stability limit on the concentration changes considerably due to the precipitation of solute at the droplet surface. Lithium chloride had more pronounced effect on the observed charge limit than calcium chloride.

10AP.5

The Effects of Small Scale Interactions on Liquid Particle Formation in Spray. WANJIAO LIU, Sean Garrick, Michael Cloeter,*University of Minnesota*

Droplet formation in sprays has been extensively studied in the past because of broad interest and applications. These include pharmacological applications, fuel spray inside engines, agricultural sprays, food processing, and chemical coatings. The effects of small scale interactions are critical to primary atomization and the break-up of the liquid jet. A clear understanding can provide guidance to the formation of liquid droplets and tailoring of droplet size distributions. However, the complicated interfacial or topological interactions — including primary breakup, secondary breakup and droplet coalescence — make the problem difficult to solve. High velocity, three dimensional character and dense distribution of liquid particles in gas medium also adds difficulty to experimental investigation. In this work we use the recently developed numerical tool - coupled level set and volume of fluid method (CLSVOF), to solve multiphase turbulent interfacial flow. Specifically, we will investigate the physical mechanisms underlying the liquid jet breakup process and the effect of small-scale interfacial structures on particle formation. Despite its critical role in droplet formation, the effect of small scale interactions in multiphase flows has not been extensively studied. We perform analyses on the effects of small scale interfacial structures, by carrying out a sub-grid scale analysis on the data from direct numerical simulation.

10AP.6

The Effect of Shape on the Electrical Mobility "Diameter" of Mineral Dust. Swarup China, Kristopher Bunker, Claudio Mazzoleni, ALEXANDER KOSTINSKI, Will Cantrell, *Michigan Technological University*

While a spherical particle's electrical mobility is unambiguous, this is not the case for irregularly shaped aerosols such as mineral dusts. For such particles, the Stokes drag depends on the orientation of the particle in the flow, which in turn, depends on the placement of an attached electric charge. What are the quantitative implications of such shape and orientation dependence for mobility?

To that end, we have compared the sizes of Arizona Test Dust and kaolinite derived from electrical mobility measurements with those derived from scanning electron microscope (SEM) images. Specifically, we select the size of the dust with a differential mobility analyzer (DMA), then collect the dust on a Nucleopore filter, which is then examined with the SEM. The discrepancy between the sizes (and distribution of sizes) derived from the DMA and SEM is striking. The projected Area Equivalent Diameter, Daeq, as derived from the SEM images, is as much as a factor of three greater than the electrical mobility diameter for the sizes examined for both dusts. The factor itself is size dependent, decreasing with increasing size of the dust. The distribution of sizes seen in SEM images for a given electrical mobility diameter is also quite broad, extending up to a factor of seven (i.e. particles with a Daeq seven times greater than the electrical mobility diameter comprise a non-negligible fraction of the particles deposited to the filter). Like the ratio of the diameters derived from the two methods, the spread of the SEM-derived size distribution diminishes with increasing size of the dust. Furthermore, kaolinite, which has a plate-like structure and tends to be less compact than the Arizona Test Dust, exhibits a larger discrepancy.

10CA.1

Differences in the Carbon Finger Print for Different Soot Sources. AMEWU A. MENSAH, Joel Corbin, Berko Sierau, *Institute of Atmospheric and Climate Science*

Soot particles significantly contribute to the total ambient aerosol particle loading. However, little is known about the chemical characteristics of soot particles originating from different soot sources. The recent development of the Soot Particle Aerosol Mass Spectrometer (SP-AMS) based on the well-known Aerodyne AMS allows analysis of soot particles in real time. As an example of a prominent ambient soot source we present the first high resolution mass spectrometric analysis of direct turbine emission soot particles sampled under controlled conditions in the turbine maintenance facility of SR Technics, Switzerland, as part of an Aircraft Exhaust Emissions Measurement Committee (E-31) campaign. We compare these results to different standard soot sources produced in the laboratory. This includes particles generated by a CAST burner under fuel-rich (brown) and fuel-lean (black) conditions, a GFG spark generator, nebulized Regal Black, and nebulized fullerene soot.

We show that the soot sources can be partly characterized by the analysis of the signal intensities of the mass to charge ratios (m/z) 12 and m/z 36. The ratio m/z 12 to m/z 36 ranges from 0.57 for CAST brown to 0.95 for CAST black. Intermediate values are determined for the other laboratory generated soot particles. Interestingly, the m/z 12 to m/z 36 ratio of a CFM56 7B airplane turbine has a value of 0.79, which is closest to the value of GFG particles (0.85). Furthermore, we present more detailed analyses of the mass spectrometric patterns such as positive matrix factorization (PMF) analysis.

10CA.2

The Examination of Mass Spectral Signatures With Different Black Carbon Sources Utilizing a SP-AMS Instrument.EDWARD FORTNER, Timothy Onasch, Leah Williams, Paola Massoli, William Brooks, Manjula Canagaratna, Puneet Chhabra, Jonathan Franklin, Achim Trimborn, Scott Herndon, John Jayne, Douglas Worsnop, *Aerodyne Research, Inc.*

The soot particle aerosol mass spectrometer (SP-AMS) instrument developed recently by Aerodyne Research, Inc. has participated in a number of field campaigns as well as laboratory studies where specific sources of black carbon-containing particles have been examined to give insight into the chemical makeup of these particular black carbon particle sources. The SP-AMS instrument combines the ability to measure black carbon with the ability to determine the chemical composition of the PM associated with black carbon particles. A 1064 nm. laser beam, based on SP2 design, is used to vaporize refractory particles such as black carbon soot particles, while a conventional heated tungsten vaporizer is used to vaporize nonrefractory particles by impaction on the hot surface (600o C). The SP-AMS may be run with or without the conventional vaporizer installed. When the conventional vaporizer is installed, the SP-AMS measures both refractory and non-refractory particles while with the conventional vaporizer removed, only black carbon-containing particles, including associated PM on those particles, are measured.

The field measurements conducted include biomass burning, flare emissions and internal combustion engine sources. Experiments with black carbon samples coated with ammonium nitrate and specific organic compounds have also been conducted in the laboratory. Campaigns examining ambient air conditions have been conducted with the SP-AMS and individual black carbon plumes have been detected. The mass spectrum measured in these ambient black carbon rich plumes will be examined and compared to different specific source mass spectral signatures.

10CA.3

Characterization of Black Carbon Containing Particles Measured by the Soot Particle Aerosol Mass Spectrometer on Board the R/V Atlantis during the 2010 CalNex Study. TIMOTHY ONASCH, Paola Massoli, Shao-Meng Li, Katherine Hayden, Christopher Cappa, Ibraheem Nuaanman, Donna Sueper, Douglas Worsnop, *Aerodyne Research, Inc.*

Black carbon (BC) containing particles formed in combustion processes are strong light-absorbers with climate forcing impacts and have a complex nature which makes their characterization (microphysical, chemical and optical) challenging. Detailed measurements of the mass, size, chemical composition, and optical properties of BC-containing particles were made as part of the CalNex 2010 study onboard the R/V Atlantis. The Atlantis was deployed to characterize inflowing and outflowing air masses along the California coast and to assess emissions from sources (e.g. ships) in coastal waters and urban ports.

We deployed a suite of particle instruments sampling behind a thermal denuder on a common inlet to investigate aerosol volatility and absorption enhancement due to BC particle coatings. Measurements obtained using an Aerodyne Soot Particle Aerosol Mass Spectrometer (SP-AMS) provided mass, size, and chemical composition of BC-containing particles. We present several cases of coastal pollution outflow events (morning and afternoon) as the R/V Atlantis often sampled air masses as they moved offshore from Santa Monica and Monterey Bays. We track changes in size, mass, volatility, and chemical composition of BC-containing particles as a function of atmospheric aging, with implications for their optical properties. We also characterized black carbon emissions from ship plumes encountered during the deployment.

10CA.4

Transformation of Diesel Soot Investigated in a Smog Chamber. JOAKIM PAGELS, Axel Eriksson, Jenny Rissler, Jonathan Carlsson, Cerina Wittbom, Erik, Z Nordin, Patrik Nilsson, Pontus Roldin, Birgitta Svenningsson, Erik Swietlicki, *Lund University, Lund, Sweden*

Atmospheric processing of soot particles ultimately leads to transformation of the agglomerated soot structure to close to spherical particles with an embedded elemental carbon core. These processes affect climate (e.g. optics and cloud formation) and health relevant properties but the dynamics and time scales of the processes are poorly known. In this work we investigated the transformation of diesel soot using photo-oxidation studies in a smog chamber.

The experiments were conducted in a 6 m3 Teflon (FEP) smog chamber, using black lights to initiate OH-chemistry. Diesel exhaust from an idling Euro II light duty vehicle was injected using a heated inlet. Varying concentrations of the secondary organic aerosol (SOA) precursors toluene and m-xylene were injected to the smog chamber to investigate different degrees of aging. The composition of the soot core, its coatings and the vacuum aerodynamic size distribution was analyzed with a Soot Particle Aerosol Mass Spectrometer (SP-AMS) (Aerodyne Inc.). The soot morphology and size dependent condensed mass fraction was investigated using a Differential Mobility Analyzer-Thermo Denuder-Aerosol Particle Mass Analyzer and TEM.

During condensation of SOA the effective density increased from values typical for fresh diesel agglomerates to 1.4 g/cm3 asymptotically, indicating that the agglomerates had been transformed to near spherical particles. The results have been summarized in a parameterization of the dependence of particle morphology (dynamic shape factor and effective density) on the condensed mass fraction and particle size during aging in the smog chamber. Humidifying the particles from the smog chamber to 90% RH using a hygroscopic tandem DMA, showed that uptake of water vapor leads to progressed compaction of the soot core at certain stages of aging.

Vacuum aerodynamic sizes of soot fragments detected with the SP-AMS increased with aging in the smog chamber. These results were compared with recent field measurements in a street canyon in Copenhagen which show one vacuum aerodynamic size mode consistent with fresh agglomerated soot and another mode of larger soot containing particles consistent with aged compacted particles.

10CA.5

Speciated Characterization of Primary Organic Aerosol Emissions from on Road Gasoline and Diesel Vehicles. DAVID WORTON, Gabriel Isaacman, Drew Gentner, Arthur Chan, Chris Ruehl, Timothy Dallmann, Thomas Kirchstetter, Kevin Wilson, Robert Harley, Allen H. Goldstein, *University of California, Berkeley*

Emissions from on road gasoline and diesel vehicles are major sources of primary organic aerosol (POA) to the atmosphere. Characterizing the chemical composition of this POA source has implications for the rate of secondary organic aerosol (SOA) formation and its resultant composition when these compounds evaporate during atmospheric dilution. Samples of vehicle exhaust particulates were collected in the Caldecott Tunnel (California highway 24) in July 2010 and analyzed by gas chromatography with high resolution time of flight mass spectrometry and vacuum ultraviolet ionization (GC/VUV-HRTOFMS). This “soft” ionization technique allows for improved identification of hydrocarbons because they display a significant parent ion peak facilitating compound classification according to carbon number, degree of saturation and number of rings in their structure. Here, POA was broadly classified into straight and branched alkanes, straight and branched cycloalkanes and aromatics. The composition of POA was dominated by hydrocarbons with between 20 and 30 carbon atoms, consistent with being derived from motor oil with minimal influence from unburnt diesel fuel and no influence from unburnt gasoline. The calibrated sum of all speciated measurements agreed with the total measured organic carbon within analytical uncertainties indicating full mass speciation of POA. These results are important for improving the representation of POA in models and have implications for the formation rate and product composition of SOA produced from the semi-volatile organic vapors because of the different atmospheric oxidation trajectories of the identified functional groups.

10CA.6

Chemical Characterization of Aircraft Engine Soot from JP-8, Fischer-Tropsch and Alternative Fuel Surrogates by Micro-FTIR Spectroscopy. JEREMY CAIN, Alexander Laskin, Edwin Corporan, David Blunck, Paul Gassman, William Roquemore, *Air Force Research Laboratory/Propulsion Directorate*

Aircraft are the major source of black carbon in the upper troposphere and lower stratosphere. These non-refractory particles impact the Earth’s climate and atmospheric environment through absorption of solar radiation and modification of cloud forming processes. As alternative fuels are explored to supplement the current jet fuel feedstock, it is important to assess the environmental impact of particulate matter (PM) emissions relevant to these fuels. PM emissions from an Allison T63-A-700 turboshaft engine are chemically characterized in this work. Six fuels were tested: a JP-8, Fischer-Tropsch (F-T) and four alternative fuel surrogates (n-dodecane blends). Soot samples were deposited on silicon frame windows inside an inertial cascade impactor and subsequently analyzed by micro-FTIR spectroscopy. The chemical group functionalities present in the PM samples, i.e., aliphatic C-H, acetylene C-H, C-O and C=O, were quantified. Results show similar ordering of the relative (to aromatic C-H) functionalities for JP-8 and the F-T fuel spanning the particle size and engine power ranges: aliphatic C-H (0.3-7.0) ≈ C-O (0.2-5.0) > acetylene C-H (0.07-0.7) > C=O (0.01-1.0). This trend was slightly different for the alternative fuel surrogates: [aliphatic C-H] > [C-O] > [C=O] > [acetylene C-H]. No trends in engine power or particle size were consistently observed with the relative abundances of these groups for all fuels tested. However, relative concentrations of most functionalities increased with particle size and engine power. Comparisons of particle emission rate and composition of soot from JP-8 and F-T fuels suggest that the F-T fuel might have less environmental impact, primarily due to lower emission rates. However, spectroscopy results reveal that both JP-8 and F-T produced soot particles may have ample aliphatic hydrocarbon bonds to serve as surface sites for heterogeneous reactions at cruise altitudes.

10HA.1

Motion of Ellipsoidal Fibers in Human Tracheobronchial Tree. LIN TIAN, Goodarz Ahmadi, Philip K. Hopke, Yung-Sung Cheng,*Clarkson University*

Fate of the inhaled asbestos fibers has been of considerable research focus during the past few decades due to its malignant pathological response in living beings. Extensive earlier studies, has been identified links between the inhalation of asbestos and the occurrence of lung cancer; however, details of the pathological correlation are still to be uncovered. The understanding is further hampered by the lack of tools to reveal the details of motion of the asbestos fibers and their interaction with the airflow within the tracheobroncial airways. This computational work is intended to provide a better understanding of the motions of elongated fibers in the human lung, so that the fate of these fibers can be assessed. System of coupled nonlinear equations governing the fibers translational and rotational motions were described and solved numerically. Correlations between the deposition pattern, fiber characteristics, breathing conditions, and airway morphology in human upper tracheobronchial airways were derived. The simulation results were compared with the experimental data, and good agreement was found.

10HA.2

Respiratory Deposition of Fine and Coarse Particles During Moderate Exercise. CHONG KIM, Shu-Chieh Hu, *USEPA*

During exercise breathing patterns change by increasing ventilation rate and this has a direct impact on risk to exposure to ambient pollutants. Although the number of people increases participating in more active life styles, specific data for lung deposition of particulate matter are lacking for exercise conditions.

We measured total lung deposition (TDF) of micron-sized aerosols (Dp=1, 3 and 5 um diameter) in 15 healthy individuals (8M/7F) with breathing patterns of both resting (Vt =500-750 ml and f = 12-15 min-1) and moderate exercise (Vt =1000-1500 ml and f = 20-30 min-1) conditions. The minute ventilation (Vmin) was 7.5 and 30 l/min, respectively. Subjects inhaled the test aerosols via the mouth while both aerosol concentration and breathing pattern were being continuously monitored. TDF for each breath was determined and deposition rate (Drate) was calculated by TDF x Vmin, an indicative of lung deposition per minute.

TDF was 0.18, 0.48 and 0.64 at rest and 0.15, 0.53 and 0.80 during exercise for Dp = 1, 3 and 5 um, respectively. TDF decreased for Dp=1 um (-20%) but increased for Dp = 3 um (+12%) and 5 um (+25%) during exercise. Drate was 1.38, 3.56 and 4.79 at rest and 4.44, 16.0 and 23.9 during exercise for Dp = 1, 3 and 5 um, respectively. Compared to resting, Drate increased by 3.2, 4.5 and 5.0 times during exercise for Dp = 1, 3 and 5 um, respectively and the increase was smaller by 20% for Dp = 1 um, comparable for Dp = 3 um and greater by 25% for Dp = 5 um than Vmin ratio of 4 (exercise vs. resting).

In conclusion, during exercise lung deposition rate increases more rapidly for larger size particles and this may result in a greater risk to exposure to coarse than fine particles.

10HA.3

Deposition of Carbon Nanotubes in a Human Nasal Airway Replica. WEI-CHUNG SU, Bahman Asgharian, Yung-Sung Cheng,*Lovelace Respiratory Research Institute*

Carbon Nanotubes (CNTs) aerosols may appear in related workplaces in nanometer size range where they could be inhaled by the workers causing potential health problems. Therefore, investigating the deposition of CNTs in the human airway is important and necessary to assess the health risk posed by the occupational exposure to these particles. This study used a nebulizer to aerosolize Stacked-cup Carbon Nanotube (SCCNT) and Single-walled Carbon Nanotube (SWCNT), and employed an electrostatic classifier to classify the CNT aerosols by electrical mobility. The size-classified CNT aerosols were then measured by a sequential mobility particle sizer (SMPS), an electrostatic precipitator (ESP), a micro-orifice uniform deposition impactor (MOUDI), and a TEM to obtain their physical characteristics and morphology. The deposition study was conducted by delivering the size-classified CNT aerosols into a well-defined human nasal airway replica. The deposition fractions and deposition efficiencies of the CNT aerosols in the nasal airway were determined by the concentration ratios of the CNT aerosols measured at the inlet and the outlets of the replica. The deposition results showed that very few CNT aerosols were deposited in the nasal airway which implies that most of the size-classified CNTs in this study could easily transport down to the lower human airway. The results suggest that the deposition mechanism for the size-classified CNT aerosols, studied in this work, is likely diffusion. These data acquired will be used in the development of a human respiratory tract deposition model for related CNTs.

10HA.4

Comparative Total Lung Deposition for the Two In-vivo Nano-Aerosol Inhalation Studies. VLADIMIR MIKHEEV, William Forsythe, Kevin Minard, Wei Wang, *Battelle Memorial Institute*

Two in-vivo inhalation studies were conducted on BALB-C Mice using nano-aerosol generated out of superparamagnetic iron-oxide nano-particles (SPIO NP). SPIO NP were prepared by chemical co-precipitation and surface modified with carboxylic groups using two different methods.

Aerosol was generated from water suspension of SPIO NP via Collison nebulizer using helium carrier-gas applied at 80-100 psi. Aerosol laden helium flow was mixed with HEPA-filtered air and oxygen, dried, and delivered to the nose-only exposure carousel. Exposure carousel consisted of multiple tiers (8 nose-ports per tier) that allowed simultaneous exposure of several dozens of rodents.

Aerosol number concentration and count median diameter (CMD) was monitored using Scanning Mobility Particle Sizer (SMPS). Aerosol mass concentration was determined using gravimetric filter analysis. Aerosol mass median diameter (MMD) was measured using Nano Micro-Orifice Uniform Deposition Impactor (MOUDI). Scanning Electron Microscopy images of the NP deposited on the MOUDI stages were taken. Spatial uniformity of aerosol distribution across the exposure carousel was measured using SMPS.

Rodents were exposed for 4 hours per study. Respiratory physiology measurements (tidal volume - TV, respiratory rate - RR, minute volume - MV) were taken using whole body plethysmography. MV and aerosol mass concentration were used to estimate total inhaled mass (TIM). Magnetic Particle Detection (MPD) was used to measure iron mass deposited in the lungs.

Parameters of the aerosol generated for the first study, respiratory physiology, and MPD data were: CMD=93.4 nm (GSD=1.7), MMD=164 nm (GSD=2.4), mass concentration 8.7 mg/m^3, MV=72 ml/min, TIM=3.2 microgram. Parameters of the second study were: CMD=68.6 nm (GSD=1.6), MMD=207.0 nm (GSD=2.5), mass concentration 19.9 mg/m^3, MV=76 ml/min, TIM=13.8 microgram.

Results have demonstrated non-linear dependence of total lung deposition upon inhaled mass. Based on lung deposition models particle size difference may not fully explain obtained results. Influence of NP surface properties could also affect lung deposition efficiency.

10HA.5

Idealized Infant and Child Throats for Mimicking Average Extrathoracic Deposition. Warren Finlay, Laleh Golshahi, Emad Javaheri, CONOR RUZYCKI, *University of Alberta*

Deposition in the extrathoracic region is an important factor in determining the dose of inhaled aerosol that reaches the lungs. While realistic throat replicas are sometimes used in bench-top testing of inhalation aerosols, such replicas are too complex to be accurately and inexpensively manufactured from durable conducting materials. In addition, they only mimic deposition in one particular individual. To address these limitations, we have developed idealized child and infant extrathoracic airways. The idealized child geometry was developed by scaling the adult Alberta Idealized Throat homogeneously such that the ratio of volume to surface area is equal to the average value of this parameter in computed tomography (CT) scans of 9 orally inhaling children aged 6-14 years. Deposition in this scaled, idealized child throat for flow rates of 30-150 l/min and particle sizes of 0.5 -5.3 micrometers is found to match average values seen in realistic replicas of these 9 children (Golshahi et al., J. Aerosol Sci. 49:21-31, 2012). A comparison is also made with published in vivo deposition scintigraphic data with Turbuhaler and Qvar inhalers. Good agreement with this in vivo data is seen. An idealized infant geometry is also defined by examining CT scans of 10 infants (age 3-18 mo.) in which we have previously characterized nasal airway deposition (Storey-Bishoff et al. J. Aerosol Sci. 39:1055-1065, 2008). Deposition in this idealized infant geometry is measured with representative tidal breathing patterns and particle sizes 0.8-5.3 micrometers and found to match average values seen in the 10 realistic replicas. The present pediatric idealized throats may be useful for bench-top estimation of average extrathoracic deposition in infants and children.

10HA.6

Evaluation of Drug Particle Deposition in Mouse Lung via Inhalation. JINGJIE ZHANG, Da-Ren Chen, Yian Wang, *Washington University in St. Louis*

The inhalation of drug aerosols is one of administration routes for drug delivery, especially for the diseases in the respiratory tracts and the lung. The efficacy of a given drug via aerosol administration depends on many factors such as the particle size distribution, total particle mass concentration, and the physiochemical properties of drug particles. Genetically-engineered mice play an important role in drug screening and preclinical studies. Limited studies have been focused on particle deposition in mouse lungs. Because of much smaller dimension of the mouse respiratory system than human being’s, the deposition data obtained for human respiratory systems are not applied to the cases of mice. It is thus necessary to measure the mass deposition of particles in mouse lung.

In this study, Cisplatin-loaded polymer particles produced by aerosol generators were used. Cisplatin is an anticancer drug. Various polymers were also applied in the spray solutions to extend the retention time of Cisplatin in the mouse lung. We used electrospray aerosol generator to produce monodisperse drug particles of various sizes. For the comparison we also used Collison atomizer to generate polydisperse Cisplatin-loaded polymer particles. Generated particles were delivered to a custom-built nose-only exposure chamber and inhaled by the mice. The mice were sacrificed immediately after specified exposure time periods. The lungs of exposed mice were harvested and flash-frozen in liquid nitrogen lobe by lobe. The collected lung tissue samples were weighed and homogenized to extract Cisplatin. The extracted drug was then analyzed by ICP-MS. The deposition efficiency of drug particles was then derived from the mass measurement of Cisplatin contained in collected tissue samples for each mouse lung. At the same time, the size distributions of Cisplatin-loaded polymer particles were characterized via Scanning Mobility Particle Sizer (SMPS; TSI Inc). The airborne mass concentration of test particles in the exposure chamber was measured by a portable dust monitor (Kanomax, Model 3521). The result of this study will be given in this presentation.

10IM.1

The Effects of Ammonium Nitrate Equilibrium on Real-Time Measurements Particulate Nitrate. YONG J. LI, Berto Lee, Chak K. Chan, *Hong Kong University of Science and Technology*

The volatile characteristic of nitrate can result in multiple-mode distribution in the presence of coarse particles due to re-partitioning from fine particles to gas phase, followed by chloride depletion or reactions with crustal aerosols (Zhuang et al. 1999; Yao et al. 2001). The multiple-mode distribution of nitrate may influence nitrate measurements due to different inlet size-cuts used among different instruments. Here we present measurement results of particulate nitrate by AMS and MARGA at a coastal site in Hong Kong. While most of other species showing reasonable agreements between the two instruments, nitrate measurements had a large discrepancy, with the largest discrepancy during daytime. We used several parameterization methods to estimate the partitioning coefficient ($K_p = p_{NH3} \times p_{HNO3}$) of ammonium nitrate, from temperature dependent (solid only) (Mozurkewich 1993), T-relative humidity dependent (solid/liquid) (Mozurkewich 1993), to T-RH-ionic strength ($Y = n_{NO3}/(n_{NO3} + 3n_{SO4})$) (Seinfeld and Pandis 2006) dependent estimations. Results showed that even with T, RH and Y taken into account (lowest K_p), gas-particle equilibrium could not be reached based on measured NH_3 and HNO_3 by MARGA. The product of total ammonium and total nitrate were compared with $K_p = f(T, RH, Y)$. It is deduced that equilibrium was reached during nighttime, but still not daytime. It is possible that daytime re-partitioning of nitrate is more prominent and shifts the nitrate to the larger sizes by heterogeneous reactions. These results suggest that the multi-mode distribution of nitrate has a strong effect on the real-time measurements of nitrate.

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10IM.2

Evaluation of a Particle Trap Laser Desorption Mass Spectrometer (PT-LDMS) for Online Measurements of Aerosol Composition. NOBUYUKI TAKEGAWA, Takuma Miyakawa, Naoki Takeda, Masahiko Takei, Noritomo Hirayama, *RCAST, University of Tokyo*

We have developed a new aerosol composition analyzer, a particle trap laser desorption mass spectrometer (PT-LDMS), for online measurements of sulfate, nitrate, and organic carbon (OC). The main components of the instrument include an aerodynamic lens, a particle trap (micro-machined mesh layers coated by platinum), a quartz cell, an electron impact ionization quadrupole mass spectrometer (QMS), and a carbon dioxide (CO2) laser. Aerosol particles collected on the particle trap are vaporized by the CO2 laser and the ion signals from the evolved gas are detected by the QMS. The quantification of sulfate and nitrate is performed by detecting major fragments of these compounds. The quantification of OC is performed by catalytically converting organic compounds to relatively simple, low-molecular-weight compounds on the heated surface of the particle trap. The cycle time of the particle collection and laser desorption is typically 10 min. The concept of the PT-LDMS and first evaluation of its performance in the laboratory was given by Takegawa et al. (Aerosol Sci. Tech., 2012). Here we present further improvements and evaluation of the instrument. The fragment patterns of ammonium sulfate, ammonium nitrate, and some selected organic compounds (oxalic acid, oleic acid, glucose, etc.) were tested in the laboratory. The mass-to-charge ratios (m/z) of 48 (SO) + 64 (SO2) and 30 (NO) were the major fragments of sulfate and nitrate, respectively, and the yields of these signals per unit mass loading were reproducible. The fragments of the selected organic compounds were predominantly found at lower m/z (< 50), mostly at m/z 44 (CO2). The optimizations of the laser desorption process and the structure of the trap are now being performed to achieve high conversion efficiency for various organic compounds. Preliminary results from the ambient measurements and intercomparison with other instruments will also be discussed in the presentation.

10IM.3

Photophoretic Trapping of Absorbing Particles in Air and Measurement of Their Single-Particle Raman Spectra. YONG-LE PAN, Steve Hill, Mark Coleman, *US Army Research Laboratory*

A new method is demonstrated for optically trapping micron-sized absorbing particles in air and obtaining their single-particle Raman spectra. A 488-nm Gaussian beam from an Argon ion laser is transformed by conical lenses (axicons) and other optics into two counter-propagating hollow beams, which are then focused tightly to form hollow conical beams near the trapping region. The combination of the two coaxial conical beams, with focal points shifted relative to each other along the axis of the beams, generates a low-light-intensity biconical region totally enclosed by the high-intensity light at the surface of the bicone. Particles within this region are trapped by the photophoretic forces that push particles toward the low-intensity center of this region.

Using this system, individual micron-sized particles or aggregates of Johnson grass smut spores (an example fungal spore), riboflavin, carbon black, nigrosin, and carbon nanotubes were trapped in open air for times up to hours. Raman spectra from individual trapped particles made from carbon nanotubes were obtained in less than 1 second. The strong photophoretic force, which has been calculated to be orders of magnitude larger than the radiation pressure force, could supply a stronger optical trap than laser tweezers. This photophoretic trapping technique could lead to the development of an on-line real-time single-particle Raman spectrometer for characterization of absorbing aerosol particles.

10IM.4

Laboratory Evaluation of Selected Methods for Determining Black Carbon Source Emissions. JOHN KINSEY, Jelica Pavlovic,*U.S. EPA*

A number of studies have been conducted which compare various methods for the determination of black carbon in the atmosphere. Relatively little attention has been paid, however, to similar measurements of black carbon from different types of emission sources. Of particular interest are the non-volatile emissions from commercial aircraft engines. In this research, four different techniques were compared in the laboratory using a flow tunnel system and a soot aerosol generated by a propane diffusion burner (Mini-CAST). The four methods evaluated were: NIOSH Method 5040, multi-angle absorption photometry (MAAP), laser-induced incandescence (LII), and photoacoustic detection (Micro Soot Sensor). All of these techniques were compared to Teflon filter gravimetric analysis corrected for organic carbon content. Six tests were conducted at soot concentrations of 10, 50, 100, 500, and 1000 µg/m3 both with and without pre-treatment using a catalytic stripper. Study results showed excellent correlation between all techniques and the filter gravimetric method. In addition, the data also suggest the possibility of some sensitivity of the instrumental methods with varying levels of organic carbon in the aerosol.

10IM.5

The Use of Cavity Ring-Down Spectroscopy to Quantify Mineral Dust Optical Properties. Daniel P. Veghte, MIRIAM A. FREEDMAN, *The Pennsylvania State University*

It is currently unknown whether the direct effect of mineral dust aerosol results in a net warming or cooling of the Earth system. This uncertainty arises in part due to the varied composition and shape of dust aerosol as well as particle aging during atmospheric transport. Cavity ring-down spectroscopy is currently the most sensitive technique available to measure aerosol optical properties, but it has only rarely been used to quantify the extinction cross sections of non-spherical particles. We have used a combination of cavity ring-down spectroscopy, transmission electron microscopy, and computation to determine the extinction cross sections of size-selected calcium salts and other mineral dust species. We find that microscopy is essential for the determination of experimental parameters for cavity ring-down spectroscopy. For irregularly shaped calcium carbonate particles, we see little deviation from the optical properties of spherical particles. Our results demonstrate a method that can be used to extend cavity ring-down spectroscopy for the measurement of the optical properties of non-spherical particles.

10IM.6

A Balloon-Borne Platform for Measuring Vertically Resolved Concentrations of Black Carbon in the Troposphere. DANIEL WILSON, Odelle Hadley, Craig Corrigan, Jeff Blair, Thomas Kirchstetter, *Lawrence Berkeley National Laboratory*

Sunlight-absorbing black carbon (BC) particles emitted during combustion of fossil and biomass fuels contribute to climate change. Modeling studies agree that the climate impact of BC depends on its vertical distribution in the atmosphere. This project is developing a balloon-borne platform for the routine vertical profiling of aerosols that aircraft-based platforms cannot perform because they are too costly. Our current platform includes an improved micro-Aethalometer and a miniaturized optical particle counter integrated with a data acquisition and tracking system, altogether weighing less than six pounds. At this weight, the payload is unrestricted by the Federal Aviation Administration. Compared to its predecessor, the improved micro-Aethalometer has increased sample flow rate, inlet humidity control, and improved firmware, all of which increase stability and sensitivity for high altitude operation. In addition to aerosol data, temperature, pressure, humidity and location are recorded. At 12 km, the payload is released from the balloon, a parachute deploys, and the payload descends gently back to the Earth’s surface. Transceivers incorporated into the instrument package transmit the location of the payload to a ground operator’s laptop throughout the flight allowing the payload to be recovered after each mission. This presentation will feature a description of the technology and several test flights in California.

10RA.1

Regional Signatures from Seawater in Atmospheric Particles. AMANDA FROSSARD, Lynn Russell, Patricia Quinn, Timothy Bates, Scott Elliot, *Scripps Institution of Oceanography*

Marine aerosol particles play an important role in the earth's radiative balance, yet the sources and composition of the organic fraction remain largely unconstrained. Recent measurements have been made in order to characterize the sources, composition, and concentration of particles in the marine boundary layer. The organic compositions of submicron particles derived from multiple seawater regions have been measured using Fourier Transform Infrared (FTIR) spectroscopy. Cluster analysis of FTIR organic spectra suggest different spectral signatures based on collection location, seawater composition, and ambient conditions. Measurements including aerosol composition from a high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS), seawater composition, and wind speed were used to interpret the cluster results, depending on the availability from each campaign. Recent measurements used in the comparison include ambient and generated marine aerosol particles measured on board the R/V Atlantis during CalNex in May and June 2010. The ambient clean marine particles had an average organic mass (OM) of 0.80 micro-gram m^{-3} and average chlorophyll and wind speed values of 6 m s^{-1} and 7 micro-gram L^{-1}, respectively. Additional remote ambient marine aerosol particles were collected 100 miles off the coast of Monterey in the eastern Pacific on board the R/V Point Sur during the EPEACE experiment in July 2011 and had an average OM of 0.64 micro-gram m^{-3} and an average wind speeds of 7 m s^{-1}. These particles are compared with those measured in the southeastern Pacific during VOCALS and the north Atlantic during ICEALOT. One spectral cluster from the eastern Pacific showed the highest fraction of hydroxyl functional groups (77%), which corresponds to periods of high relative chlorophyll concentrations and high wind speeds (>10 m s^{-1}).

10RA.2

Chlorophyll-a and Other Ocean Color Products as Predictive Tools of the Organic Mass Fraction in Submicron Sea Spray.MATTEO RINALDI, Sandro Fuzzi, Stefano Decesari, Salvatore Marullo, Rosalia Santoleri, Antonello Provenzale, Jost von Hardenberg, Darius Ceburnis, Colin O'Dowd, M. Cristina Facchini, *CNR-ISAC*

Initial efforts towards developing a combined organic-inorganic sea-spray source function parameterization for large-scale models utilized chlorophyll-a and wind speed as input parameters to combine oceanic biology and atmospheric dynamics. These first studies, performed using satellite derived chlorophyll-a fields with low temporal resolution (monthly averages), reported only a modest correlation coefficient (at best 0.55) between Chlorophyll-a and organic matter enrichment in sea-spray, suggesting that Chlorophyll-a is only partially suitable for this aim.

In order to check if better biological activity surrogates are available from satellite measurements, the following research activity has been carried on, using aerosol data collected at Mace Head research station (Ireland) and satellite ocean color products from ESA GlobCOLOUR. A reconstructed Chlorophyll-a field of the North-Atlantic Ocean, based on daily data, revealed an improved correlation of 0.73 between the fractional mass contribution of organics in sea-spray and chlorophyll-a concentration. A similar analysis, using "colored dissolved and detrital organic materials absorption" and "particulate organic carbon" concentration, revealed slightly lower correlation coefficients (0.70 and 0.69). These results indicate that, to date, chlorophyll-a is the best biological surrogate for predicting sea-spray organic enrichment. In fact, considering the minimal difference between the correlation coefficients obtained with the three ocean color products, there is no reason to substitute chlorophyll-a, which is the most accurate parameter obtained from ocean color data, with other biological surrogates which in general can be affected by larger and less known errors.

A new relationship describing the organic enrichment of sea spray aerosol, as a function of both wind speed and sea surface chlorophyll-a concentration, to be implemented in large scale models, is proposed as a conclusion of this study.

10RA.3

Aerosol Hygroscopicity in a Mixed-Deciduous Forest During CABINEX 2009. George R. Mwaniki, Rosenkrance Chelsea, Mark E. Erupe, Shelley Pressley, TIMOTHY M. VANREKEN, *Washington State University*

During Summer 2009 the Community Atmosphere-Biosphere Interactions EXperiment (CABINEX) was carried out at the PROPHET research facility at the University of Michigan Biological Station (UMBS). The PROPHET site at UMBS is a forested atmospheric chemistry research station located in the northern part of Michigan's Lower Peninsula; its remote location offers a unique opportunity to study atmospheric chemistry in a region dominated by biogenic emissions of volatile organic compounds. However, despite a 15+ year history of atmospheric chemistry field work at PROPHET, virtually no aerosol measurements had been reported at the site prior to the 2009 CABINEX campaign. During CABINEX, we measured several aerosol physical and chemical properties at the site, including particle size distribution, bulk aerosol water-soluble composition, CCN concentration at five supersaturations, and the aerosol scattering coefficient.

Here we present an overview of the aerosol properties during CABINEX and a detailed hygroscopic closure analysis for the study period. We calculated the hygroscopicity parameter (κ) of the aerosol using two distinct approaches: 1) by comparing the measured CCN concentration at a given supersaturation to the particle size distribution; and 2) using measurements of aerosol water-soluble composition along with reasonable approximations of aerosol properties that were not directly measured. The κ-values resulting from these two approaches are compared. Wet aerosol volumes are also calculated using these calculated κ-values and compared to observations of aerosol scattering coefficient. Finally, the observed variability in aerosol hygroscopicity is related to broader patterns in meteorological conditions and atmospheric pollution.

10RA.4

LADCO Winter Nitrate Study – Sensitivity of 2009 Winter PM2.5 to Modeled Reductions in NOx and and Ammonia.CHARLES STANIER, Scott Spak, Yoo Jung Kim, Jessica Carlson, Jaemeen Baek, Gregory Carmichael, Abigail Fontaine, Mark Janssen, Michael Koerber, Nicole Riemer, Stephanie Shaw, *University of Iowa*

The Winter Nitrate Study was a measurement campaign with subsequent model-based analysis designed to understand wintertime episodes of elevated fine particulate (PM2.5) concentrations in the upper Midwest. These episodes occur several times per year throughout the upper Midwest, and hinder compliance with the 24-hour average federal air quality standard for PM2.5 of 35 micrograms per cubic meter. These episodes are often regional and are characterized by low wind speeds, near-freezing temperatures, and elevated levels of ammonium nitrate. From December 2008 to March 2009, an intensive monitoring campaign was conducted including continuous measurements of ammonia, ammonium, nitrate, nitric acid at an urban site (Milwaukee, Wisconsin), and an upwind rural site. We analyze results from 12 km resolution simulations using WRF v3.1 with CAMx v5.3 and CMAQ v4.7 chemical transport modeling to address the question: How effective are NOx, NH3, and SO2 emission reductions on PM2.5 concentrations? A method of observationally constraining total ammonia and total nitrate in conjunction with the forward sensitivity model is implemented and comparison to direct forward model sensitivity will be presented.

For the upper Midwest, equal percentage reductions of NH3 emissions and NOx emissions do not result in equal reductions in PM2.5, and the spatial patterns of the reductions are also different. NH3 emissions reductions lead to larger PM2.5 reductions than the corresponding NOx controls by a factor of about four for Mayville and Milwaukee. NOx reduction leads to PM2.5 reductions mainly west of the Mississippi in ammonia-rich regions. Ammonia controls are simulated to have reductions mainly east of the Mississippi river. These features (of NOx and NH3 reductions) are predicted in both the CAMx and CMAQ model runs. Localized reductions of both NH3 and NOx were simulated.

10RA.5

Current and Future Impacts of Natural Gas Drilling in the Marcellus Shale on Regional NOx, VOC and PM2.5 Emissions.

ANIRBAN ROY, Peter Adams, Allen Robinson, *Carnegie Mellon University*

Recent discovery of reserves of shale gas, combined with advances in drilling technology, are leading to extensive development of natural gas from the Marcellus Shale formation which straddles Pennsylvania, West Virginia, Ohio and New York. However, drilling for natural gas raises several air quality problems. We constructed a regional emission inventory for the development and production of gas from the Marcellus formation, including emissions for VOC, NOx and PM2.5. The most important emissions sources for NOx and PM2.5 include diesel powered drilling rigs, hydraulic fracturing pumps, and natural-gas fired compressors. Completion venting, condensate tanks and compressors are major sources for VOCs. We projected these emissions in 2020, using well-drilling and gas production forecasts from published reports. NOx emissions in 2009 were predominated by truck traffic and by compressors in 2020. PM2.5 emissions were dominated by trucks in 2009, and were equally split between drilling, fracing, trucks and compressors in 2020. Completion venting was seen to be a major source of VOCs in both years. It was seen that Marcellus development could contribute to 7-27% of regional NOx and 6-24% of regional VOC emissions in 2020. Relative contribution of PM2.5 emissions from Marcellus development was smaller (1-6%), but elemental carbon (EC) emissions are potentially a concern. EC emissions in 2020 from Marcellus development could not only offset the reductions in EC emissions due to control strategies, but also raise them above the 2009 values. Diesel-powered drill rigs, fracturing pumps and truck traffic were the predominant contributors to EC emissions.

10RA.6

Real-World Emission Characterization in the Canadian Oil Sands Region.

XIAOLIANG WANG, Steven Kohl, Judith Chow, John Watson, *Desert Research Institute*

The Athabasca Oil Sands Region of northern Alberta, Canada, contains about 170 billion barrels of recoverable bitumen. Crude oil derived from this bitumen is projected to increase from 1.5 to 3.5 million barrels/day from 2010 to 2025. This large-scale oil production and processing has raised environmental concerns, including potential adverse effects on air and water quality, ecosystems, human health, and climate change. Emissions from different types of heavy haulers, major stacks at mining and upgrading facilities, and fugitive dust from roads, tailings ponds, construction, and natural surfaces were characterized in this study. Dilution sampling systems were used to measure emissions from heavy haulers and stacks. It was found that emissions from most tested trucks were within the voluntary Canadian off-road Tier 1 emission limits for carbon monoxide (CO), non-methane hydrocarbon (NMHC), oxides of nitrogen (NOx), and PM2.5. Stack emission rates of major air pollutants were found to be lower than the emission guidelines for each stack during the test period, except that one of the stacks emitted 10% higher NOx than the guideline during the winter testing period. Major components in the stack emitted PM2.5 included ammonium sulfate or sulfuric acid droplets. Geological materials were collected from potential fugitive dust generation surfaces and resuspended for chemical analysis. Compared to background soil samples, most samples near oil sands operations were enriched with sulfate, high molecular weight n-alkanes, hopanes, and steranes. Real-world emission characterization aims to improve the accuracy of emission rates and chemical compositions that can be used to improve emission inventories, model emission transport and dispersion, verify source contributions, and evaluate effectiveness of emission reduction measures.

11AC.1

Laboratory and Field Studies of Organic Aerosol Aging Using Nanospray-DESI High-Resolution Mass Spectrometry.ALEXANDER LASKIN, Julia Laskin, Peter Eckert, Tran Nguyen, Paula Lee, Katelyn Updyke, David Bones, Sergey Nizkorodov, Rachel O'Brain, Allen H. Goldstein, *Pacific Northwest National Laboratory*

Nanospray Desorption Electrospray Ionization (nano-DESI) is a recently developed ambient pressure surface ionization technique integrated with high resolution mass spectrometry (HR-MS) that enables molecular-level analysis of organic aerosol (OA) samples. The nano-DESI technique offers advantages of simplicity, ease of use, sensitivity, and signal stability, and eliminates the requirement for special sample preparation. OA deposited on common substrates are readily analyzed using this approach and provide high-quality HR-MS spectra using less than10 ng of analyte. In this presentation, we demonstrate the utility of the nano-DESI/HR-MS approach in a number of our recent studies focused on molecular identification of organic compounds in laboratory-generated and in field-collected OA samples reacted with gas-phase and particle-phase ammonia. We show that reactions of OA with ammonia yield highly conjugated nitrogen-containing species that have light-absorbing properties, and possibly contribute to the formation of “brown carbon”. Understanding of the OA composition at the molecular level allowed us to identify key aging reactions, including the transformation of carbonyls to imines, carbonyl-imine oligomerization, and intramolecular “four centered” carbonyl-imine cyclization that were detected in OA samples from both field and laboratory studies. Our results indicate that the reactions between carbonyl groups and ammonia play an important role in atmospheric aging of OA and contribute substantially to the formation of brown carbon in the atmosphere.

11AC.2

Brown Carbon Formation from Reactions of Limonene-derived Ketoaldehydes with Ammonium Sulfate and Amino Acids.TRAN NGUYEN, Sergey Nizkorodov, *University of California, Irvine*

Limonene (C10H16), an important monoterpene, forms SOA that produces secondary brown carbon through reactions with ammonium sulfate (AS) and amino acids. Brown carbon is believed to make a significant contribution to light absorption by aerosols but the sources of brown carbon are poorly understood. We hypothesize that the reactive ketolimononaldehyde (KLA), the most abundant compound in the aerosol phase, is the species responsible for the brown carbon formation in limonene SOA. Synthesized and purified KLA was demonstrated to produce identical chromophores to limonene SOA when reacted with AS and glycine. Limononaldehyde (LA), a first-generation ketoaldehyde product in limonene oxidation, was also synthesized and used as a control to demonstrate that the unique structure of KLA is necessary to produce brown carbon. UV-Vis, FT-IR and NMR spectroscopy were used to characterize the chemical structures of the chromophores after separation with reverse-phase HPLC-UV. The kinetics of reaction were also quantified in both aqueous and evaporative reactions. The results suggest that KLA is likely the only precursor in the formation of brown carbon for this type of SOA and that the chromophores are nitrogen-containing organic compounds. Results of this study provide useful information on the mechanism of formation of brown carbon from secondary organic aerosols.

11AC.3

Real Refractive Indices and Volatility of Secondary Organic Aerosol Generated from Ozonolysis and Photooxidation of Limonene, Alpha-Pinene and Toluene upon Heating.

Hwajin Kim, SUZANNE PAULSON, *University of California Los Angeles*

Recent studies have suggested chamber SOA particles processed with a thermodenuder (TD) result in particles that are more representative of the atmosphere. We generated particles via homogeneous nucleation from toluene, alpha-pinene and limonene using high and low NOx photochemistry and ozonolysis, and monitored both their refractive index (a fundamental optical property) and their volatility over the range 65 - 98 C. Angular scattering was monitored with a polar nephelometer using parallel and perpendicular polarized 532 nm light, and retrievals were performed with a genetic algorithm method using Mie-Lorenz scattering theory and measured particle size distributions. Overall range of retrieved real refractive indices for the SOA was from about 1.35 - 1.62 depending on parent hydrocarbon and oxidation chemistry. Several types of particles exhibit substantial increases in refractive index as the particles grow initially, particularly limonene (1.35 – 1.56) and toluene (1.37 – 1.62) photo-oxidation and to a lesser degree alpha-pinene ozonolysis (1.38 – 1.48) and photooxidation (1.42 – 1.53). Because of the complications of retrievals from particles with rapidly changing size distributions we thermo-denuded particles only after initial rapid growth was complete. Toluene was not affected by heating in the range investigated, while alpha-pinene and limonene SOA was much more volatile, losing 30 – 60 % of their mass depending on parent hydrocarbon, oxidation chemistry and temperature. Generally as the biogenic SOA are heated the size of the particles decrease and the refractive index of the smaller particle returns to about the same value as observed for unheated particles with matched size observed earlier in the experiment, although there are a few exceptions. The possible factors controlling refractive index, its changes upon heating and its relationship with volatility will be discussed.

11AC.4

Measurements of Nitrogen-Containing Organic Particle and Gas Phase Compounds with a New MOVI-HR-ToF-CIMS.

CLAUDIA MOHR, Felipe Lopez-Hilfiker, Julia. D. Wargo, Nga Lee Ng, Lu Xu, Matthew Kollman, Peter Zotter, Andre Prévôt, Scott Herndon, Jonathan Franklin, Mark Zahniser, Leah Williams, Douglas Worsnop, Joel A. Thornton, *University of Washington, Seattle, WA*

Organic compounds are ubiquitous in the atmosphere and present in both gas and particle phase. Their evolution in time is determined by emissions, oxidation, deposition, and gas/particle partitioning especially for semi-volatiles (SVOCs). A fundamental understanding of this highly dynamic system requires quantitative measurements of organic compounds in both gas and particle phases.

Here we present data from an improved version of the Micro Orifice Volatilization Impactor High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (MOVI-HR-ToF-CIMS). While particles are impacted on a post for subsequent thermal desorption and analysis using chemical ionization mass spectrometry (CIMS), gases are drawn into the MOVI and analyzed in real time using CIMS, alternating ~every 15 min. Continuous switching between positive and negative ion proton transfer chemical ionization allows the detection of organic compounds with a variety of functional groups.

The instrument was recently deployed in a month-long field campaign (ClearfLo) in Detling, UK, from January 16 to February 15, 2012. The measurement site is influenced by local emissions from nearby roads and villages, continental air masses or the London plume. A high number of organic acids, as well as other compounds such as organonitrates and organosulfates, in both gas and particle phase up to an m/Q of ~500 Th could be detected and quantified. Nitrophenols, light-absorbing compounds in the UV, were detected at significant concentrations (a few nanograms per m3) in the particle phase. The consistency of their diurnal pattern with levoglucosan, syringic acid, and the absorbance of particulate matter at 370 nm measured with a 7-wavelength Aethalometer relates them mainly to biomass burning emissions and indicates their significance for the identification of “brown carbon” and its implications for the climate.

Initial statistical pattern analyses of the multi-dimensional field data set are also discussed.

11AC.5

Quantification of Organosulfate Formation in the SOA with Preexisting Acidic Sulfate Aerosol. JIAYING LI, Myoseon Jang,*University of Florida*

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

11CA.1

Primary to Secondary Organic Aerosol: Evolution of Emissions from Combustion Sources. ALBERT A. PRESTO, Timothy Gordon, Christopher Hennigan, Marissa Miracolo, Allen Robinson, *Carnegie Mellon University*

Mobile combustion sources such as automobiles and diesel trucks contribute to ambient organic aerosol in two ways. These sources directly emit primary organic aerosol (POA). The photo-oxidation of organic vapors that are co-emitted with the POA produces secondary organic aerosol (SOA). Several studies [1-3] have shown that SOA formation from the photo-oxidation of diluted exhaust is larger than POA emissions by a factor of 4-50. This importance of SOA from mobile sources is consistent with ambient AMS measurements that indicate SOA, in the form of the various OOA factors, dominates ambient organic aerosol in nearly all environments. [4]

This presentation investigates the evolution of the aerosol mass spectra of dilute POA and the resultant SOA from smog chamber experiments conducted with various combustion sources, including gasoline automobiles, diesel trucks, gas-turbine engines, and wood smoke measured with an Aerodyne quadrupole AMS. Contributions and mass spectra of SOA and POA are estimated using Positive Matrix Factorization [5] and analyzed using the f_{44}/f_{43} triangle of Ng et al. [6, 7]

The gasoline and diesel data can be explained with two PMF factors – one for POA and one for SOA. The determination of a single SOA factor suggests that SOA formed in the chamber is dominated by “first-generation” chemistry, consistent with an effective atmospheric timescale of several hours. The experiments do not have significant multi-generational chemistry or oxidative aging that would occur over several days. The POA factor is spectrally similar to the ambient HOA factor, with high f_{43} (~0.07 – 0.1) and low f_{44} (<0.05). The SOA factors have higher f_{44} and lower f_{43} and are spectrally similar to mildly oxidized SV-OOA. When plotted in Van Krevelen space, the SOA and POA factors exhibit a slope of approximately -0.5. This suggests that SOA formation chemistry in these experiments includes the addition of both acid and alcohol/peroxide functional groups, and is chemically similar to ambient SOA. [6]

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11CA.2

Road Vehicle Primary and Secondary Organic Aerosol. ANDRE PRÉVÔT, Stephen Platt, Alessandro Zardini, Clairotte Michael, Covadonga Astorga, Robert Wolf, Imad El Haddad, Jay Slowik, Brice Temime-Roussel, Nicolas Marchand, Irena Jezek, Luka Drinovec, Grisa Mocnik, Ottmar Möhler, Urs Baltensperger, *Paul Scherrer Institute*

A large fraction of ambient PM consists of organic aerosol (OA), either primary (POA), from direct emissions, or secondary (SOA), formed from gaseous precursors. Therefore any attempt to mitigate the effect of on-road vehicle emissions on public health and the environment should consider not only primary aerosol emissions but also secondary aerosol production potential (SAPP). However, only the primary aerosol from on-road vehicles is currently subject to direct legislation.

We determined emission factors (EFs) (g kg -1 fuel) for primary PM and for SOA, from two- and four-stroke scooters, a gasoline car and a truck, all complying with the latest European emissions standards. We also quantified the effect of using alkylated gasoline in scooters, liquid petroleum gas (dual fuel) in trucks and the effect of ambient temperature on SOA formation from gasoline cars and from trucks.Vehicle exhaust was introduced into the new PSI mobile smog chamber during regulatory driving cycles on chassis dynamometers at the European Joint Research Centre Ispra, Italy. A high-resolution time-of-flight aerosol mass spectrometer equipped with a PM 2.5 lens was used to quantify OA. Black carbon was measured using a multi angle absorption photometer and an Aethalometer (AE 33 prototype). A high resolution proton transfer time-of-flight mass spectrometer was used to investigate volatile organic compounds gases including the determination of the OH clock using deuterated n9-butanol (Barmet et al., 2012). Primary exhausts of 2-stroke scooter emissions could be shown to be very high whereas the SAPP versus primary organic emissions of gasoline cars and 4-stroke scooters were strongly enhanced. Results for various technologies will be presented in detail at the conference.

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Barmet et al. (2012) Atmos. Meas. Tech. 5, 647-656.

11CA.3

Organic Aerosol Formation and Processing in the Los Angeles Basin: Role of Gasoline vs. Diesel Emissions. ROYA BAHREINI, Ann Middlebrook, Joost de Gouw, Carsten Warneke, Michael Trainer, Charles Brock, Harald Stark, Steven Brown, William P. Dube, Jessica Gilman, Katharine Hall, John Holloway, William C. Kuster, Anne Perring, Andre Prévôt, Joshua P. Schwarz, J. Ryan Spackman, Soenke Szidat, Nick Wagner, Rodney Weber, Peter Zotter, David D. Parrish, *CU CIRES- NOAA ESRL*

Laboratory experiments have shown that organic compounds in both gasoline fuel and diesel engine exhaust can form secondary organic aerosol (SOA); however, the fractional contribution from gasoline and diesel exhaust emissions to ambient SOA in urban environments is poorly known. Here we use airborne and ground-based measurements of organic aerosol (OA) in the Los Angeles (LA) Basin, California made during the CalNex field project (“Research at the Nexus of Air Quality and Climate Change, May and June 2010) to assess the amount of SOA formed from diesel emissions. Airborne black carbon (BC) measurements indicate that diesel emissions in the LA Basin are lower on weekends by 54%. Despite the lower contribution of diesel emissions on weekends, formation of OA in air masses with similar degrees of photochemical processing is the same on weekends and weekdays, within the measurement uncertainties. This result indicates that the contribution from diesel emissions to SOA formation is zero within our uncertainties. Using these uncertainties, we estimate that the maximum weekday contribution from diesel engine emissions to SOA is 20%. Therefore, a decrease in the emission of organic species from gasoline engines may significantly reduce SOA concentrations on local and global scales.

11CA.4

Unresolved Complex Mixture Emissions from Combustion Sources and Their Potential to Form Secondary Organic Aerosol. SHANTANU JATHAR, Havala Pye, Peter Adams, Allen Robinson, *Carnegie Mellon University*

The Center for Atmospheric Particle Studies (CAPS, Pittsburgh PA) has undertaken numerous studies to investigate secondary organic aerosol (SOA) formation from various combustion sources (aircraft, gasoline and diesel light-duty vehicles, biomass). Across the different sources, we make two robust conclusions. One, a significant fraction of the gas- and vapor-phase organic emissions remain unspeciated or unresolved; these include semi-volatile and intermediate volatility organic compounds and are referred to as an unresolved complex mixture (UCM) And two, after a few hours of photochemical processing, SOA accounts for a significant fraction of the (primary+secondary) aerosol mass, most of which cannot be explained by speciated SOA precursors. We hypothesize that the unexplained SOA arises from the gas-phase oxidation of these UCM emissions. In this work, we propose a simple method to model SOA formation from UCM emissions and use it to quantify UCM’s influence on the regional and global SOA budget.

The UCM SOA is parameterized similar to the SOA formation from single species like benzene or alpha-pinene, where the UCM is considered as a single species. We estimate that at atmospherically relevant organic aerosol concentrations (5-20 microgram per cubic-metre), gasoline vehicle, diesel vehicle, aircraft and biomass burning emissions have a substantial SOA yield (10-30%). We use three independent sources (Schauer et al., 1999-2002, EPA’s SPECIATE, CMU) to estimate UCM emissions from combustion sources. Globally, we find that UCM emissions could be two-thirds of total anthropogenic SOA precursor emissions (~33 Tg/yr). If these UCM emissions were included in existing SOA models (very few of which explicitly account for UCM emissions), a simple calculation suggests that it could result in doubling the anthropogenic SOA production worldwide.

11CA.5

On-Road Gasoline and Diesel Engine Exhaust Naphthalene Emissions: Contributions to Regional SOA Formation in Southern California. Alexander Cohan, Donald Dabdub, Arantzazu Eiguren-Fernandez, ANTONIO H. MIGUEL, *University of California, Irvine*

Naphthalene is the simplest and most abundant polycyclic aromatic hydrocarbon (PAH) in the polluted urban atmosphere (Arey et al., 1998; Atkinson et al., 1988). Naphthalene is the predominant PAH in California fuels, with concentrations of up to 2600 mg L-1 in gasoline and 1600 mg L-1 in diesel fuel (Marr et al., 1999). Present primarily in the vapor-phase, naphthalene is defined as a hazardous air pollutant by the U.S. Environmental Protection Agency (EPA), and classified as possibly carcinogenic to humans (International Agency for Research on Cancer (IARC, 2002). Naphthalene may constitute an important contributor to secondary aerosol formation (SOA) (Chan et al., 2009; Kautzman et al., 2010; Odum et al., 1997). Naphthalene emission factors for gasoline and diesel vehicles measured in summer 2004 and winter 2005 in the Caldecott Tunnel in Berkeley, California (Miguel & Eiguren-Fernandez, AAAR 29th Annual Conference, Portland, OR) are combined in this work with an activity-based automobile inventory to characterize anthropogenic naphthalene emissions in the South Coast Air Basin of California (SoCAB). A 3-dimensional air quality grid model is used to examine transport and chemical reaction losses of naphthalene in the SoCAB. Only naphthalene emissions from gasoline and diesel vehicles, which account for ca. 40% of the total naphthalene emissions to the SoCAB, were included in the model. SOA formation from naphthalene engine exhaust emissions is predicted using a two product semi-empirical partitioning model. Gas- and particle-phase modeled predictions are evaluated against measurements obtained in the spring of 2005 in the SoCAB. The inclusion of roadway driven gas-phase naphthalene in the emissions inventory was found to increase SOA growth by up to 10%, and to correlate better inland than on the coast. Gasoline vehicles make up 96% of the estimated 28 million California vehicle fleet. Hence, reductions of naphthalene from gasoline fuels may be an effective means of reducing the emissions of an important SOA-forming precursor to the atmosphere of large urban centers.

11HA.1

An in Vitro Model for Tracking Translocation of Industrially Relevant Engineered Nanomaterials across the Alveolar Epithelium: The Importance of Size, Surface Chemistry, and Particle Kinetics. JOEL COHEN, Ramon Molina, Joseph Brain, Philip Demokritou, *Harvard University*

Relatively little is known about the intracellular fate and function of industrially relevant engineered nanomaterials (ENMs). These interactions are important when considering inhalation exposure and subsequent translocation of ENMs across the nano-thin epithelial lining layer of the lung. Limited studies suggest a correlation between particle size and cellular uptake, though with conflicting results. Discrepancies in the literature may be attributable to limitations of fluorescent tracer particle models currently used. Herein we present a novel method for tracking well-characterized industrially relevant metal oxide ENMs by neutron activation. Nano-sized ceria dioxide of various sizes and silica dioxide coated-ceria dioxide particles generated by flame spray pyrolysis were neutron activated, forming the isotope 141Ce. Non-irradiated ENMs were characterized for specific surface area by nitrogen adsorption (BET), surface chemistry by x-ray photoelectron spectroscopy (XPS), crystallinity by x-ray diffraction (XRD), and morphology by transmission electron microscopy (TEM). ENMs were dispersed in liquid suspension following a previously described protocol and characterized for agglomeration and zeta potential by dynamic light scattering (DLS). ENM dispersions were applied to a monolayer of A549 cells in a transwell in vitro system. ENM trafficking was evaluated following 4, 24, and 48 hours of exposure by gamma spectrometry. A mass balance of particles was determined for various intra- and extracellular compartments to determine the fraction of ENMs that translocated across the cellular monolayer. Our results demonstrate the influence of particle size and chemical composition on ENM delivery to cells, cellular uptake, and cellular trafficking, with implications for preferential translocation across the alveolar epithelium following inhalation exposure.

11HA.2

Transport Properties of Airborne Nanomaterials. BON KI KU, Pramod Kulkarni, *Centers for Disease Control and Prevention, NIOSH*

Airborne engineered nanomaterials such as multi-walled carbon nanotubes (MWCNTs), functionalized MWCNT, graphene, fullerene, and silver nanorods were characterized to understand their lung deposition characteristics. These nanomaterials were aerosolized using different generation methods such as electrospray, pneumatic atomization, and dry aerosolization techniques so as to span a range of morphologies of workplace aerosols and to measure diffusional and aerodynamic diameter, fractal dimension, and effective density of nanomaterial aerosols. Laboratory experiments were conducted to measure diffusion and aerodynamic diameters of airborne carbon nanotube and nanomaterial aerosols using tandem mobility-mass measurements. Fractal dimensions and aerodynamic diameter of mobility-classified particles were calculated from particle mass measured using aerosol particle mass analyzer and the mobility diameter. Microscopy analysis using Transmission Electron Microscopy (TEM) was performed to obtain morphological descriptors of particles, such as envelop diameter, porosity, aspect ratio, and projected area. The morphological information from the TEM was compared with measured aerodynamic and diffusion diameters of the particles. The results showed that aerodynamic diameter is smaller than mobility diameter for all nanomaterials except silver nanorods. Various equivalent diameters and shape factors for all the materials studied are presented and their implications for lung deposition are discussed.

11HA.3

Aerosol Emission Monitoring in the Production of Silicon Carbide Nanoparticles by Induction Plasma Synthesis. DREW THOMPSON, Jing Wang, Jelena Buha, Christian Jaeggi, Marc Leparoux, David Pui, *University of Minnesota*

With the proliferation of products incorporating nanomaterials comes growing concern about occupational health and safety at workplaces where nanomaterials are produced or used. Key to evaluating the potential health risks posed by nanomaterials is the nature of inhalation exposure to airborne engineered nanoparticles. This is not only needed for establishing safer nanomaterial work practices, toxicology studies also require doses relevant to actual workplace exposures. In this study aerosol emissions were monitored at a research laboratory during the production of silicon carbide (SiC) nanoparticles by inductively coupled plasma (ICP) synthesis.

The use of direct-reading particle instruments was found to be an effective means by which to identify emission events and to assess the efficacy of the engineering controls and best practices guidelines in the production of nanoparticles by ICP synthesis. No particles were released during the synthesis of SiC nanoparticles due to the reactor being operated in a closed system under slight vacuum. However, aerosol emissions were identified in other related production tasks. A release of submicrometer particles was detected when a nanoparticle collection filter was disconnected from the reactor system. The use of compressed air when cleaning nanoparticle contaminated equipment was also investigated. When compressed air was used for cleaning in moderately closed ventilated systems, like the interior of the reactor, no particles were emitted. When compressed air was used for cleaning in open spaces, such as the cleaning of the nanoparticle collection filters in a ventilated walk-in enclosure, emissions of submicrometer particles were identified and particle number concentrations exceeded 250,000 cm^{-3}. Particle emissions in this facility were found to be largely submicrometer and exhibited a mode size of approximately 170 nm. Observation of filter samples under scanning electron microscope confirmed that the particles released were agglomerates of SiC nanoparticles.

11HA.4

An Inhalation Toxicological Characterization of Nano CeO2 Using the Harvard VENGES Toxicological Platform. Georgios Pyrgiotakis, Samuel Gass, William Goldsmith, David Frazer, Jane Ma, Walter McKinney, Mark Barger, Bridget Dolash, Vincent Castranova, PHILIP DEMOKRITOU, *Harvard University*

Ceria nanoparticles are increasingly used for a number of industrial and commercial applications including catalysts, chemical mechanical polishing, UV-shielding, and nanocomposites. As the number of consumers and factory workers exposed to CeO2 nanoparticles increases, the need for a comprehensive toxicological characterization is pressing. While most in-vitro models predict minimal toxicity for nanosized CeO2, preliminary in-vivo animal models using instillation of CeO2 nanoparticles point to fibrogenicity. However, to date, most evidence is limited to intratracheal instillation studies that may not represent real-world exposure scenarios. Here, we present the first ever whole-body systematic animal inhalation study of nano-CeO2. In addition, the use of a nanothin amorphous SiO2 coating as means of mitigating CeO2 toxicity was evaluated as a safer formulation concept. CeO2 (uncoated and SiO2-coated) nanoparticles were synthesized using the Harvard Versatile Engineered Nanomaterial Generating System (VENGES), which enables the synthesis and coating of industrially relevant nanoparticles in the aerosol phase with precise control over primary particle size, aggregation, and aerosol concentration. The generated aerosol was diluted and introduced into a customized exposure chamber. The generated CeO2 particles (SiO2 coated and uncoated) were characterized (1) in-situ with respect to aerosol size distribution and number concentration (SMPS), aggregate morphology (TEM, SEM), and charge and aerosol length (AED) and (2) ex-situ with respect to crystallinity and chemical composition (XRD, XPS, EDX), surface area (BET), and morphology (TEM, SEM). Exposure atmospheres in the chamber were monitored in real time and characterized with respect to number and size aerosol concentration (CPC, SMPS), mass concentration (Gravimetric Filter Measurements), Mass Size Distribution (MOUDI), temperature, humidity, CO, CO2, (Q-Track) and NOx concentrations. Sprague Dawley rats (n=12/group) were exposed to either coated or uncoated CeO2 (2.7 mg/m3, 2 h/day, 4 days). Exposed animals, along with particle free- controls, were sacrificed at either 1 or 84 days post exposure. Pathophysiological analysis was performed and inflammatory and cytotoxic biomarkers were measured in the bronchoalveolar lung lavage of the animals.

11HA.5

Evaluation of the Toxicological Potential of Silver Nanoparticles. STEFANIE KASURINEN, Pasi, I Jalava, Kari Kuuspalo, Ari Leskinen, Kati Huttunen, Jorma Jokiniemi, Kari Lehtinen, Maija-Riitta Hirvonen, *University of Eastern Finland, Kuopio, Finland*

Combustion emissions and nanoparticles are widely recognized as harmful to human health and there is a growing need for the development of alternative and more realistic in vitro exposure models for the research of their adverse health effects.

We used a Vitrocell® exposure system with A549 alveolar epithelial cells for the in vitro exposures.

The Ag/Ag_2O-aerosol for the experiments was produced using a Carbolite MTF12/38B tube furnace with a tube length of 45 cm and inner diameter of 22 mm. A laminar N_2-flow was lead trough the tube furnace and compressed pure air was used in the porous tube diluter to quench the carrier gas. The size distribution of the generated particles was characterized and their morphology was studied.

A549 cells were cultivated at air lifted conditions prior, posterior and during the exposure experiments. Ag/Ag_2O-aerosol flow was adjusted to the desired speed and the cells were exposed to the PM for various durations. After exposure, the cells were removed from the Vitrocell® module and allowed to recover for 24 h. Culture medium aliquots were taken and levels of different pro-inflammatory cytokines were determined using the Meso Scale Discovery multi-spot assay system. A PM concentration dependent increase in both IL-6 and IL-8 release was found, indicating the induction of pro-inflammatory processes in A549 cells upon exposure to silver nanoparticles.

The system is easily adjustable for the air-liquid exposure of lung cell models to exhausts from cars, wood burning devices and others.

11IM.1

Development of Variable-Flow Rate Isokinetic Sampling System for 0.5-15 Micro-Meter Particles. HIROKAZU ICHITSUBO, Yoshio Otani, *Japan Tobacco Inc.*

Isokinetic sampling is required when evaluating the aerodynamic sizes of particles released from dry powder inhalers (DPI) under simulated breathing condition since anisokinetic sampling may lead to significant sampling error for coarse particles. We propose an isokinetic measuring system for aerosol particles from a stream in a narrow conduit of variable flow rates (Variable Flow rate Aerosol Sampler, VFAS) combined with Aerodynamic Particle sizer(C) APSTM spectrometer (model 3321, TSI Inc.). VFAS was capable of generating variable sampling flow rates by adjusting the flow resistance of makeup air to produce constant flow rate of aerosol to APS. The penetrations through the VFAS-APS system were measured using monodisperse particles with a size range between 0.7 to 15 micro-meter by applying a rectangular flow rate-time pattern of sampling air and we found that the VFAS-APS system can measure the concentration of particles with the particle detection efficiency (particle penetration through the system) of almost unity. The VFAS-APS system may be a powerful tool to measure the size and concentration of powder released by the DPI in the size ranges of 0.5 to 15 micro-meter.

11IM.2

Aspiration Efficiency Evaluation of Two Specific Personal Samplers. YUE ZHOU, Hammad Irshad, Chuen-Jinn Tsai, Shao-Ming Hung, Bean Chen, Yung-Sung Cheng, *Lovelace Respiratory Research Institute*

Personal aerosol samplers are used to estimate the exposure of workers to airborne particles in workplaces. The most widely used personal sampler is the Institute Occupational Medicine (IOM) sampler which collects particles that inhaled into human respiratory system. To assess worker exposure to bio-aerosols or nano-particles, special personal samplers are needed. For bioaerosol sampling application, a two-stage cyclone personal sampler with microcentrifuge tube and regular centrifuge tube was developed by NIOSH. For nano-aerosols, a prototype sampler was also developed by National Chiao Tung University, Taiwan. Laboratory tests have been performed for collection efficiency during development of these samplers. Since personal samplers are used in workplaces, the sampler’s aspiration efficiency should also be evaluated. This study presents the aspiration efficiencies of these two specific samplers at different wind speeds and wind directions. A full size mannequin was sued in our wind tunnel facility. Samplers were mounted in front, side, and back of the mannequin. The operation wind speeds were 0.5, 1.0, and 1.5 m/s. Results were also compared with the aspiration efficiency of the IOM and the inhalable convention curve. At the wind speed of 0.5 m/s which is in most cases of indoor workplaces, the direction-averaged aspiration efficiencies agreed with the inhalable convention curve, although there is a large variability. When wind speed increased, the aspiration efficiency of the prototype sampler was below the inhalation convention curve for small particles, because of low efficiency of the sample located at the back of mannequin.

11IM.3

Examination of Sampler Efficiency of Thin-Walled Reference Samplers in Low Velocity Freestreams. KIMBERLY ANDERSON, T. Renee Anthony, *University of Iowa*

Background: Particle aspiration efficiency is calculated as the ratio of the concentration over the concentration in the freestream. This equation relies on the assumption that the reference sampler measuring the freestream concentration captures a representative sample of the aerosol in the freestream. The performance of the thin-walled reference sampler in moving air has been extensively investigated; however, the performance of these samplers in low velocities has not been studied. If the thin-walled reference sampler under-aspirates the true concentration of large particles in low velocity environments, then the calculated sampler efficiency or human aspiration efficiency will be higher than it should be at these particle sizes. If particle bounce significantly contributes to the measured reference concentration, then the resulting calculated efficiency will be lower than it should be.

Objective: The objective of this study is to (1) evaluate large particle aspiration for a thin-walled reference sampler in low freestream velocities and (2) quantify the effect of particle bounce on secondary aspiration.

Methods: CFD modeling was used to investigate aspiration efficiency of a thin-walled reference sampler for three freestream velocities: 0.1, 0.2, and 0.4 m/s, seven particle sizes: 7, 22, 52, 68, 82, 100, and 116 micro-meters, and two CoR values: 0.0 (no-bounce) and 0.9 (bounce). Fluid simulations used the standard k-epsilon turbulence model. Particle trajectories were simulated using laminar particle tracks and used to determine the upstream critical area. These areas were used to calculate sampler efficiency.

Results: Thin-walled sampler efficiency was significantly different when secondary aspiration (from particle bounce) was allowed ($p=0.011$). Aspiration at 0.1 m/s was significantly lower from unity at the no-bounce condition ($p=0.012$) and approaching significance for the bounce condition ($p=0.07$). Sampler efficiency was not significant different from unity at 0.2 and 0.4 m/s for either the bounce or no bounce condition.

11IM.4

Experimental Study of a Miniature Dumbbell Electrical Aerosol Classifier (Dumbell EAC). SIQIN HE, Da-Ren Chen,*Washington University in St. Louis*

As the rising concern of the health effect due to the exposure of ultrafine particles, it is demanding to have the ultrafine particle sizers which are capable of measuring spatial distribution of particles. Low-cost ultrafine particle sizers make it feasible to achieve the measurement task. In our group we have developed the low-cost sizers of precipitator type (electrical mobility-based technique). To improve the sizing resolution while covering the particle size ranging from 10 to 500 nm, a miniature electrical aerosol classifier (i.e., Dumbbell EAC) has been proposed to replace the mini-disk precipitator in the developed low-cost ultrafine sizers. Different from the conventional EACs the dumbbell EAC has a curved classification region. The design of dumbbell EAC and its performance modeling had been presented in the AAAR 2011. In this study we have constructed the prototype EAC and experimentally evaluated its performance.

We evaluated the performance of the Dumbbell EAC using single-charged particles classified by a DMA. In the evaluation the concentration of charged particles at the downstream of the Dumbbell EAA operated at various voltage setting was measured by a CPC (TSI 3025). The penetration of charged particles through the EAC was then derived by the ratio of particle concentration at applied voltage and that at zero voltage. The performance of dumbbell EAC was then determined by its transfer functions describing the particle penetration as a function of the product of applied voltage and particle electrical mobility. The detailed result of this study will be discussed in this talk.

11IM.5

Bipolar Charge Measurement for DPI (Dry Powder Inhaler) Particles. JONNA KANNOSTO, Ville Niemelä, Henna Isherwood, Jaakko Yli-Ojanperä, Jorma Keskinen, Risto Hillamo, Anna Frey, Steve Layzell, David Prime, Ari Ukkonen, *Dekati Ltd., Tampere, Finland*

Recently, delivery of various drugs to lungs has been of increased scientific interest and it has become a more and more common way to treat different diseases, not only respiratory diseases like asthma. According to computer simulations, electrostatic deposition of inhaler drug particles dominates in the lower lung regions (Balachandran et al. 1997), particularly in the alveoli where the most efficient systemic absorption exists. Earlier charge studies have focused on particle net charge measurements (Telko et al. 2007) since a method for measuring bipolar charge has not been available.

The Dekati® Bipolar Charge Analyzer (BOLAR™) is the first commercial instrument available for measuring aerosol particles' bipolar electrical charge as a function of particle size. The instrument separates negatively and positively charged particles in 5 size fractions in electrical collection tubes. After the measurement, the electrical collection tubes can be uncoupled and positive and negative particles can be recovered and analyzed separately. Thus, the bipolar charge in respect of mass can be assigned as well as the particles' composition in different size ranges.

In this presentation, the detailed operating principle and calibration results including impactor stage collection efficiencies, the tube collection efficiencies and the flow divider penetration are shown. The quality of flow dividing has been studied by net charges and analyzing the amount of particles in each branch. The particle deposition (losses) in different parts of the instrument has also been studied in detail. The BOLAR™ was used together with ELPI™ (Electrical Low Pressure Impactor) to determine size distribution and net charge of lactose particles. The results from the two instruments show good correlation for both size and net charge data. Furthermore, the BOLAR™ results show high bipolar charge levels of lactose particles indicating inadequacy of net charge measurements when studying charging behavior of DPI particles.

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11NM.1

The Sintering Rate of Aerosol Nanoparticles. Beat Buesser, Arto Groehn, SOTIRIS E. PRATSINIS, *ETH Zurich*

The basic sintering mechanism and growth rate of aerosol nanoparticles is investigated by accelerated molecular dynamics. Primarily, the sintering or coalescence of TiO2 nanoparticles, the dominant photocatalytic material and a promising candidate for photovoltaics and organic vapor sensors, is elucidated by monitoring the detailed motion of Ti and O atoms with accelerated molecular dynamics. It is shown how rutile nanoparticles realign themselves during sintering to match their fusing lattice plains (1). It is revealed that sintering by surface diffusion dominates the growth of such particles with minimal displacement of inner atoms (sintering by grain boundary diffusion). This is in stark contrast with classical ceramics where compacts of particles are used in sintering studies. In addition, a long-standing question on the significance and sequence of these two sintering mechanisms for TiO2 is resolved contributing a quantitative expression for the accelerated sintering rate of nanoparticles that beautifully converges to that of much larger ones (2,3) at only about 5 nm instead of 10 or 20 nm. This expression can be readily used in phenomenological sintering models for the design, scale-up and optimization of gas-phase manufacture of nanoparticles. Furthermore it is extended to metal nanoparticles and multiparticle structures exploring the role of geometry in deciphering sintering mechanisms and extracting their sintering or coalescence rates.

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11NM.2

A Safer Formulation Concept for Flame-Generated Engineered Nanomaterials (ENMs). Samuel Gass, GEORGIOS PYRGIOTAKIS, Joel Cohen, Georgios A. Sotiriou, Sotiris E. Pratsinis, Philip Demokritou, *Harvard University*

Engineering less toxic nanomaterials that maintain valuable functional properties is crucial to the sustainability of the nanotech industry. We have therefore devised a safer formulation concept for flame-generated nanomaterials based on the encapsulation of potentially toxic nanomaterials by a biologically inert nanothin amorphous SiO2 layer. The core-shell particles maintain specific properties of their core material but exhibit surface properties of their SiO2 shell. The SiO2-coating process was performed using a modified flame spray pyrolysis (FSP)-based Versatile Engineered Nanomaterial Generation System (VENGES) in which core ENMs are coated in-flight by the swirl injection of hexamethyldisoloxane (HMDSO). We first demonstrate the versatility of the proposed SiO2-coating process by applying it to several ENMs (CeO2, Fe2O3, ZnO, Ag) marked by their prevalence in consumer products as well as their range in toxicity. We then investigate (1) the effect of the SiO2-coating on core material structure, composition and morphology (XRD, BET, and TEM), (2) the mobility and aggregation of SiO2-coated and uncoated ENMs in DI-water, biological media (DLS) and air (SMPS), and (3) the coating efficiency (XPS, Chemisorption) of the process for each ENM (XPS and Isopropanol Chemisorption). Finally, we provide valuable in-vitro toxicological evidence for the safety of this novel formulation concept by evaluating the relative toxicity of SiO2-coated vs. uncoated ENMs using a number of cellular assays (MTT, LDH, Live/Dead) and several cell-lines (A549 cancer alveolar epithelial cells and THP-1, macrophages). Our results show that the proposed method can be used to effectively coat flame generated ENMs with a nanothin layer of amorphous SiO2 thereby resulting in a significant reduction of their toxicological profile. Moreover, the proposed method can readily be scaled up and used by NT industry in the production of safer ENMs.

11NM.3

Highly Efficient Pt-TiO2 Nanostructured Films for CO2 Conversion to Hydrocarbon Fuels. WEI-NING WANG, Woo-Jin An, Balavinayagam Ramalingam, Somik Mukherjee, Dariusz M. Niedzwiedzki, Shubhra Gangopadhyay, Pratim Biswas, *Washington University in St. Louis*

A facile development of highly efficient platinized titania (Pt-TiO2) nanostructured films via versatile gas phase deposition methods is described. The films have one-dimensional (1D) structure of TiO2 single crystals, deposited by an aerosol chemical vapor deposition route, which is a continuous and low energy method designed to deposit metal oxide films with controlled morphologies. Platinum nanoclusters (NCs) were coated onto the TiO2 single crystals using a unique tilted target sputtering method. Ultra-small Pt sizes ranging from 0.5 to 2 nm with uniform distribution could be finely tuned which are not readily achieved and controlled using conventional liquid phase synthesis methods. These Pt-TiO2 nanostructures demonstrated high photoreduction efficiency with selective CH4 formation. The size of the Pt nanoclusters plays an important role in the CO2 photoreduction process. The mechanistic pathways of CO2 photoreduction have been explained in detail. The high surface area and single crystallinity of the TiO2 single crystals and the efficient electron-hole separation by the Pt NCs were the main reasons attributable for the enhancement, which have been confirmed by experimental results including femtosecond time-resolved transient absorption spectroscopy measurements.

11NM.4

Ultrasonic Spray Pyrolysis Synthesis of Ag-Ce Co-modified TiO2 Nanocomposites for Syngas Production Under Solar Irradiation. Daniel Pitts, Cunyu Zhao, Huilei Zhao, Lianjun Liu, YING LI, *University of Wisconsin-Milwaukee*

Silver and cerium co-modified titanium dioxide (Ag-Ce/TiO2) composite nanoparticles have been synthesized through an ultrasonic spray pyrolysis (USP) method. Pure phase anatase TiO2 and mixed-phase anatase-brookite TiO2 nanoparticles were first prepared through a hydrothermal method and then used as the precursor for USP. The materials were characterized by XRD, UV-vis diffuse reflectance, SEM and TEM for crystal phase, particle size and morphology, and optical behavior. The Ag-Ce/TiO2 nanoparticles were tested as photocatalysts for syngas (H2 + CO) production from CO2 and water via two reaction routes: (1) hydrogen production from water splitting and (2) CO2 reduction for CO production. A 150 W Solar Simulator was used as the light sources. A Gas Chromatograph (GC) equipped with TCD/FID detectors was used to identify the products and measure the yields of solar fuels. The activities of catalysts with different Ag-Ce compositions and different TiO2 crystal phases were investigated. The H2/CO ratio of the produced syngas was correlated with the nanomaterial properties.

11NM.5

In situ Ambient Pressure XPS Investigations of PdAg Alloy Nanoparticles: Towards Cheaper Catalysts. MARIA E MESSING, Sara Blomberg, Natalia M Martin, Johan Gustafson, Jesper Andersen, Lars Erik Walle, Anne Borg, Henrik Grönbeck, Michael E Grass, Zhi Liu, Edvin Lundgren, Knut Deppert, *Lund University*

Due to the huge economic and environmental rewards, one major goal in catalysis related research is to create cheaper catalysts. As catalysis happens on the surface of the catalyst, one possible way to realize this would be to dilute the more expensive active material with a less costly one, providing that the active material stays at the surface. This could be achieved by using a material which is less prone to interact with the reactant gases, such as a cheaper noble metal. In most catalysts, the active material is dispersed in a high area complex oxide support as nanoparticles. In order to maintain the high activity, it would be necessary to ensure that the active material is at the surface of the nanoparticle.

We report on our findings from attempts to produce PdAg alloy particles using aerosol generation. The use of PdAg is motivated by the fact that Pd segregates to the surface in the presence of a reactive gas while Ag segregates in ultra-high vacuum (UHV) and that Ag is considerably less expensive than Pd.

TEM images reveal that most particles are single crystalline. From XEDS the composition are measured to approximately 75 atomic% Pd and 25 atomic% Ag. Ag $3d_{5/2}$ core level XPS spectra from the PdAg particles are compared to the corresponding spectra of a $Pd_{75}Ag_{25}$ (100) single crystal and a (110)-oriented Ag crystal. The Ag $3d_{5/2}$ binding energy for the nanoparticles compares well with the bulk contribution for $Pd_{75}Ag_{25}$ (100) which in turn is shifted by 0.5eV relative to the bulk value in pure Ag. From this observation, we therefore conclude that the PdAg alloy particles consist of a proper alloy and not Ag and Pd in separate phases. In addition, corresponding Pd 3d spectra strongly indicate that the active Pd is present at the surface of the PdAg particles in the presence of reactant gases.

11RA.1

Influences of SO2 and NH3 Levels on Ambient Isoprene Epoxydiol (IEPOX)-Derived SOA Formation in the Rural Southeastern United States. YING-HSUAN LIN, Eladio Knipping, Eric Edgerton, Stephanie Shaw, Jason Surratt, *University of North Carolina at Chapel Hill*

Recent work through organic synthesis and controlled chamber studies has confirmed that reactive uptake of gaseous isoprene epoxydiols (IEPOX) are key intermediates in the formation of isoprene-derived SOA constituents under low-NOx conditions (Lin et al., 2012). Heterogeneous oxirane ring-opening reactions of IEPOX have also been reported to be atmospherically relevant under typical tropospheric conditions, with reaction rates enhanced by aerosol acidity. In the present study, ambient fine aerosol (PM2.5) samples were collected and analyzed to investigate the effects of aerosol acidity on isoprene SOA formation in the rural atmosphere influenced by anthropogenic sulfur dioxide (SO2) and ammonia (NH3) emissions. Filter samples were collected from Yorkville, GA, a rural site with high isoprene emissions located in the Southeastern Aerosol Research and Characterization Study (SEARCH) network during the summer of 2010. Conditional sampling strategies were employed to collect aerosol samples under pre-defined environmental thresholds (i.e., high vs. low SO2/NH3 conditions) to distinguish the influences of different ambient SO2 and NH3 levels on isoprene SOA formation. IEPOX-derived SOA constituents, including 3-methyltetrahydrofuran-3,4-diols, 2-methyltetrols, C5-alkene triols, dimers, as well as their organosulfate derivatives, are chemically characterized and quantified by advanced off-line analytical techniques (i.e., UPLC/ESI-HR-Q-TOFMS, GC/MS). In situ aerosol pH is estimated by aerosol thermodynamic models (i.e., E-AIM models). Important results regarding correlations between SOA constituents and aerosol acidities, as well as available complementary chemical and meteorological measurements will be presented in order to help provide insights into the atmospheric formation of IEPOX-derived SOA.

Reference:

Lin, Y.-H.; Zhang, Z.; Docherty, K. S.; Zhang, H.; Budisulistiorini, S. H.; Rubitschun, C. L.; Shaw, S. L.; Knipping, E. M.; Edgerton, E. S.; Kleindienst, T. E.; Gold, A.; Surratt, J. D., Isoprene epoxydiols as precursors to secondary organic aerosol formation: Acid-catalyzed reactive uptake studies with authentic compounds. Environ. Sci. Technol. 2012, 46 (1), 250-258.

11RA.2

Performance of High Resolution Time-of-Flight Aerosol Mass Spectrometer during Chemical Characterization of Particle Emissions from Controlled Biomass Burning. POORNIMA DIXIT, Seyedehsan Hosseini, Ping Tang, David R. Cocker III, Li Qi,*University of California, Riverside*

A total of forty-nine burns were conducted at the Missoula Fire Sciences Lab consisting of nine fuel types; i.e., chamise scrub oak, ceanothus, maritime chaparral, coastal sage scrub, California sage brush, Manzanita, oak savanna, oak woodland and masticated mesquite. This paper focuses on assessing the performance of the high resolution Time-of-flight Aerosol Mass Spectrometer in determining the chemical characterization of fine particle emissions collected for flaming, mixed and smoldering phases of biomass burning. Levoglucosan, an anhydrous sugar evolves during wood burns, which was used as a tracer to evaluate PM emissions from the burns. The AMS reported an interference ion in the UMR m/z 73, a fragment normally attributed to levoglucosan. The sum of ions $C_2H_4O_2{}^+$ (m/z 60.021) and $C_3H_5O_2{}^+$ (m/z 73.029) performed better in estimating the contribution of levoglucosan on an online basis. For our offline analysis, we used a Gas chromatography mass spectrometer to quantify levoglucosan collected on quartz filters during all of the wood burns. Both the online and offline were compared using the amount of levoglucosan quantified, to understand the performance of the HR-TOF-AMS. The online and the offline co-relation for the amount of levoglucosan showed a factor of 0.67, which was considered a good estimate. Additionally the polycyclic aromatic hydrocarbons and organic carbon content from both the online and offline measurements were compared to get a more distinctive understanding of the performance of HR-AMS-TOF. Nitrates, sulfates & Ammonia evolving from the different phases of real time wood burns were instantaneously measured by the HR-TOF-AMS. Those measured values provided a deeper knowledge of emissions from real time biomass burning. The results of the offline and online comparisons showed an agreement, thus strengthening the measurement abilities of the HR-TOF-AMS for instantaneous real-time analyses.

Keywords: HR-TOF-AMS, levoglucosan, offline GC-MS

11RA.3

Characterization of Transboundary Biomass Burning Smoke on Organic Aerosols in a Tropical Urban Environment: Dicarboxylic Acids, Malic Acid, and Photooxidation Intermediates of Levoglucosan. Liming Yang, Wei Hong Fan, Shiguo Jia, Duc Minh Nguyen, Jeffrey Reid, LIYA YU, *National University of Singapore*

Biomass burning (BMB) smoke in Southeast Asia has been reported to contain unique chemical composition, which could be due to special composition of peatland in this region. Biomass burning in Southeast (SE) Asia occurs annually, depending on weather and countries, intensity and chemical composition of the smoke in SE Asia vary significantly, so as the transboundary smoke reaching Singapore, an urban receptor site. This work investigates impacts of the transboundary smoke on urban aerosols based on the observations in 2008. Data obtained in this year represent “light” presence of transboundary BMB smoke in the urban environment and can serve as a lower bound of impacts imposed by the transboundary BMB smoke.

Daily ambient PM2.5 was collected during 8 September to 5 October (Julian Days, JDs 252–279), 2008 in Singapore; based on backward trajectory analysis of smoke and fire counts of in the region, Singapore was affected by the smoke for 12 out of the 28 sampling days. Although PM2.5 varied marginally, the smoke increased C2–C5 total dicarboxylates (TDCAS, summation of dicarboxylic acids and dicarboxylate salts) on average more than two times, and levoglucosan, more than five times. During the presence of the transboundary smoke, C2-TDCAS accounted for around 80% of the C2–C5 TDCAS; oxalate salts exhibited the highest concentration (355.0 ng/m^3), which is more than 13 times of oxalic acid. The transboundary smoke increased malic acid concentration more than 3.5 times, the largest relative increase among the quantified TDCAS, indicating more prominent photooxidation incurred by the smoke. Quantifiable photooxidation intermediates of levoglucosan, including malic acid, show consistent temporal trends with levoglucosan throughout the study period. Among the identifiable intermediates, ribonolactone concentration exhibits the highest linear correlation with levoglucosan during the presence of the smoke with R^2 of 0.8.

11RA.4

Long Term Measurements of Aerosol Optical Properties in Amazonian. PAULO ARTAXO, Luciana Rizzo, Erik Swietlicki, Andrea Arana, Elisa Sena, Glauber Cirino, Alfred Wiedensohler, *Institute of Physics, University of Sao Paulo*

Aerosol physical and chemical properties were measured in two sites in Amazonia since January 2008. The clean site is at Central Amazonia (Manaus) and is located in a pristine Amazonian forest site. A second sampling site is located in Porto Velho, Rondonia, an area strongly affected by biomass burning emissions. Long term measurements, from February 2008 are being carried out in these two sites, as part of the EUCAARI and AEROCLIMA projects.

In the pristine Amazonian atmosphere, aerosol scattering coefficients ranged between 1 and 200 Mm-1 at 450 nm, while absorption ranged between 1 and 20 Mm-1 at 637 nm. A strong seasonal behavior was observed, with greater aerosol loadings during the dry season (Jul-Nov) as compared to the wet season (Dec-Jun). During the wet season in Manaus, aerosol scattering (450 nm) and absorption (637 nm) coefficients averaged, respectively, 14 and 0.9 Mm-1. Angstrom exponents for scattering were lower during the wet season (1.6) in comparison to the dry season (1.9), which is consistent with the shift from biomass burning aerosols, predominant in the fine mode, to biogenic and dust aerosols, predominant in the coarse mode. Single scattering albedo, calculated at 637 nm, did not show a significant seasonal variation, averaging 0.86. In Porto Velho, even in the wet season it was possible to observe a strong impact from anthropogenic sources. AOT values at 550 nm above 3 are frequently observed in Porto Velho with AERONET sunphotometers. Black Carbon was measured at 20 ug/m3 in the dry season, showing strong aerosol absorption.

This work presents a general description of the aerosol optical properties in Amazonia, both during the Amazonian wet season, when the aerosol population is dominated by particles of biogenic origin, and during the dry season, when there is a strong influence of biomass burning emissions.

11RA.5

Fine Particles Over an Ecologically Sensitive Zone in Bhopal, India-Characterization and Temporal Variability. RAMYA SUNDER RAMAN, Balram Ambade, Masood Ayub Kaloo, *Indian Institute of Science Education and Research, Bhopal*

Bhopal, India is home to a large concentration of industries. Additionally, the city lies in a semi-arid region and is in close proximity to marble quarries with the likelihood of high dust contributions to particulate matter (PM) mass, even in the fine mode. Consequently, it is hard to predict whether the source contributions to fine particulate matter ($PM_2.5$) and its precursors are dominated by industrial/vehicular emissions or by mineral dust. Thus, a $PM_2.5$ monitoring station was set-up at Van Vihar National Park (ecologically protected zone), Bhopal to measure $PM_2.5$ and apportion its sources.

Measurements for $PM_2.5$ mass, its chemical constituents, and optical properties commenced in January 2012 and will continue for a period of two years. 12 hour integrated samples are collected every-other-day on multiple filter substrates (Teflon, Quartz Fiber, and Nylon) using co-located Airmetrics Mini-Vol® Tactical Air Samplers. Fine PM mass will be measured using gravimetry and the filter samples will be subjected to a variety of chemical analyses. Concentrations of organic and elemental carbon (OC/EC), inorganic anions/cations, water soluble organic anions, and trace element concentrations will thus be obtained.

Additionally, visibility degradation due to ambient PM at Van Vihar National Park is also being monitored using an ensemble of techniques that include on-site photography, transmissiometry (long path transmissometer, OPTEC, LPV3), and nephelometry (OPTEC, NGN3A). These measurements in conjunction with on-site meteorological data (measured using a Vaisala® WXT520 automatic weather station) will ultimately be used for source apportionment of fine PM measured at the receptor site.

Preliminary results for all measurements made between January and August 2012 will be discussed. Fine PM mass concentrations, its chemical and optical properties, and their temporal variability will be examined. The relationships between meteorological parameters and fine PM concentrations will also be discussed.

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12AC.1

Kinetics and Products of Multiphase Aging Reactions of Organic Aerosol. JESSE KROLL, James Hunter, Kelly Daumit, Sean Kessler, Anthony Carrasquillo, Eben Cross, Theodora Nah, Douglas Worsnop, Kevin Wilson, *MIT*

Atmospheric organic aerosol (OA) tends to be substantially higher in mass loading and carbon oxidation state than OA produced in laboratory studies. Further, oxidized OA is produced on timescales on the order of one day in the atmosphere, significantly faster than has been achieved in the laboratory. This suggests major gaps in our understanding of the chemistry underlying OA formation and evolution, and has led to several suggested multiphase mechanisms for the rapid generation of high yields of highly oxidized OA. Here we present a series of laboratory studies of the formation and aging of oxidized organic aerosol, focusing on both the particulate reaction products (abundance and average oxidation state of particulate organic carbon), and the rate at which such products are formed. Oxidative "aging" of secondary organic aerosol mixtures (in which gas-phase reaction products are exposed to sustained concentrations of hydroxyl radicals) is found to lead to increases in both particle mass and degree of oxidation, but over timescales substantially longer than a day for the mixtures studied. Heterogeneous oxidation of a wide range of particulate organics is similarly found to be too slow to account for observations of oxidized OA formation. Aqueous-phase chemistry also provides a pathway for the formation of highly oxidized organics, but first requires that organics partition into the condensed phase prior to being oxidized, and so can also be quite slow under atmospheric conditions. Consideration of both kinetics and partitioning together is needed to predict potential channels for the rapid formation of highly oxidized, low-volatility organics.

12AC.2

Aging of Secondary Organic Aerosol from Small Aromatic VOCs: Changes in Chemical Composition, Mass Yield, Volatility and Hygroscopicity. LEA HILDEBRANDT RUIZ, Andrea Paciga, Benjamin Murphy, Kate Cerully, Athanasios Nenes, Neil Donahue, Spyros Pandis, *Carnegie Mellon University*

Secondary organic aerosol (SOA) undergoes additional reactions in the atmosphere after its initial formation, changing its chemical and physical characteristics. This aging of SOA is currently not well understood and poorly represented in chemical transport models (CTMs). We conducted laboratory chamber experiments in which we formed and aged SOA from toluene and other small aromatic VOCs under different oxidizing conditions. We measured the amount of OA formed and its oxidation state (approximated by elemental ratios O:C and H:C) using a high resolution time-of-flight aerosol mass spectrometer (AMS) from Aerodyne, Inc., the aerosol volatility using a home-built thermodenuder system, and the hygroscopicity of the denuded and non-denuded OA using a cloud condensation nuclei counter from Droplet Measurement Technologies.

Under stronger oxidizing conditions the mass yield and oxidation state of organic aerosol is higher and its volatility is lower. The O:C ratio in the OA formed is close to 1, suggesting that LV-OOA observed in the atmosphere could partly be due to aged SOA from aromatic VOCs. Approximately 15 percent of the OA mass formed in these high-NOx experiments is due to NO and NO2 fragments in the AMS which originate from organic nitrate, suggesting that organic nitrates could compose approximately 50 percent of the OA mass in these experiments. The organic nitrates are more volatile than the rest of the OA. Using an evaporation model to quantify changes in the volatility we find that the OA formed under the different conditions differs in volatility by at least an order of magnitude. The hygroscopicity of the OA changes under the different conditions but is correlated with O:C.

We use these data to constrain SOA formation and transformation in a box model of our chamber experiments, and we will update mass yields and chemical transformation mechanisms in our CTM PMCAMx.

12AC.3

Rapid Modification of Cloud-Nucleating Ability of Aerosols by Biogenic Emissions. SARAH D. BROOKS, Yan Ma, German Vidaurre, Alexei F. Khalizov, Lin Wang, Jun Zheng, Renyi Zhang, *Texas A&M University*

Emissions of biogenic volatile organic compounds (VOCs) lead to formation of secondary organic aerosol, contributing to a major fraction of the global tropospheric aerosol loading. The extent to which VOC oxidation products condense onto preexisting primary aerosols and modify their cloud-nucleating properties, however, remain highly uncertain. In chamber studies we show that water-soluble organic acids produced from the reaction between alpha-pinene and ozone rapidly accumulate onto preexisting soot particles. In less than 30 minutes, initially hydrophobic aerosols are converted to aerosols containing a mass fraction of 80-90% organics which activate efficiently as cloud condensation nuclei under representative atmospheric conditions. Our results imply that the microphysical properties of aerosols present in continental air masses are largely controlled by the composition and thickness of coatings (approximately 30 nm in 30 minutes) formed during aerosol aging processes, rather than by the size or composition of original primary particles. Current atmospheric models may considerably underestimate the indirect climate forcing from biogenic emissions.

12AC.4

Sustained Chemical Evolution of alpha-Pinene Ozonolysis Products - Evidence for Bulk Phase Reaction. PETER DECARLO, Torsten Tritscher, Lisa Pfaffenberger, Arnaud Praplan, Peter Barmet, Kaytlin Henry, Josef Dommen, Neil Donahue, Andre Prévôt, Urs Baltensperger, *Drexel University*

During the MUltiple CHamber Aerosol CHemical Aging Study 2 (MUCHACHAS-2) at the Paul Scherrer Institute, aerosol products generated from the ozonolysis of alpha-pinene (AP) were observed to undergo continual chemical aging, in the absence of light and additional oxidant injection. Particle size and chemical composition were monitored with standard instrumentation including an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) and a Volatility Hygroscopic Tandem Differential Mobility analyzer (VHTDMA). Gas phase evolution was monitored with a PTRMS and ozone monitor. AMS results show continued chemical evolution of ozonolysis generated secondary organic aerosol (SOA) without additional OH exposure and after the precursor had been consumed. Showing that the AP ozonolysis system does not reach a equilibrium but continues to react. Increases in signal intensity with time was observed for several high molecular weight (150-250 amu) species. These observations indicate that while glassy aerosol may be important from a volatility reduction perspective, chemical change of the SOA needs to also be considered.

12AC.5

New Information on Cr Speciation in the Presence of Ozone and Reactive Oxygen Species during Atmospheric and Sampling Aging. Mehdi Amouei Torkmahalleh, Lin Lin, Thomas M. Holsen, Don H. Rasmussen, PHILIP K. HOPKE, *Clarkson University*

Cr(III) and Cr(VI) are the two stable oxidation states of chromium in the environment. Cr(VI) was found to be toxic for human body such that exposure to Cr(VI) may lead to cancer, nasal damage, asthma, bronchitis, pneumonitis, inflammation, dermatitis and skin allergies. On the other hand, Cr(III) is a trace element essential for the proper function of living organisms. Little is known about chromium chemistry in the atmosphere as well as during sampling and storage. Exposure of chromium to ozone at 24oC and 10% RH showed approximately 40 ± 8% and 17.1 ± 1.7% loss of Cr(VI), at pH 4 and 9, respectively. Compared with control experiments, ozone added to the conversion of Cr(III) to Cr(VI) at pH 4 and 9. The aging of chromium in the presence of ozone at pH 4 and12oC after 2 hours, showed a statistically significant ($P = 0.002$) reduction in Cr(III) conversion from 7.1 % to 0.7% compared with aging at 24oC. ROS exposure resulted in 15.4 ± 5.7% loss of Cr(VI) at 24oC, pH 9 and 10% RH during chromium aging. Overall, ROS and ozone added to the conversion of Cr(III) to Cr(VI) during sampling of chromium in airborne PM and atmospheric aging such that aging at a lower temperature reduced the Cr(III) conversion fraction compared to a higher temperature. All of the reactions were complete in less than 1 to 2 hours.

12CA.1

Phase, Viscosity, Morphology, and Room Temperature Evaporation Rates of SOA Particles generated from different Precursors, at Low and High Relative Humidities, and their Interaction with Hydrophobic Organics. ALLA ZELENYUK, Dan Imre, Josef Beranek, Jacqueline Wilson, Evan Abramson, *Pacific Northwest National Laboratory*

Formation, properties, transformations, and temporal evolution of secondary organic aerosols (SOA) particles strongly depend on particle phase. Recent studies by our group indicate that laboratory-generated alpha-pinene SOA particles and fresh ambient SOA characterized in a recent field campaign are in semi-solid phase and their evaporation rates are orders of magnitude slower than predicted. These results demonstrate that assumptions used by all current models that SOA form solution that can be modeled with Raoult's law, and that the particles maintain equilibrium with the gas-phase at all times need to be significantly changed.
We extend these studies to include SOA particles generated by oxidation of a number of different precursors that include limonene, n-alkenes, cyclo-alkenes, and isoprene and characterized their phase, morphology, and room temperature evaporation rates. To examine the effect of relative humidity on SOA properties and evaporation rates we conducted the experiments at low and high (~90%) relative humidities.

In addition, we examine the interaction between SOA particles and different hydrophobic organics that represent typical anthropogenic emissions. We find that when hydrophobic organic vapors are present during SOA formation, they become incorporated into SOA particles and significantly slow the particle evaporation rates. We demonstrate that it is possible to directly measure the diffusion rates of these molecules in SOA, and use them to calculate a reasonably accurate value for the SOA viscosity, from which particle coalescence rates are also calculated.
Similar measurements were also conducted on aged SOA particles, including those doped with hydrophobic organics. The data indicate that aging further slows the rates of evaporation and results in decreased diffusion rates and increased viscosity, indicating hardening occurs with time, which is consistent with observed decrease in water uptake.

12CA.2

Effect of Relative Humidity on the Evaporation Kinetics of Alpha-Pinene Secondary Organic Aerosol. ELLIS SHIPLEY ROBINSON, Neil Donahue, *Carnegie Mellon University*

The effect of relative humidity (RH) on the evaporation kinetics of secondary organic aerosol (SOA) from alpha-pinene ozonolysis was investigated using a two-chamber dilution method. Recent studies have pointed to the slow evaporation of alpha-pinene SOA as indicative of a highly-viscous physical state, and we employ the plasticizing effects of water to test this theory. Our hypothesis was that if particle-phase diffusion were responsible for slow evaporation this diffusion limitation would be eliminated at high relative humidity, where the SOA particles are known to take up substantial water. The evaporation rate, however, does not correlate with RH, and thus the data do not support the idea that diffusion limitations are controlling the evaporation timescale.

Our two-chamber dilution approach allows for near-instantaneous dilution of both particles and gases, which eliminates wall-bound particles as a source of confusion for in-chamber dilution studies. Upon SOA formation, aerosol suspensions were transferred from the reaction chamber into a clean smog chamber, instantaneously diluting the gas-particle mixture by a large, but finite, amount. Measurements of the particle size distribution were taken with a Scanning Mobility Particle Sizer (SMPS) to determine mass-loss due to evaporation as a function size. The chemical composition of the SOA was measured using a High-Resolution Aerosol Mass Spectrometer (HR-AMS).

We present here a new experimental technique for performing dilution experiments on aerosols. Additionally, we demonstrate that a highly viscous, or “glassy,” physical state is not responsible for the observed SOA evaporation rate.

12CA.3

Implementing Volatility Basis Set Algorithm for Organic Aerosol Formation in CMAQ 5.0. BONYOUNG KOO, Greg Yarwood, Eladio Knipping, *ENVIRON International Corporation*

A volatility basis set (VBS) approach is implemented in the Community Multiscale Air Quality (CMAQ) model version 5.0 to provide an alternative framework of organic particulate matter (PM) formation. Of the various components of atmospheric PM, organic aerosol (OA) is among the most abundant and the least understood and is usually under-predicted substantially in current air quality models. Traditionally, primary organic aerosols (POA) have been treated as non-volatile and non-reactive. However, environmental chamber studies that vary temperature and aerosol dilution have shown that POA can be semi-volatile and undergo gas-particle partitioning in the atmosphere similar to secondary organic aerosols (SOA). Also, it is now known that further oxidation of semi-volatile organic compounds (SOA and POA) can create products with lower volatility leading to increased OA formation downwind. The organic aerosol (OA) module in CMAQ 5.0 uses a two-product model for semi-volatile SOA with polymerization decreasing SOA volatility over time and assumes non-volatile POA with oxidative aging increasing the mass of POA over time. The VBS approach provides a unified framework for gas-aerosol partitioning of both POA and SOA including chemical aging. The VBS implementation in CMAQ 5.0 uses four separate basis sets to differentiate anthropogenic POA and SOA, biogenic SOA, and OA from biomass burning. Each basis set consists of five volatility bins including zero-volatility bin for non-volatile compounds. Molecular weight increases as volatility decreases to account for mass gain from chemical aging. The new organic PM module is evaluated with a modeling database provided by US EPA which simulates a 2006 summer episode over the entire continental US, and its effect on modeled OA formation is discussed.

12CA.4

Contribution of Uncertainties in Anthropogenic Emission Inventories to SOA Simulations for the Los Angeles Basin. RAVAN AHMADOV, Stuart McKeen, Roya Bahreini, Ann Middlebrook, Joost de Gouw, Carsten Warneke, Jose-Luis Jimenez, Patrick Hayes, Allen Robinson, Michael Trainer, *NOAA ESRL*

In recent years significant research has been focused on understanding of secondary organic aerosol (SOA) formation and evolution processes in the atmosphere. The appropriate representation of chemical and physical processes pertinent to SOA in the atmospheric models is an essential task. However, uncertainties of the anthropogenic emission inventories can have a large impact on the prediction of SOA concentrations from urban areas. Inaccuracies in the emission inventories arise due to several factors: mainly changing economic activity, impact of regulations on the vehicle emissions, contrast between week-end and week-day emissions.

An intensive field campaign CalNex took place during May-June 2010, focusing on Los Angeles basin. The available measurements for meteorological fields, gas-phase and particle species from the NOAA P3 aircraft and the Caltech supersite in Pasadena during CalNex provide us with valuable datasets to evaluate models and emission inventories.

The state-of-the-art SOA parameterization based on volatility basis set and updated SOA yields are implemented in the WRF-CHEM model. We perform full meteorology and chemistry simulations including SOA species for the Los Angeles area by using different emission inventories. The reference simulations are done using U.S. EPA National Emission Inventory version 2005 processed according to EPA recommendations. Initial comparison of the model results with the observations of gas and particle species reveal a significant overestimation of the emissions by the inventory, consequently affecting simulated SOA concentrations over the region. The emission inventory used for WRF-CHEM is corrected for CalNex period using various datasets, such as observations, the fuel sale, the trend information and updated inventory from EPA. We present the sensitivity of SOA simulations to the change in anthropogenic emissions. We also discuss the contribution of different emission categories (point, mobile-onroad, mobile-nonroad, and area) to primary and secondary organic aerosol budget over the Los Angeles region.

12CA.5

Assessment of Biogenic Secondary Organic Aerosol in the Himalayas. ELIZABETH STONE, Tony Nguyen, Bidya Banmali Pradhan, Pradeep Man Dangol, *University of Iowa*

Biogenic contributions to secondary organic aerosol (SOA) in the Southeast Asian regional haze were assessed by measurement of particle-phase isoprene, monoterpene, and sesquiterpene photooxidation products in fine particles (PM2.5) at a mid-latitude site in the Himalayas. Organic species were measured in solvent-extracts of filter samples using gas chromatography mass spectrometry (GCMS) and chemical derivatization; this analysis was used to quantify molecular markers for primary aerosol sources—including motor vehicles, biomass burning, and detritus—and SOA tracers. Authentic standards of most SOA products were not commercially available at the time of this study, so surrogate standards were used for semi-quantitation. Using an empirical approach to uncertainty estimation based on homologous series of atmospherically-relevant model compounds, analytical uncertainties ranged from 32% for SOA tracers with structurally-similar surrogates to more than 100% for tracers with a poorly-matched surrogate. Biogenic SOA contributions to PM2.5 mass and organic carbon content in the 2005 monsoon and post-monsoon season ranged from 2-19% for isoprene, 1-5% for monoterpenes, and 1-4% for sesquiterpenes. High concentrations of isoprene derivatives in aerosol, particularly in the late summer months, point to biogenic SOA as a significant source of organic carbon in the Himalayan region.

12HA.1

Multistage Cyclone Array for the Simultaneous Collection of Aerosol Mass in the Ultrafine, Submicron, Respirable, and Coarse Region. EMANUELE CAUDA, Steven Mischler, *NIOSH*

The impact of exposure to occupational aerosol on workers' health needs to be evaluated by simultaneously investigating the toxicity of the aerosol and the physical characterization of the particles. While current real-time monitors and off-line analysis can perform accurate physical characterization of the particles on very small samples, in-vitro toxicological analysis generally requires large amount of sample to be analyzed. This requirement induce the use of samplers that collect rapresentative and significant portion of the aerosol on media or substrates. For aerosols characterized by particles both in the micron and ultrafine region, the collection and analysis of size-segragated samples is also extremely useful for the investigation of different size-cut of the aerosol. This is typicall accomplished by using multistage impactors that collect particles on plates or filters. It is known that the collection of large amount of sample on a single impactor stage can modify the collection efficiency of the impactor by shifting its characteristics. This study investigated the use of a multi-stage cyclone system to collect crystalline silica particles from the coarse region to below 200 nm. The collection efficiency of the four stages - ultrafine, submicron, respirable, and coarse - was characterized by using real-time monitors, microscopy analysis, and dynamic light scattering on aerosol samples dispersed in liquid form prior the toxicity analysis. The study showed that the system is capable of providing sufficient amount of sample for toxicity analysis – in the order of milligrams – for every cut size, while maintaing consistent and accurate stage collection efficiency characteristics during the test.

12HA.2

Contribution of water-soluble and insoluble species and their hydrophobic/hydrophilic sub-fractions in the toxicological properties of ambient atmospheric aerosols. VISHAL VERMA, Neel Kotra, Laura King, Jiumeng Liu, Roberto Rico-Martinez, Terry Snell, Rodney Weber, *Georgia Institute of Technology*

The present study assesses the relative contributions of water soluble and insoluble compounds and their hydrophobic/hydrophilic sub-fractions in the toxicological properties of ambient fine aerosols (D_p<2.5 micro-meter). Toxicity of the particulate matter (PM) was measured by both chemical (dithiothreitol; DTT assay) and biological methods [acute toxicity test using aquatic organisms - Brachionus calyciflorus (rotifers)]. The particles were collected at an urban site near downtown Atlanta using a high-volume sampler and were extracted in both water and methanol. Hydrophobic and hydrophilic fractions of the PM were segregated by passing the extracts through a C-18 column. The responses of both toxicity assays (DTT and rotifers) were significantly higher for the methanol extract than water extract. A substantial fraction of aerosol toxicity was associated with the hydrophobic compounds as evident from a remarkable attenuation in DTT response (~60 % for water and ~75 % for methanol extract) after passing the PM extracts through C-18 column. The DTT activity of water and methanol extracts were correlated with WSOC (water soluble organic carbon; R = 0.86) and WIOC (water insoluble organic carbon; R = 0.94) content of the PM, respectively. Brown carbon (BrC) content of the PM, which predominantly represents the hydrophobic organic fraction, was also correlated with DTT activity of both the water (R=0.78) and the methanol extracts (R=0.83). Conversely, regression results of the rotifers assay didn't yield any consistent association with the measured PM constituents. However, considerable reductions (>90%) were obtained in the rotifers mortality also by removing the hydrophobic PM species. These findings suggest that the hydrophobic components of both the water-soluble and the insoluble organic aerosols contribute substantially to the ambient PM toxicity and could have significant ecological impacts (e.g. on rotifers and other important animals in aquatic food webs). More research should be focused on this fraction than done in the toxicological studies conducted so far.

12HA.3

On-line Measurements of Particle Bound Reactive Oxygen Species in Ambient and Combustion Aerosols. STEPHEN FULLER, Jenny Nutter, Stephen Platt, Lisa Pfaffenberger, Peter Barmet, Josef Dommen, Urs Baltensperger, Andre Prévôt, Markus Kalberer, *University of Cambridge*

Adverse health effects associated with aerosol particles in ambient air are well documented by epidemiological studies. However, due to the large variability in ambient particulate matter it is unknown what physical or chemical properties are responsible for these negative health effects. Previous studies have highlighted reactive oxygen species (ROS) in components of organic particulate matter, as being potentially a major cause.

An online measurement system was developed in the study presented here that collects water-soluble aerosol components and determines the ROS concentration by reaction with the fluorescent probe 2-7 dichlorofluorescein (DCFH). Particles were collected and continuously extracted on a wetted hydrophilic filter. The particles are collected and extracted in a solution of horseradish peroxidase (HRP) that allows immediate reaction of ROS on collection. The concentration of ROS is determined following subsequent reaction of the oxidised HRP with DCFH yielding a fluorescent reaction product, which is quantified in the continuous flow set-up using fluorescence spectroscopy. The detection limit of the system is approximately 10 nMoles of hydrogen peroxides per cubic meter of air.

This system was used to measure particle bound ROS concentrations during the ageing of primary moped combustion emissions in the presence of UV light and NOx in smog chamber experiments. The reactivity seen during the ageing experiments was found to be purely due to secondary organic aerosol with ROS concentrations of about 1nMole per microgram of SOA. The ROS concentration in these primary emissions are comparable with pure SOA systems from biogenic and anthropogenic precursors.

12HA.4

The Complex Role of Vegetation in Mitigating Near Road Air Pollution. ZHEMING TONG, Max Zhang, Patrick MacRae, Thomas Whitlow, *Cornell University, Ithaca, NY, USA*

Air pollution is a major environmental concern in cities across the world. Urban vegetation may help mitigate local particulate pollution. We conducted a near-road study to investigate the impact of vegetation barriers next to a major highway in New York City. Three real time optical particle counters were placed next to the highway, behind a vegetated buffer, and in the open field. Particle number size distributions were measured from 0.3 µm to 20 µm. Average PM2.5 concentration declined with distance from the road. The particle concentration was lowest in the open field 34 meters downwind of the barrier. Vegetation did little to attenuate transient spikes caused by traffic and acted as a “low pass” filter by reducing the number of low concentration events. In addition, the gradient in particle concentration away from the road was strongly dependent on wind velocity and direction, where greater concentration usually corresponded to lower wind speed and wind directions that are more perpendicular to the highway.

12HA.5

Relation Between Carbonaceous Aerosol Characterization and Lung Injury Endpoints in an In Vivo Model. ANDRÉS HENRÍQUEZ, Matías Tagle, Felipe Reyes, Thomas Kuhlbusch, Bryan Hellack, Claudio Hetz, Pedro Oyola, *Centro Mario Molina*

Particulate air pollution is a major problem to public health (Brunekreef and Holgate. 2002). Lately, the carbonaceous compounds of aerosols have attracted interest not only for their implications in the adverse health effects, but also for the contribution to global climate change. The carbonaceous aerosol is a dominant component of fine particle matter ($PM_2.5$), and consists of both elemental and organic carbon. Elemental carbon (EC) is produced by incomplete combustion and comprises graphitic carbon particles, otherwise organic carbon (OC) is a mixture of many compounds; several of them with known health hazard. Nevertheless, there are still gaps in knowledge about how the carbonaceous components induce pulmonary toxic responses.

We collected samples of $PM_2.5$ in the two most populated cities in Chile (Santiago and Concepción) during summer and winter in 2010. Samples were analyzed for mass concentration, EC, OC, monosaccharides, $^{14}C/^{12}C$, among others at NILU (Norwegian Institute for Air Research) and Lund University. With these measurements, a source apportionment of fossil and non-fossil (Biomass) OC and EC was done using Latin Hypercube Sampling Method (Szidat et al. 2009).

Additionally to the aerosol characterization and $PM_2.5$ sampling, toxic responses of constant doses of $PM_2.5$ in an in vivo model were measured using acute lung injury endpoints as lactate dehydrogenase (LDH), total protein and cell count in the bronchoalveolar lavage of Sprague Dawley rats exposed by intratracheal instillation. Also, we analyzed the relation with oxidative stress measuring the intrinsic $PM_2.5$ potential to produce hydroxyl radical generation detected by Electron Paramagnetic Resonance spectrometry (EPR).

The results point out that $PM_2.5$ concentration does not correlate with in vivo endpoints but with EPR. Levoglucosan concentrations, a widely used wood smoke tracer (Naeher et al. 2007), correlate with in vivo endpoints but not with the EPR signals (or concentration). Among sources, non fossil OC and Fossil EC correlated significantly with two in vivo endpoints.

In conclusion, this work highlights the importance of carbonaceous compounds and its relation with health effects of $PM_2.5$.

12IM.1

Ultrafine Particle Generation Through Atomization Technique: The Influence of the Solution. LUCA STABILE, Giorgio Buonanno, Conchita Vargas Trassierra, Gianfranco Dell'Agli, Aldo Russi, *University of Cassino and Southern Lazio*

Aerosol particle generators represent the key devices in the complex calibration apparatus for aerosol measurement instruments. Therefore, several aerosol generation techniques were designed to produce either monodisperse and polydisperse aerosols carrying liquid and/or solid particles. In the sub-micrometer range the most reliable, repeatable (and, hence, marketed) technique is based on the atomization of a properly prepared solution. In particular, in the widely used TSI 3940 submicrometer monodisperse aerosol generator, aerosol is produced through the atomization of a solution made up of a salt in deionized distilled water. After the atomization the aerosol passed through a diffusion dryer to produce a dried polydisperse aerosol. Then, in case, a monodisperse aerosol can be selected classifying a specific particle diameter through an Electrostatic Classifier. Different solutes could be used in the solution preparation, anyway such generator system was only characterized for few solutes.

In the present work the characterization of the TSI 3094 aerosol generation system was performed using different solutions in terms of both solute type and its molar concentration. In particular, different soluble salts selected mainly amongst sulfates, nitrates, carbonates and halides were considered. Moreover, molar concentrations ranging from 0.000017 to 0.017 mol/L were tested for each solute. Polydisperse and monodisperse aerosol measurements in terms of particle number distributions and total concentrations were performed through a Scanning Mobility Particle Sizer spectrometer (SMPS 3936, TSI) and a further Condensation Particle Counter (CPC 3075, TSI), respectively, both set (in series) downstream of the generation system.

Results in terms of polydisperse aerosol characteristics (mode and total concentration) as a function of both solute type and its molar concentration were compared in order to detect solutes able to produced polydisperse aerosol showing sufficiently high concentrations in the range 5-20 nm: it usually represents the range characterized by the lowest amount of particle produced.

12IM.2

A Piezoelectrically Actuated Nebulizer for Inductively Coupled Plasma (ICP) Spectrometry. SANAZ ARABZADEH, Hamid Badiei, Kaveh Kahen, Javad Mostaghimi, *PerkinElmer Inc.*

Pneumatic nebulization of liquid samples is the most commonly used method of sample introduction in ICP atomic emission spectroscopy and mass spectrometry. Their performance, however, is plagued by poor sample transport efficiency due to the wide size distribution of primary aerosol and the need to remove large droplets. In addition, the nebulizer gas used to generate the primary aerosol is also used to transport the droplets to the plasma, which dictates a compromise between the nebulization efficiency and the residence time in the plasma.

Unlike a pneumatic nebulizer, a piezoelectrically actuated nebulizer generates the sample aerosol by vibrating a meshed membrane situated behind a typical injector tube of an ICP torch. The piezo nebulizer generates a narrow distribution of droplets (6-10 microns dia.) which can be introduced directly into ICPs.

In addition to transport efficiency, the characteristics of the electronic nebulizer approach those of an ideal sample introduction system in many aspects, including: a) the use of an active mechanism of aerosol generation that yields a narrow size distribution droplets with a low initial velocity (<5 m/s), b) unlinking the parameters that affect both the aerosol generation and transport processes, which allows independent optimization of nebulizer and plasma parameters to achieve the best analytical performance, c) eliminating signal noise sources such as those originating from peristaltic pump pulsations, d) improved long-term signal stability and short term precision, e) providing a dynamic adjustment of the amount of aerosol generated (by controlling the duty cycle in the drive waveform) and allowing multipoint calibration curves to be constructed from a single standard solution, and f) high tolerance to matrices with high dissolved solids in a variety of acidic solutions.

Design and development of the piezo nebulizer for ICP sources are discussed in detail and the performance characteristics of the system are presented.

12IM.3

A Micro-Liter Vaporization Condensation Aerosol Generator. JOHN CARPIN, *US ARMY*

A generation system has been developed for producing a highly concentrated output of a nearly monodisperse aerosol from a small volume (less than one milliliter) of low volatility material. The approach used is a modification of the classic vaporization/condensation technique in which a material is vaporized and allowed to recondense onto non-volatile “seed” particles resulting in the formation of an aerosol of narrow size distribution. A high vaporization rate is achieved with small volumes of liquid through the use of a custom designed saturator cell and oven. This has proven to be a highly efficient approach for producing test aerosols in the 1 to 5 micrometer size range with high output mass concentrations. Stable operation can be achieved for 60 minutes with loading volumes as low as 200 microliters. This technique has potential applicability to aerosol testing when it is desirable to keep working quantities of test materials to a minimum.

12IM.4

Measurements of Particulate Matter in Diluted Cigarette Smoke and Diesel Exhaust Emissions Using a MEMS-Based Microfluidic Sensor. IGOR PAPROTNY, Frederick Doering, Paul A. Solomon, Richard White, Lara Gundel, *University of California, Berkeley*

The goal of this project is developing a PM sensor that is small enough to be incorporated with other sensors into very lightweight, low power devices that can communicate through wireless networks for community-based monitoring of air pollution and other applications. The MEMS*-based PM sensor measures mass concentration in real-time, and it incorporates the most recent designs emerging from a collaboration between the researchers at the University of California, Berkeley and Lawrence Berkeley National Laboratory. The sensor consists of two main components: a rectangular jet virtual impactor that removes coarse particles, and a thermophoretically-induced deposition-area, where a film bulk acoustic resonator (FBAR) is used to measure the mass of the deposited particles based on changes in the initial resonating frequency of 600 MHz/s of the FBAR. Microfabrication techniques reduced the size of the sensor to a few cm2, enabling portable (perhaps wearable) real-time monitoring of airborne particles. In this work, we present the results of testing two prototypes of our MEMS sensors using cigarette smoke and diesel exhaust, and compare the performance of our sensor to state-of-the-art real-time PM measurement devices. Our prototypes demonstrate low limits of detection in the single microg/m3 range using a flow rate of only 7 mL/min. The sensitivity coefficient of the rate of the frequency change (the output signal) of our sensors ranged from 1.4 to 5.8 Hz/min per microg/m3. The results indicate that the sensitivity increases with increasing flow rate because the efficiency of the thermophoretic deposition is very high. Co-locating a temperature sensor improves the already good agreement between the MEMS PM sensor and other real-time PM devices by enabling removal of the temperature dependence of the FBAR output. The presentation concludes with brief mention of how the capabilities of current PM sensor system could be expanded for more detailed characterization of airborne particles. *MEMS=microelectromechanical systems

12IM.5

Computational Fluid Dynamics Analysis of High-Volume Inlets for Atmospheric Aerosol Sampling Application. IGOR NOVOSSELOV, Riley Gorder, Anna Gannet Hallar, *Enertechnix Inc*

A comparative analysis of five high-volume omni-directional inlets was performed using transient 3D Computational Fluid Dynamics simulations. The modeled inlets included:

1. Enertechnix size-controlled inlet
2. DOE Atmospheric System Research program inlet
3. Sphinx Observatory located in Jungfraujoch, Switzerland inlet
5. Original Storm Peak Laboratory inlet
5. Modified Storm Peak Laboratory inlet

Each of the inlets was placed in a numerical wind tunnel with varied wind speeds from 2.5-15 m/s. The sampling rate was set at 1000 lpm, which is typical for atmospheric aerosol sampling applications. The transmission efficiencies were evaluated for particles in the 10 nm to 20 μm range. Two different turbulence models (k-ε and detached eddy simulations) were used and the effect of particle – turbulence coupling on the transmission efficiency was examined. The modeling results show that for all investigated inlets the particle transmission decreases with the increase of particle size. This is due to particle inertial impaction on the inner walls of the inlets. Additionally the transmission efficiency decreases at higher wind speeds due to the formation of strong recirculation zones and unstable flow behavior inside the inlet geometry. The "Random Walk" turbulent dispersion model was used in the wind tunnel CFD simulations. The model has been previously validated for external flow application against experimental wind tunnel data for one of the modeled inlets and has shown good agreement, especially at wind speeds above 10 m/s. The turbulent dispersion model significantly influences transmission efficiency, especially for the larger internal volume geometries.

12NM.1

Laser-Plasma Synthesis of Sb Nanoparticles. A.M. Baklanov, O.V. BOROVKOVA, G.N. Grachev, A.A. Onischuk, A.L. Smirnov, M.I. Zimin, *Institute of Chemical Kinetics and Combustion, Novosibirsk*

Developing nanotechnology requires more complex methods for the synthesis of nanomaterials, which make it possible to vary the composition, size, morphology and other properties of nanosystems. One of promising approaches for large-scale and inexpensive production of nanomaterials is a laser-plasma synthesis. This type of synthesis can be used for production of refractive nanoparticles for nanoceramics, semiconducting nanomaterials for gas sensing, photocatalysis, solar cell, etc. The laser synthesis is a perspective method of nanoproduction because it is easy to control the final product structure and composition by doping with different elements.

This work is aimed at Sb and Sb_2O_3 nanoparticles synthesis as the Sb based compounds of interest due to semiconducting or thermoelectric properties. Laser-plasma synthesis of these nanoparticles was carried out by evaporation from Sb target in the plasma of optical pulsating discharge ignited in flow of oxygen or argon/oxygen with the flow rate up to 30 l / min. The laser irradiation frequency was from 15 to 60 kHz. The sampling of produced particles was performed using an ejecting device through a tube of inner diameter 0.8 mm placed at the distance of 10 mm from the surface. The ejecting way of sampling was used to dilute the aerosol and suppress the coagulation.

The diluted aerosol was analyzed by the automatic diffusion battery coupled with a condensation chamber and photoelectric counter to obtain particle size distribution in the range 3 - 200 nm. Morphology of the obtained nanoparticles was studied by transmission electron microscope.

12NM.2

Preparation of Novel SiC and Carbon Nanostructures by Induction Heating of Preceramic Silicon-Carbon Nanoparticles.ANNA LÄHDE, Mirella Miettinen, Jouni Hokkinen, Tommi Karhunen, Unto Tapper, Jorma Jokiniemi, *University of Eastern Finland*

Silicon carbide (SiC) is an important high temperature structural material and high performance semiconductor, which can be operated at high temperatures, high power and high frequencies and in harsh environments. Furthermore, SiC can be used as a precursor material for more advanced structures such as graphene layers. In this study, we report the formation advanced SiC and carbon nanostructures by induction heating. Pre-ceramic Si/C nanoparticles synthesised with the chemical vapour synthesis were annealed in an argon atmosphere at temperatures between 1900 and 2600 oC. The evolution of the particle structure, composition and crystalline phases at different annealing temperatures was studied with SEM/EDS, HR-TEM, XRD and Raman spectroscopy. The annealing caused an increase in the crystallite size from a few nanometers of the untreated precursor to several micrometers in the annealed particles. In addition, the annealing temperature had an effect on the crystalline phase of the formed particles. Below the melting temperature of amorphous silicon carbide (Tm = 2172 ºC), the crystalline phase of SiC-3C was dominant (>96 w-%) while above the decomposition temperature (Tdec = 2577 ºC) a separation of carbon and silicon was observed. Carbon nanoflowers were formed in the sample vessel (T=2600 ºC) while SiC-3C and SiC-6H were formed at lower temperatures near the exit of the sample vessel.

12NM.3

Low-Temperature Hydrolysis of AlCl3 Vapor in an Aerosol Reactor to Produce Spherical Preforms for Ceramic-Grade Alumina. HOEY KYUNG PARK, Kyun Young Park, Kyeong Youl Jung, *Kongju National University, South Korea*

Fumed alumina has been commercially produced by hydrolysis and oxidation of $AlCl_3$ vapor in a flame as high as 1800 degrees C, and used as reinforcing fillers and abrasives. The fumed alumina is highly agglomerated and too low in bulk density to be used for ceramics. In the present study, $AlCl_3$ vapor was hydrolyzed in an aerosol reactor at a lower temperature of 300 - 500^oC to produce spherical preforms, $AlO_xCl_y(OH)_z$, for ceramic-grade alumina. The reactor is tubular, 2.4 cm in diameter and 30 cm in length, and electrically heated. The solid $AlCl_3$ was evaporated continuously with a LabVIEW programmed controller and mixed with water vapor in nitrogen. Investigated on the morphology and size of the preforms were the effects of the reaction temperature, the H_2O to $AlCl_3$ molar ratio, the $AlCl_3$ concentration, and the axial position of mixing $AlCl_3$ vapor with H_2O vapor. The obtained preforms were spherical, loosely agglomerated, and distributed in the size range of 50 to 200 nm. The chlorine content was 0.34 to 0.43 at%. The preforms were calcined at 1200^oC to obtain an α-alumina nearly 100 % in α-transformation degree and free of chlorine. The weight loss upon calcination was 35 to 45 %. The surface area equivalent diameter of the calcined particles was about 100 nm. We have demonstrated the preparation of ~ 100 nm α-alumina particles for potential application in functional ceramics, using the new preforms derived from $AlCl_3$ through an aerosol route.

12NM.4

Monodisperse Poly(lactide–co–glycolic acid)–based Nanocarriers for Gene Transfection. JEONG HOON BYEON, Jeffrey Roberts, *Department of Chemistry, Purdue University*

This contribution describes a simple, aerosol–based method for fabricating monodisperse particles containing mixtures of poly(lactide–co–glycolic acid) [PLGA], protamine sulfate (Prot), and poly(L–lysine) [PLL] as nanocarriers for gene transfection. Aqueous solutions of PLGA, Prot, and PLL were collison–atomized, and the resulting aerosolized droplets were dried “on the fly” to form solid particles, which then were electrostatically size–classified into 50 nm, 100 nm, and 200 nm samples. Agarose gel retardation assay confirms that collected particles bind plasmid deoxyribonucleic acid (pDNA), and measurements of cell viability and transfection reveal that the fabricated nanocarriers have a lower cytotoxicity (>85% in cell viability) and a higher transfection efficiency ($>8.7 \times 10^5$ in relative light units, RLU, per mg) than does 25 kDa polyethyleneimine (~50% and 6.8×10^5 RLU per mg). The strategy outlined in this work is potentially generalizable as a new platform for creating polymeric therapeutic nanocarriers using only clinically–approved starting materials in a single–pass configuration.

12NM.5

A Novel Method to Measure Effective Density of Engineered Nanomaterials in Liquid Suspensions: Implications for In Vitro Dosimetry and Nanotoxicology. Glen DeLoid, Joel Cohen, PHILIP DEMOKRITOU, *Harvard University*

With the ever-increasing number of engineered nanomaterials (ENMs) entering the consumer market, efficient and inexpensive in vitro toxicity assays are necessary tools for correlating ENM properties with biological activity. However, results from in vitro assays often vary substantially among different studies and from in vivo data. These discrepancies may be attributable to inadequate characterization of ENM transformations in suspension and the subsequent effects on particle delivery to cells in culture. ENM agglomeration influences in vitro dosimetry by reducing the effective density of ENMs, thereby limiting particle delivery to cells. In this study, we present a novel method for measuring the effective density of ENM agglomerates by volumetric centrifugation. Employing a standardized dispersion protocol recently developed in our group, a panel of well-characterized metal oxide ENMs was suspended in various cell culture media with and without serum proteins. ENM agglomerates were characterized for hydrodynamic diameter by dynamic light scattering. ENM suspensions were then centrifuged in packed cell volume (PCV) tubes equipped with volumetric pellet capturing capillaries. Effective densities were determined from the total volume of the ENM pellet, the known mass of suspended ENM, and the known densities of the ENM raw material and the suspension media. Empirically measured effective densities are reported for a large panel of ENMs dispersed in various media. Particle transport was modeled incorporating values for effective density, and demonstrates large discrepancies between administered and delivered doses. Our method allows for simple determination of effective density, an important step towards linking particle properties to bio-interactions in vitro.

12RA.1

Long-term Trends in the Chemical Composition of Finnish Arctic Aerosols. JAMES R. LAING, Philip K. Hopke, Liaquat Husain, Vincent A. Dutkiewicz, Jussi Paatero, Tanveer Ahmed, *Clarkson University*

The Arctic has experienced dramatic changes in the past half century. According to the Intergovernmental Panel on Climate Change (IPCC), the Arctic is warming at a rate twice as fast as the global average. Currently there is a lack of long-term datasets of atmospheric aerosol composition collected in the Arctic. We present a 47-year dataset characterizing Arctic aerosols. Week-long historical filter samples collected at Kevo, Finland from 1964-2010 have been analyzed for various chemical species. Major ions including methane sulfonate (MSA) have been analyzed for by ion chromatography (IC), trace elements by inductively coupled plasma mass spectrometry (ICP-MS), and BC by light transmission. Portions of the filters were both acid digested and water extracted to provide semi-total and soluble elemental concentrations. The solubility of certain elements can provide information about the particle origins and formation processes. Trends of various species, specifically SO4 and BC, have implications for global climate models. To evaluate the importance of changes in transport routes to Kevo, correlations between North Atlantic Oscillation (NAO) values and concentrations of anthropogenic origins will be discussed. Positive phases of the NAO have been found to coincide with increased transport from Northern Eurasia to Alert, Canada and Barrow, Alaska [Eckhardt 2003; Hirdman 2010]. In addition positive NAO indexes increase heat flux into the Barents Sea [Dickson 2000], which has implications for MSA production. Correlations between MSA and sea surface temperature anomalies as well as NAO indexes will be evaluated. Stocks et al. [1998] predicted increased boreal forest fires in Russia due to global warming. The long-term trend of BC concentrations during the summer months will provide insight to this claim. This complete dataset will be able to provide insight into the long term trend of Arctic aerosol chemical species and the possible implications of global climate change in the Arctic.

12RA.2

Ultra-High Resolution Mass Spectrometry Analysis of PM1 Finnish Boreal Forest Aerosol. IVAN KOURTCHEV, Stephen Fuller, Juho Aalto, Taina Ruuskanen, Willy Maenhaut, Markku Kulmala, Markus Kalberer, *University of Cambridge*

A substantial fraction of atmospheric fine particulate matter is comprised of organic compounds which cover a wide range of polarities, volatilities and masses. Our knowledge on the organic chemical composition of atmospheric aerosols is rather limited; only about 20-30% of the organic matter has been characterised at the molecular level. Because of this limitation, recent efforts have focused on methods that classify bulk organic aerosols. Ultra-high resolution mass spectrometry (UHR-MS) allows determination of thousands of individual organic aerosol constituents at once, providing their elemental formulae from accurate mass measurements.

In this study, we applied UHR-MS for the analysis of PM1 samples collected during a two-week summer period (August, 2011) at a boreal forest site (Hyytiälä), southern Finland. Almost for all samples negative ionisation spectra contained significantly more ions than those of positive, and the majority of these ions were found below 350 Da. More than 1000 elemental formulae were assigned in both modes, and no apparent diel variations in the elemental compositions were observed. The majority of the peaks were attributed to oxygenated or nitrogen containing compounds. The peak assignments were examined using a van Krevelen approach, which allows describing the distribution of functional groups in organic aerosol (OA). On average, the O:C ratios were found to be around 0.5 and 0.2 in the negative and positive modes, respectively. The molecular composition of the examined samples was influenced by the air mass back trajectories. In general, the O:C ratio was within the range obtained for secondary OA generated in laboratory experiments with a number of biogenic volatile organic compounds (BVOCs) reported in recent studies for alpha-pinene and isoprene. The additional LC/MS analysis revealed more than 30 species, which were mainly attributed to oxidation products of BVOCs (i.e., alpha-, beta-pinene and delta-3-carene) supporting the results from the analysis of the bulk OA.

12RA.3

Long-term Volatility Measurements of Submicron Atmospheric Aerosol in Boreal Forest. SILJA HÄKKINEN, Mikko Äijälä, Katrianne Lehtipalo, Heikki Junninen, John Backman, Aki Virkkula, Tuomo Nieminen, Mika Vestenius, Hannele Hakola, Mikael Ehn, Douglas Worsnop, Markku Kulmala, Tuukka Petäjä, Ilona Riipinen, *University of Helsinki*

The volatility of atmospheric submicron aerosol particles was investigated in a boreal forest site in Hyytiälä, Finland, in order to get information on aerosol chemical properties and composition. Measurements were performed continuously between January 2008 and May 2010. Ambient sample air was heated step-wise to six temperatures ranging from 80 to 280 degrees Celsius and the total mass concentration of aerosol particles was determined from the measured particle number size distribution before and after heating. On average 19% of the total aerosol mass stayed in the condensed or solid phase even after heating the aerosol to 280 degrees Celsius. Black carbon explained 55 to 90% of the non-volatile mass. Especially during colder months noticeable amount of non-volatile material, something else than black carbon, was observed. Using additional information on ambient meteorological conditions and air mass trajectories, as well as results from aerosol mass spectrometry (AMS) the chemical composition of the non-volatile residual and its seasonal behavior was further examined. However, no single explaining factor was found. During winter and spring months the non-volatile aerosol residual had a significant positive correlation with pollutant trace gases, such as carbon monoxide, and polycyclic aromatic hydrocarbons (PAH). This indicates a strong anthropogenic influence on the non-volatile aerosol residual. From campaign-based AMS data it was seen that during fall 2008 aerosol particles were relatively more non-volatile when the aerosol mass fraction of organic nitrate and organics was high compared to the sulfate contribution. Thus, the existence of very low-volatile organic compounds can be speculated.

12RA.4

An Investigation of Secondary Organic Aerosol Precursors and Formation Processes in and above Deciduous Forest Canopies. RICK SAYLOR, Ariel Stein, *NOAA Air Resources Laboratory*

The deciduous forest canopies of the southeastern U. S. are significant emission sources of biogenic volatile organic compounds (BVOCs) and have the potential to significantly influence the formation and distribution of secondary organic aerosol (SOA) mass in this region. The biogenically-derived SOA formed as a result of emissions from the widespread forests in the southeastern U. S. can affect air quality in populated areas, degrade atmospheric visibility throughout the region, and may also affect regional climate through both direct and indirect forcings. In an effort to better understand the formation of SOA mass from forest emissions in this area, a 1-D column model of the physical and chemical processes occurring within and just above a deciduous forest canopy has been created. This model, the Advanced Canopy Chemistry and Exchange Simulation System (ACCESS), includes processes accounting for the emission of BVOCs from the canopy, turbulent vertical transport within and above the canopy, detailed chemical reaction, mixing with the background atmosphere and deposition to the canopy and forest floor. In this presentation, the model formulation will be described and results will be presented investigating the canopy concentrations and fluxes of gas-phase precursors of SOA and how those concentrations may be affected by background anthropogenic nitrogen oxides (NOx) and VOCs and by biogenic NOx emitted at the surface. The model results will be used to estimate how well current 3-D air quality and atmospheric chemistry models account for the complex physical and chemical processes occurring within forest canopies and if a more complete parameterization of these processes is required for improved SOA simulations from these models.

12RA.5

Spatial Extent of New Particle Formation and Growth Events. JAMES SCHWAB, G. Garland Lala, Kenneth Demerjian, Brian P. Frank, H. Dirk Felton, Oliver Rattigan, *University at Albany, SUNY*

We measured particle number concentrations and size distributions at two locations in New York State separated by a little over 300 km. The sites are Pinnacle State Park in Addison, NY in southwestern upstate New York, and Queens College in the borough of Queens, New York City. Relevant measurements at the Addison site consisted of paired nano- and long-tube SMPS systems to cover the size range from 5 to ~700 nm mobility size, and a 3783 water-based Enviromental Particle Counter (EPC) for concentrations of particles greater than 7 nm diameter. At the Queens College site the size distributions were measured with a Fast Mobility Particle Sizer, and an identical 3783 EPC. Simultaneous measurements at the two sites were planned from April through September 2012.

The simultaneous nature of the measurements, combined with the mid-range separation distance between the sites allow us to pose and address a number of questions related to the spatial extent of new particle formation and growth events. For example, how well correlated (if at all) are particle formation and growth events at these two sites? If they are related, do they tend to occur simultaneously, or separated by some “transit” time? What are the frequencies of rural versus urban events? These and other questions will be addressed in this presentation.