

11A.1

Simultaneous On-line Size and Chemical Analysis of Gas Phase and Particulate Phase of Mainstream Tobacco Smoke.

JOHN McAUGHEY, Conor McGrath, British American Tobacco; Thomas Adam, Christoph Mocker, Ralf Zimmermann, University of Augsburg.

Tobacco smoke is a complex and dynamic matrix consisting of gaseous and particulate material, in which about 4800 constituents have been identified. The chemical composition and partition between phases of the smoke can change continuously and is strongly influenced by time, temperature, chemistry and dilution of smoke.

We present an experimental set-up consisting of gas phase and particulate phase on-line instrumentation for comprehensive analysis of mainstream tobacco smoke, that is, the smoke that emerges from the mouth end of the cigarette during a puff.

Cigarettes comprising Burley, Virginia or Oriental tobacco at 3 filter ventilation levels were smoked at two flow regimes, with particle diameter and concentration measured by electrical mobility. Chemical composition was characterised on-line by resonance-enhanced multi-photon ionisation (REMPI) and single photon ionisation (SPI) techniques with time-of-flight mass spectrometry (TOFMS).

Count median diameter (CMD) averaged over the cigarette varied from 182 - 260 nm and increased with increasing filter ventilation and lower puff flow rates; a consequence of increasing smoke residence time and coagulation within the rod. Puff-by-puff data showed increasing particle concentration and decreasing diameter as the tobacco was consumed and the coagulation period decreased.

Initial mass spectrometry data show that most smoke constituents feature a continuous increase from the first to the last puff. However, there are some substances, in particular unsaturated hydrocarbons e.g. butadiene, isoprene, and propyne, which show a completely different behaviour by having the highest amounts in the first puff. This is likely to be related to the different combustion and pyrolysis conditions when the cigarette is lit.

11A.2

Highly Time-Resolved Ambient Measurements of Organic Molecular Markers and Air Toxics in Pittsburgh Using Thermal Desorption Aerosol GC-MS (TAG).

ANDREW T. LAMBE, Jennifer M. Logue, Allen L. Robinson, Neil M. Donahue, Carnegie Mellon University; David R. Worton, Brent J. Williams, Allen H. Goldstein, University of California, Berkeley; Nathan M. Kreisberg, Armond Gauthier, Susanne V. Hering, Aerosol Dynamics Inc.

A significant fraction of airborne PM_{2.5} consists of organic carbonaceous material, with hundreds of individual compounds identified in ambient aerosols including source specific molecular markers and known carcinogens such as PAHs. Speciation of organic aerosol traditionally involves offline GC-MS analysis of solvent extracted samples, which is labor-intensive and results in measurement resolution of 12-24 hours. This study builds on work introduced by Williams et al (AS&T, 2006; JGR, 2007) using Thermal Desorption Aerosol GC-MS, a novel method for automated collection of ambient particles with online GC-MS analysis. TAG affords hourly resolution and has the advantage of fully automated operation, therefore holding promise as an alternative to traditional organic speciation techniques.

TAG has two modes of operation: ambient sampling with concurrent GC-MS analysis of the previously collected sample, and thermal desorption of the previously collected sample onto the GC column. Particles are humidified to increase adhesion and minimize bounce before inertial impaction onto a collection substrate. During ambient measurements, sampling is set on a 26-hour cycle that includes collection of ambient samples as well as filtered ambient samples to determine contribution of gas-phase compounds and zero air blanks to determine internal contamination levels. In this work we monitor ambient aerosol loadings in the vicinity of a large construction project on the Carnegie Mellon campus. These highly time-resolved measurements provide insight into the relative contribution of local point sources to an area dominated by regional transport. The extent of this contribution would be more difficult to discern using traditional analysis techniques with measurement resolution approaching regional mixing timescales, and demonstrates an application uniquely suited to TAG. We also evaluate instrument performance for nonpolar compounds (i.e. n-alkanes, hopanes and steranes, PAHs) relative to solvent extracted samples collected concurrently during ambient measurements and smog chamber experiments.

11A.3

Analysis of Organic Aerosols Using Methods of High-resolution Mass Spectrometry. YURY DESYATERIK, Pacific Northwest National Laboratory; Maggie L. Walser, Sergey A. Nizkorodov, University of California, Irvine; Julia Laskin, Alexander Laskin*, Pacific Northwest National Laboratory.

Traditional methods for characterization of the chemical composition of PM_{2.5} are limited to relatively low molecular weight (MW) thermally stable compounds. However, recent studies demonstrated that up to 80% of unidentified organic matter in field-collected aerosols corresponds to high-MW humic-like substances (HULIS). Development of new analytical approaches is crucial for accurate determination of chemical composition of PM_{2.5} and estimating the effects of prescribed burning on the air quality and climate. This presentation reports on our efforts aiming to develop a novel analytical platform for unequivocal identification of high-MW molecules in aerosol samples using high-resolution mass spectrometry combined with electrospray ionization. The presented work is focused on characterization of the chemical composition of secondary organic aerosol formed during the ozonolysis of undecylenic acid and limonene in laboratory experiments, and then on molecular speciation of organic compounds characteristic of field collected biomass burning aerosols. Accurate mass measurement using high-resolution (100,000 mass resolution) mass spectrometry is used for determination of the elemental composition of high-MW constituents while tandem mass spectrometry (MS/MS) experiments are used for structural characterization of complex molecules. High mass resolving power of the LTQ/Orbitrap™-MS instrument allows us to assign the empirical elemental composition of hundreds to thousands of peaks in each given sample. The complexity of the spectra can be partially reduced using the Kendrick diagram, in which groups of homologous species that differ by the number of repeating or additional groups (e.g., -CH₂-, -CH=CH-, -OH, -COOH etc.) can be identified.

11A.4

Measurements of Organic Nitrogen Budget in Atmospheric Aerosol. ANDREY KHLYSTOV, Ming-Yeng Lin, Duke University.

Ammonium and nitrate are the main inorganic nitrogen-containing aerosol constituents. However, measurements of only inorganic nitrogen do not provide complete information on the total nitrogen content of ambient aerosol. Despite growing evidence that organo-nitrogen compounds may constitute a significant fraction of the aerosol nitrogen, very little is known about this fraction. We report high time resolution measurements of chemical composition of PM_{2.5} aerosol at the Duke Forest Research Facility with the emphasis on quantification of the contribution of organo-nitrogen compounds (ONC) to the total nitrogen budget in the aerosol as well as its dynamics as a function of ambient temperature and relative humidity. The main water-soluble inorganic components (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺), total and water soluble carbon, as well as organic nitrogen are measured using a modified Steam-Jet Aerosol Collector (SJAC). The total concentration of aerosol carbon and nitrogen are measured using a high sensitivity TOC/TN unit. The concentration of organo-nitrogen in the aerosol is determined as the difference between the total nitrogen concentration and the concentration of inorganic nitrogen species. The time resolution of the measurements is 30 min.

11A.5

Characterization of Nitrogen Containing Organic Species in Atmospheric Aqueous Samples and Aerosol Particles Using a High Resolution Time-of-Flight Aerosol Mass Spectrometer. Yele Sun, QI ZHANG, University at Albany, SUNY.

Despite the fact that nitrogen-containing organic species are ubiquitous in atmospheric particles and water droplets and likely play important roles in atmospheric chemistry and ecosystem health, very little is known about the concentration or composition of this class of compounds. Here we present the development of a new method that allows the quantification and bulk-characterization of water-soluble organic nitrogen (WSON) species in atmospheric fog and cloud waters using an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS). The success of this method relies on the facts that 1) the AMS mass spectra can be deconvolved to quantify and chemically characterize organic material in complex mixtures such as atmospheric aerosol particles and 2) the high resolution capability of the HR-ToF-AMS can distinguish nitrogen containing organic fragments (e.g., $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$) from ion fragments lack of N atom (e.g., $C_xH_y^+$ and $C_xH_yO_z^+$). We evaluate this method through HR-ToF-AMS analyses of a suite of WSON standard compounds, including 19 amino acids, urea, peptides and proteins. The elemental ratios of C:H:O:N are determined in the spectrum of each compound and compared to the theoretical values. In addition, we will present the application of this technique in analyses of atmospheric fog and cloud water samples and aerosol extracts. Attempts will also be made to characterize different classes of WSON species (e.g., amino compounds vs. amides) in atmospheric samples based on mass spectral signature identified in standard compounds.

11A.6

A Community Software for Quality Control and Analysis of Data from the Aerodyne Time-of-Flight Aerosol Mass Spectrometers (ToF-AMS). DONNA SUEPER, Aerodyne and University of Colorado, Boulder; James Allan, University of Manchester; Edward Dunlea, University of Colorado, Boulder; Jonny Crosier, University of Manchester; Joel Kimmel, Peter DeCarlo, Allison Aiken, Jose-Luis Jimenez, University of Colorado, Boulder; Doug Worsnop, Aerodyne.

The ToF-AMS (Drewnick et al., 2005) and high-resolution ToF-AMS (HR-ToF-AMS, DeCarlo et al., 2006) are the new versions of the Aerodyne AMS, and are rapidly superseding the quadrupole AMS (Q-AMS). The data quality control and analysis tasks are enormous for ToF-AMS datasets, due to the size (a typical dataset size is 25 GB) and dimensionality (3-4 mathematical dimensions) of the data produced. A software tool for ToF-AMS data management and analysis called SQUIRREL will be presented (Sueper et al., 2007). As was the case with the Q-AMS analysis software, SQUIRREL is also shared with the entire AMS Users Community and improved with feedback from all users. This leads to faster development and ensures consistent processing of ToF-AMS data. The architecture of SQUIRREL is centered on the premise that most data are kept in the computer hard drive, as ToF-AMS datasets are too large to completely reside in computer memory. The ToF-AMS data acquisition software saves the data in Hierarchical Data Format (HDF5), a highly structured binary format that was developed by NCSA with NASA funding for satellite applications. HDF5 files can be accessed randomly, which greatly reduces seek times over the text file system used in the Q-AMS acquisition and analysis software. The name "SQUIRREL" reflects the ability of the software to quickly move pieces of the data ("acorns") between the memory and the hard drive. The basic principles of data analysis are adapted from those from the Q-AMS (e.g. Allan et al., 2003, 2004). Along with flexible and detailed mass calibration and baseline fitting routines, SQUIRREL incorporates techniques to handle high-speed recording and multiple ionization schemes. Additional modules can be built upon SQUIRREL for specialized analyses. An example of such a module is the code to characterize the chemical information contained in the high-resolution mass spectra from the HR-ToF-AMS. Examples of application of SQUIRREL and HR-SQUIRREL to real datasets, and directions for future development will be given.

11A.7

Application of Positive Matrix Factorization (PMF) to Aerosol Mass Spectrometer (AMS) Data: Pitfalls and Results. Ingrid Ulbrich, JOSE L. JIMENEZ, Katja Dzepina, Kenneth Docherty, University of Colorado-Boulder; Qi Zhang, SUNY-Albany; Manjula Canagaratna, Douglas Worsnop, Aerodyne Research; Dara Salcedo, Univ. Estado Morelos.

Our understanding of organic aerosols (OA) is rapidly evolving, partially due to the influx of data from new real-time techniques. Zhang et al. (ES&T, 2005; ACP, 2005) first applied component analysis techniques to AMS field data, leading to the recognition of the dominance of oxygenated organic aerosols (OOA) even in urban areas. Several new component analysis techniques have been recently applied to AMS datasets (Zhang et al., GRL, 2007; Lanz et al., ACP 2007; Marcolli et al., ACP 2006). PMF is promising due to the non-negativity constraint that reduces the rotational freedom of the solutions, the availability of reliable software, and the accumulated experience of community in its use. However PMF does not produce a unique solution, but rather a matrix of solutions (with increasing number of factors and values of the rotational parameter FPEAK) from which the user has to choose the "most realistic one." Although many OA sources are known to make a contribution to ambient OA levels, it is not clear how finely these can be retrieved using unit-resolution EI AMS data. Using synthetic data, we show that PMF solutions with too many factors still produce realistic-looking time series and mass spectra, due to "mixing" of the real components and to "splitting" of the real components into subcomponents. Splitting tends to yield similar mass concentrations on both new components. The evaluation of PMF solutions through synthetic analysis is critical to the believability of the results. We apply PMF to ambient datasets from Pittsburgh, Riverside, and Mexico City. PMF reveals a small semivolatile OOA II component (8% of the OA mass) in Pittsburgh, which doesn't change the interpretation of this dataset by Zhang et al. (2005ab). PMF solutions for Pittsburgh with more than 3 components appear to split the main components, rather than to find real new components.

11A.8

Investigation of biomass combustion aerosol by H-NMR spectroscopy. James Hutchings, Pierre Herckes, Arizona State University; GAVIN MACMEEKING, Sonia Kreidenweis, Jeffrey L. Collett, Jr., Colorado State University; Wei Min Hao, Cyle Wold, US Forest Service; W.C. Malm, National Park Service.

Biomass combustion is an important emission source of particulate matter into the atmosphere with local (haze) and global (climate) impacts. In recent years many efforts have been made to characterize the particulate emissions in terms of size, hygroscopicity, optical and chemical properties. Chemical characterization has mainly focused on speciation studies, quantifying individual species while the bulk of the organic matter remained poorly characterized beyond water solubility. Consequently little is known on how the chemical properties including functionality impact physical characteristics like hygroscopicity and optical properties.

We investigated particulate matter emissions from biomass burning through a series of large scale laboratory experiments aimed at understanding the impact of fuel and combustion regime on chemistry and optical properties. For the present work, biomass samples from a variety of fuels and burning regimes were extracted with deuterium oxide. These aqueous extracts were then characterized by proton nuclear magnetic resonance spectroscopy (H-NMR). The results give insights on the variability of the chemical structure of the water soluble organic carbon (WSOC) fraction by quantifying the importance of different types of protons (e.g., aromatic vs aliphatic). Beyond functional group information, major organic species including levoglucosan can be identified and quantified at a molecular level using the discrete features in the H-NMR spectra. Finally, we will discuss how these new insights in the structure and composition relate to the variability in optical and hygroscopic properties observed in biomass burning aerosol.

11A.9

Cross flow ion mobility spectrometry. MANG ZHANG, Anthony S Wexler, University of California, Davis.

A new instrument, the cross flow ion mobility spectrometer (CF-IMS) was constructed and tested. CF-IMS is a light-weight, low cost instrument that can analyze the composition of the gas phase continuously and with high mobility resolution. Unlike the traditional ion mobilities spectrometers (IMS) and differential mobility analyzers(DMA), CF-IMS uses a higher flow velocity and parallel plated configuration that decreases the characteristic dimension in the Reynolds number to achieve higher resolution. Its electrometer sensor array eliminates voltage scanning in the DMA and the shutter gate in IMS, both of which decrease duty cycle in these instruments.

Three different CF-IMS prototypes which include two channel, 20 channel and 256 channel electrometers is tested with different chemicals. Result will be compared and presented.

11A.10

A New Automated Monitor for the Measurement of Particulate Reactive Oxidant Concentrations in the Atmosphere. PRASANNA VENKATACHARI, Philip K. Hopke, Clarkson University.

The global burden of disease as a consequence of ambient particulate matter (PM) remains a growing threat, and efforts to identify and link specific components of the PM mix with various PM-associated health effects are intensifying. A causal hypothesis for particle toxicity is through oxidative challenges to the lung, resulting in the generation of reactive oxidative species (ROS) at the target sites. However, research conducted over the past few years has shown that ROS is present on ambient particles to which we are exposed. It needs to be recognized that ROS present on particles can cause the same kind of systemic dysfunctions as endogenously produced ROS. Few measurements have been made of the particulate oxidant concentrations due to the impracticability of the manual measurement methods, and the difficulty of obtaining timely and accurate measurements is an obstacle for the research and regulatory communities. As a result, an automated instrument is needed.

In atmospheric applications, the requisite sensitivity involved in the trace determinations of atmospheric oxidants limits the choice to luminescence methods. The photoluminescence procedure involving the oxidation of the non-fluorescent form of dichlorofluorescein to its fluorescent form by ROS in the presence of a peroxidase enzyme was found to be a sensitive, non-specific, attractive method. A practical sample collection-flow injection system for the semi-continuous measurement of the total particulate oxidant concentrations in the ambient atmosphere based on this dichlorofluorescein-oxidant-peroxidase fluorescence reaction has been developed. This monitor allows the determination of the distribution of ambient particulate ROS as a function of location, time of day, and day of year, and will ultimately aid in the statistical evaluation of the role of particle-bound oxidants in the overall toxicological impact of PM. The system configuration, validation of its performance, and, measurements of atmospheric oxidant concentrations with this monitor will be presented.

11A.11

Contribution of Carboxylic Acids in Ambient Aerosol to the m/z 44 Signal of an Aerodyne Aerosol Mass Spectrometer.

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The Aerodyne aerosol mass spectrometer (AMS) employs flash vaporization (600C) followed by 70-eV electron impact ionization to detect organic and inorganic aerosols. The signal at mass-to-charge ratio (m/z) 44 (mainly CO₂⁺) is considered the most reliable marker of oxygenated organic aerosol, especially for carboxylic acids. We estimate the contribution of selected low molecular weight dicarboxylic acids (diacids) and omega-oxocarboxylic acids (omega-oxoacids) to the particle-phase m/z 44 signal of the AMS mass spectrum. Ambient measurements were conducted at a surface site in Tokyo (35.39N, 139.40E) during August 3-8, 2003. Diacids and omega-oxoacids were measured using a filter sampling followed by extraction, derivation, and gas chromatograph - flame ionization detector (GC-FID) analysis. The mass concentrations of diacids and omega-oxoacids show tight correlation with the m/z 44 signal ($r^2 = 0.85-0.94$) during the measurement period. Laboratory experiments were performed to determine the fragment patterns of selected diacids (C₂-C₆ diacids and phthalic acids) and omega-oxoacid (glyoxylic acid) in ambient aerosols. We have found that the selected organic acids could account for 14% of the observed m/z 44 signal on average during the measurement period. Oxalic acid (C₂) is the largest contributor, accounting for 10% of the observed m/z 44 signal. The mass spectra of other carboxylic acids, which include monocarboxylic acids (monoacids) and polycarboxylic acids (polyacids), have been investigated in the laboratory. Although these monoacids and polyacids were not measured during the ambient measurement, possible contributions from these compounds are also discussed to explore the missing source of the m/z 44 signal in ambient aerosols.

11A.12

Low-Pressure Chemical Ionization Mass Spectrometry of Ultrafine Aerosols. SONYA C. COLLIER, Angela I. Shibata, Denis J. Phares, University of Southern California.

Chemical analysis of organics requires an ionization mechanism that minimizes the energy transferred to the molecule that may lead to fragmentation. Chemical ionization represents one such "soft" ionization scheme. Maintaining the chemical reaction region at low pressure (1 to 10 Torr) minimizes the ion clustering that occurs at atmospheric pressure, thereby allowing for easier identification of the protonated organic molecule. In this study, we apply low-pressure chemical ionization time-of-flight mass spectrometry to the analysis of ultrafine aerosols. Particles are classified and collected using an inlet that resembles a cylindrical Differential Mobility Analyzer (DMA) in that the sample flow is introduced around the periphery of the annulus between two concentric cylinders, and charged particles migrate inward, depositing on a Nichrome filament. The particles are desorbed, and the resulting vapor is passed into the low-pressure chemical ionization cell. The ions are then focused into an orthogonal extraction TOF mass spectrometer, providing a mass spectrum for the size-resolved aerosol. Results are presented for organic aerosol standards ranging in size from 20 nm to 200 nm.

12A.1

**Bridging the Gap Between Top-Down and Bottom-Up
Characterization of Organic Aerosols.** MURRAY

JOHNSTON, Matthew Dreyfus, Katherine Heaton, Julie Lloyd,
Christopher Zordan, University of Delaware.

Ambient organic aerosol is complex and may contain hundreds or thousands of individual compounds. There are two main ways to handle this complexity: 1) bottom-up, where the distribution of molecular components is measured and properties of the total, \macroscopic\ aerosol are inferred, and 2) top-down, where macroscopic properties are measured and the distribution of molecular components is inferred. Usually, molecular level measurements are performed off-line with low time resolution. An advantage of these measurements is that individual \marker\ compounds can be linked with specific sources, facilitating source apportionment. In contrast, macroscopic measurements are usually performed on-line with high time resolution. Advantages of these measurements are that short term variations can be associated with meteorological conditions or transient events and macroscopic physical properties can be inferred. Bridging these two views and the information they provide requires additional analytical capability, specifically the ability to measure molecular distributions with high time resolution.

Our group has developed an aerosol mass spectrometer that allows molecular distributions to be measured with a time resolution of a few minutes. The current version of the instrument uses photoionization with vacuum ultraviolet radiation to characterize relatively nonpolar, semivolatile components. A new version of the instrument uses chemical ionization and matrix assisted laser desorption ionization to characterize polar and macromolecular components. In either case, rapid changes in the distribution of molecular components can be directly compared with macroscopic chemical measurements such as OC/EC and with meteorological parameters. Our group has also developed an aerosol mass spectrometer that allows the elemental composition of individual particles to be measured with high time resolution. The molecular distribution can be compared with the macroscopic elemental composition, both obtained with high time resolution, to determine how representative the measured molecular distribution is of the total aerosol. Results of laboratory and ambient studies will be discussed.

12A.2

**Tracing the Sources and Transformations of Oxidized
Organic Aerosols in the Atmosphere by Spectroscopic
methods: Results from Functional Group Analysis.** Stefano

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Emanuela Finessi, Italian National Research Council, Italy;
Fabio Moretti, Emilio Tagliavini, Centro Interdipartimentale di
Ricerca per le Scienze Ambientali, University of Bologna, Italy;
also at Department of Chemistry, University of Bologna, Italy.

The recent development of high-time resolution aerosol MS (AMS) techniques has provided a new insight to the sources and transformation of organic aerosols in the atmosphere, by showing that spectral fingerprints can be identified for specific fresh emissions and for processed, chemically aged aerosols. These findings are in substantial agreement with the results of functional group analysis by nuclear magnetic resonance (NMR) spectroscopy, showing that the \bulk\ chemical composition - and not only molecular tracers - can retain information about the sources of aerosol organic compounds. Analogously to the results of AMS measurements, distinct NMR compositions of oxidized organic aerosols can be found for biomass burning emissions and for SOA formation. Moreover, specific spectral fingerprints of fresh biogenic SOA can be extracted from field data collected in clean continental forest sites, and linked to analogous features found for synthetic biogenic SOA formed in smog chambers. Conversely, both AMS and NMR spectral fingerprints of oxidized organic aerosols in polluted environments could not be reproduced by SOA formed in smog chambers experiments employing high concentrations of aromatic hydrocarbons as precursors. NMR functional group compositions deviating from the oxidized organic aerosol types identified by AMS were also observed, especially in the free troposphere at the mid-latitudes in wintertime, and in the marine boundary layer. Finally, NMR analysis shows significant changes in the composition of oxidized organic aerosols in periods of high photochemical activity, that can only partly be attributed to the chemical aging effects - such as the oxidation of carbonyls to carboxyls - already shown in the AMS data record.

12A.3

Secondary Organic Aerosol Formation Through Cloud Processing: Acids and Oligomers from Aqueous

Methylglyoxal Photooxidation. Katye Altieri, Annmarie Carlton, EPA; Yi Tan, Sybil Seitzinger, BARBARA TURPIN, Rutgers University.

There is growing evidence that secondary organic aerosol (SOA) forms through cloud processing. Specifically, organic emissions are oxidized to form water-soluble compounds that partition into cloud water and oxidize further to form low volatility products. These products remain, at least in part, in the particle phase after droplet evaporation, forming SOA (Blando, *Atmos. Environ.*, 2000). This process could help explain the gap (Heald, JGR, 2006) between measured and modeled organic PM in the free troposphere. In-cloud SOA predictions have mostly assumed aqueous oxidation pathways and products (Ervens, JGR, 2004; Lim, *EST*, 2005). Since then, laboratory experiments have verified that low volatility products form from aqueous photooxidation of pyruvic acid and glyoxal (Carlton, *GRL*, 2006; Altieri, *EST*, 2006; Carlton, *Atmos. Environ.*, 2007). Field measurements also provide evidence for in-cloud formation (i.e., of oxalic acid; Crahan, *Atmos. Environ.*, 2004; Sorooshian, JGR, 2006).

In this work, aqueous-phase photooxidation experiments were conducted with methylglyoxal and hydroxyl radical (from the reaction of hydrogen peroxide with UV; 254 nm). Methylglyoxal is a major water-soluble product of gas-phase isoprene oxidation. Precursors and products, analyzed by HPLC, ESI-MS, FT-ICR-MS, and ESI-MS-MS, included pyruvic, acetic, formic, glyoxylic and oxalic acids and oligomers. A modified aqueous-phase reaction mechanism is proposed for methylglyoxal that is consistent with the measured concentration dynamics of products, including pathways leading to the formation of oligomers (i.e., through radical-initiated reactions) and oxalic acid. Oligomeric products have higher molecular weights (m/z 100-500) and somewhat lower organic mass (OM) to organic carbon (OC) ratios (1.6-2.1) than the organic acid products ($OM/OC=2.0-3.8$). Thus we expect the oligomers to be somewhat less hygroscopic than the organic acid products. The ESI-MS-MS fragmentation patterns of the oligomers are consistent with the presence of carboxylic acid functionalities.

12A.4

Comparison of Organic Functional Groups from FTIR and Organic Mass Fragments from AMS at Six North American

Field Studies. LYNN M. RUSSELL, Stefania Gilardoni, Lelia N. Hawkins, Scripps Institution of Oceanography, UCSD; Tim S. Bates, Pacific Marine Environmental Laboratory, NOAA; James D. Allan, University of Manchester; Darrel Baumgardner, National Autonomous University of Mexico; Peter F. DeCarlo, Edward Dunlea, Jose L. Jimenez, University of Colorado at Boulder; Tim B. Onasch, Doug R. Worsnop, Aerodyne Research Inc.

This study compares the organic composition of six different sets of collocated Fourier Transform Infrared (FTIR) spectrometry of bulk submicron particle filter samples and Aerosol Mass Spectrometer (AMS) online size-resolved submicron particle measurements during field projects. The comparison includes about 30 days of data from each of the following six field studies: International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) during July and August 2004 at Chebogue Point and aboard the R/V Ronald Brown, Megacities Impact on Regional and Global Climate (MIRAGE)/Megacity Initiative: Local and Global Research Observations (MILAGRO) during March and April 2006 aboard the NCAR C130, Paso de Cortes during March and April 2006, Intercontinental Chemical Transport Experiment (INTEX-B) during April and May 2006 aboard the NCAR C130, and Texas Air Quality Study / Gulf of Mexico Atmospheric Composition and Climate Study (TEXAQS/GoMACCS) during July and August 2006 aboard the R/V Ronald Brown. The FTIR measures wavelength-dependent carbon bond absorption by transmission to estimate functional group concentrations of aromatic C=C-H, unsaturated aliphatic C=C-H, saturated aliphatic C-C-H, organic hydroxyl O-H, organosulfur C-O-S, and carbonyl C=O using calibrated standards. The AMS measures mass fragments of compounds, including carbon, hydrogen, oxygen and sulfur atoms. The correlations of functional groups with mass fragments that result from the comparison of FTIR and AMS measurements provide enhanced information about the structure of the organic compounds in ambient aerosol particles.

12A.5

Introducing the Concept of Potential Aerosol Mass. Eunha Kang, WILLIAM H. BRUNE, Margaret Root, Pennsylvania State University; Darin Toohey, University of Colorado.

We introduce a new concept: potential aerosol mass (PAM). PAM can be defined as the as the maximum aerosol mass that precursor gases can be oxidized to form particulate matter. This concept has many uses. In the atmosphere, PAM can be used along with chemical measurements in the gas and particle phases to better understand the integrated secondary organic aerosol (SOA) formation and evolution and to test the completeness of the measured SOA sources, aerosol mass yields, and oxidation pathways. When placed in networks, the sum of aerosol mass and PAM can be used to better understand the sources and distribution of SOA. In environmental chambers, it can be used in a variety of ways to understand the behavior and completion of SOA formation and subsequent oxidation.

The PAM measurement consists of passing air containing aerosol-precursor gases through a small chamber that is irradiated with ultraviolet lamps. Rapid and complete oxidation ensues in the extreme oxidizing environment, with measured values of about 10 ppmv of O₃, 100 pptv of OH, and 2 ppbv of HO₂. The airflow exiting the chamber is sufficient that a wide range of detection has been used, including a Tapered Element Oscillating Microbalance (TEOM), an aerosol mass spectrometer (AMS), and a variety of particle sizing instruments.

We present laboratory studies that demonstrate the feasibility of the PAM concept, with emphasis on applications to SOA. These studies include dependence of aerosol mass yields on oxidant levels, relative humidity, and UV light; measurements of aerosol mass yields for several anthropogenic and biogenic hydrocarbons; and the chemical and size evolution of SOA in the PAM chamber. We discuss improvements in the PAM measurement technique that will make it useful for an even wider array of applications.

12A.6

Development and Application of a Soot Particle Mass Spectrometer. Achim Trimborn, DAGMAR TRIMBORN, Timothy Onasch, Manjula Canagaratna, Jesse Kroll, John Jayne, Douglas Worsnop, Aerodyne Research, Inc.; Gregory Kok, Droplet Measurement Technologies.

Black carbon containing aerosols play important roles in governing the optical properties of atmospheric aerosol. Absorption of incident solar radiation by elemental carbon containing aerosol can lead to a cooling effect on the ground, potentially offsetting the warming caused by greenhouse gases. In addition, the absorption can lead to heating of the air mass potentially affecting clouds. An outstanding question is the role of coatings on black carbon cores and how such coatings may alter the optical properties. Instruments like the Single Particle Soot Photometer (SP2) and Photoacoustic Spectrometer (PASS) are well suited to characterize the black carbon content inside internally mixed ambient particles (via incandescence and absorption measurements). However, these instruments lack the capability to measure the chemical composition of absorbed species in or on black carbon cores. We report here a new method for measuring the chemical composition of absorbed inorganic and organic material which is specific only to particles containing black carbon. Black carbon particles absorb and are heated by radiation in the 1 μ m wavelength range. The vaporized constituents are then ionized by electron impact ionization and detected using a time of flight (TOF) mass spectrometric approach. We report a series of measurements which demonstrate the utility of this technique for a variety of particles with and without black carbon cores and with various coatings. These measurements clearly show that the method is highly selective and sensitive only for particles containing an absorbing core. The results also show that the mass spectrometric signals vary linearly with the amount of the condensed species. This allows for the quantification of the chemical composition of this class of particles. Signals for vaporized carbon atom clusters are also observed and current work is aimed at interpreting the significance of these signals.

13A.1

Semivolatile Emissions and the Organic Aerosol Budget.

ALLEN L. ROBINSON, Neil M. Donahue, Carnegie Mellon University.

Sources of primary organic aerosols (POA) such as motor vehicles, wood combustion, and industrial processes emit substantial quantities of semivolatile organics. The amount of primary organic aerosol depends on the gas particle partitioning of this complex mixture. Photochemical aging of these emissions typically creates more polar and less volatile reaction products, generating secondary organic aerosol (SOA).

This talk combines recent field, laboratory, and modeling results to discuss the influence of semivolatile emissions on the organic aerosol budget. Although POA emissions are commonly measured with dilution sampler, these measurements are typically made at low dilution ratios. Measurements with diesel exhaust and woodsmoke indicate that this can substantially bias measured emission factors because aerosol concentrations inside the dilution sampler can be orders of magnitude higher than typical atmospheric conditions. Unfortunately, emission inventories and models currently treat the POA emissions as non-volatile, implicitly assuming that the dilution sampler measurements represent the full range of atmospheric conditions. Accounting for partitioning of POA in chemical transport models dramatically reduces POA concentrations. Smog chamber experiments indicate that semivolatile emissions may be an important source of SOA. Current SOA models do account for some SOA production from low volatility vapors, but these vapors contribute little SOA compared to oxidation products of light aromatics and biogenics. A comparison of emission inventories with partitioning and speciation data indicate that emissions of semivolatile organics are grossly under-represented in the inventories, which have largely been developed for simulating tropospheric ozone. A major challenge is that the vast majority of the low volatility organics cannot be speciated, and instead appear as an unresolved complex mixture. The talk will conclude with a discussion of how the basis set framework can be used to better account for the effects of both gas-particle partitioning and photochemical aging of semivolatile emissions on the organic aerosol budget.

13A.2

Chemical Characterization of Low, Medium, and High Volatility Biogenic Secondary Organic Aerosol Components Using an Aerosol Mass Spectrometer. EVANGELIA

KOSTENIDOU, Spyros N. Pandis, Institute of Chemical Engineering and High Temperature Chemical Processes and also University of Patras; Byong-Hyoek Lee, Gabriella J. Engelhart, Spyros N. Pandis, Carnegie Mellon University.

A thermodenuder operating at temperatures of 25-100°C (An et al., 2007) is used to separate the secondary organic aerosol (SOA) components by volatility. The chemical composition of these components is then measured using an Aerodyne Aerosol Mass Spectrometer (AMS). The SOA is produced in the Carnegie Mellon smog chamber by ozonolysis of alpha pinene, beta pinene and limonene. The mass spectra of the low, medium, and high volatility components are quantified and inter-compared. Experiments are performed at low and intermediate RH and at low and high NO_x conditions. The effect of these conditions on the mass spectra of the corresponding components is quantified. As volatility decreases the normalized organic fragments at m/z = 12, 17, 18 and 44 increase, while those at m/z = 15, 27, 29, 43, 55 and 57 show a decreasing trend.

An approach to deconvolute these spectra according to the volatility basis-set modeling framework is developed and applied to the data set. These AMS spectra of the various SOA components separated by volatility can become valuable tools in linking the smog chamber SOA measurements with field observations of organic aerosol.

Woo Jin An, Ravi K. Pathak, Byong-Hyoek Lee and Spyros N. Pandis (2007). Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol. *Journal of Aerosol Science*, Volume 38, Issue 3, Pages 305-314.

13A.3

Volatility of Primary and Secondary Organic Aerosols: Source and Field Measurements. J. ALEX HUFFMAN, Allison C. Aiken, Ken Docherty, Ingrid Ulbrich, Jose L. Jimenez, University of Colorado at Boulder Jesse Kroll, Timothy Onasch, John T. Jayne, Douglas R. Worsnop, Aerodyne Research, Inc. Paul Ziemann, University of California - Riverside.

The volatility of organic species in atmospheric particles is important for a number of reasons. Models need to properly account for the gas-particle partitioning of organic species in order to predict the organic aerosol (OA) concentrations in the atmosphere. Semi-volatile and intermediate volatility organic compounds (SVOC and IVOC) can react in the atmosphere to produce significant amounts of SOA (Robinson et al, 2007). These species are difficult to measure directly, but their relative amounts can be inferred from the slopes of TD-volatility curves near ambient temperature. Aerosol volatility also plays a large role in both dry deposition and reaction losses, because dry deposition and reactions are both typically faster for species in the gas phase. Finally, knowledge of aerosol volatility allows an estimation of losses of particle species due to ram and cabin heating when sampling into aircraft.

A custom-built fast temperature-stepping thermodenuder (TD) was coupled with an Aerodyne Aerosol Mass Spectrometer (AMS) to allow the study of chemically-resolved volatility in the lab and the field. The TD-AMS system was deployed during field campaigns in Riverside, CA (SOAR-1: July-August, 2005), Mexico City (MILAGRO/MCMA-2006: February 2006). Particles from three additional sources were also characterized: (a) primary biomass burning aerosols at the USDA Fire Sciences Lab in Missoula, MT (FLAME-1: June, 2006), (b) secondary organic aerosols (SOA) from the photochemical reaction chamber at the University of California - Riverside, and (c) primary anthropogenic particles from combustion and meat-cooking sources in Boulder, CO. Urban SOA was less volatile than urban POA. Biomass burning OA exhibited a wide variability in its volatility, but in most cases was of similar or larger volatility than urban POA. In each case of mixed aerosol, the less oxygenated species were shown to evaporate at lower temperatures than the more oxygenated species.

These results contradict the assumptions in almost all current models, which treat primary organic aerosol (POA) from biomass or anthropogenic combustion sources as completely non-volatile, and SOA as quite volatile. The use of a chemical detector after the TD allowed this study to characterize the volatility of bulk OA in ambient air for the first time.

13A.4

Hourly Measurements of Organic Marker Compounds using an In-Situ Thermal desorption Aerosol Gas chromatograph (TAG). BRENT WILLIAMS, Allen Goldstein, University of California Berkeley; Nathan Kreisberg, Susanne Hering, Aerosol Dynamics Inc.; Laura Shields, Kimberly Prather, University of California San Diego.

Thermal desorption Aerosol Gas chromatograph (TAG) is a new in-situ instrument to identify and quantify organic aerosol chemical composition with one hour time resolution. Atmospheric particles are collected by means of humidification and inertial impaction. The sample is then thermally desorbed onto a GC column, where it is separated into individual compounds which are identified and quantified using a quadrupole mass spectrometer (MS) and flame ionization detector (FID). With the exception of periodic manually applied calibration standards, TAG is fully automated, offering around the clock measurements to determine diurnal, weekly, and seasonal patterns in organic aerosol composition.

We report ambient aerosol measurements made in southern California during the 2005 Study of Organic Aerosol at Riverside (SOAR). We use hourly measurements of over 300 individual organic compounds to define both primary and secondary particle sources. The compound classes include alkanes, branched alkanes, alkenes, PAHs, branched PAHs, acids, ketones, aldehydes, phthalates, furanones, terpenes, nitrogen containing organics, sulfur containing organics, chlorine containing organics, phosphorous containing organics, and more. The particle sources defined include primary anthropogenic sources such as vehicle emissions, meat cooking, biomass burning, pesticide use, herbicide use, along with primary biogenic sources such as plant emissions and plant waxes. We also explore secondary particle sources (i.e. SOA) formed as a result of the oxidation of biogenic and anthropogenic precursor gases. These sources are then compared with similar sources independently defined by ATOFMS single particle measurements. Finally, we present ambient air observations of gas-particle phase partitioning as a function of molecular size and functional groups.

13A.5

Biomass Burning and Pollution Aerosol over North America: Organic Components and their influence on Spectral Optical Properties and Humidification Response.

ANTONY CLARKE, Cameron McNaughton, Vladimir Kapustin, Yohei Shinozuka, Steven Howell, Jingchuan Zhou, Vera Brekhovskikh, Mitchell Pinkerton, University of Hawaii; Jack Dibb, University of New Hampshire; Bruce Anderson NASA-LaRC; Harold Turner; University of Alabama.

Thermal analysis of aerosol size distributions provided size resolved volatility up to temperatures of 400C during extensive flights over North America (NA) for the INTEX/ICARTT experiment in summer 2004. Biomass burning and pollution plumes identified from trace gas measurements were evaluated for their aerosol physio-chemical and optical signatures. Measurements of soluble ionic mass and refractory black carbon (BC) mass, inferred from light-absorption, were combined with volatility to identify organic carbon at 400C (VolatileOC) and the residual or refractory organic carbon, RefractoryOC. This approach characterized distinct constituent mass fractions present in biomass burning and pollution plumes every 5-10 minutes. Biomass burning, pollution and dust aerosol could be stratified by their combined spectral scattering and absorption properties. The \non-plume\ regional aerosol exhibited properties dominated by pollution characteristics near the surface and biomass burning aloft.

VolatileOC included most water-soluble organic carbon. RefractoryOC dominated enhanced shortwave absorption in plumes from Alaskan and Canadian forest fires. The mass absorption efficiency of this RefractoryOC was about 0.63 m²g⁻¹ at 470 nm and 0.09 m²g⁻¹ at 530nm. Concurrent measurements of the humidity dependence of scattering, gamma, revealed the OC component to be only weakly hygroscopic resulting in a general decrease in gamma with increasing OC mass fractions. Under ambient humidity conditions, the systematic relations between physio-chemical properties and gamma lead to a simple dependency on the absorption per unit dry mass for these plume types that may be used to challenge remotely sensed and modeled optical properties.

13A.6

Investigating the Volatility of SOA in Different Urban

Environments. CHRISTOPHER J. HENNIGAN, Amy P. Sullivan, Richard E. Peltier, Rodney J. Weber, Christos Fountoukis, Athanasios Nenes, Georgia Institute of Technology; Delphine Farmer, Paul J. Wooldridge, Ronald C. Cohen, University of California, Berkeley.

The formation of secondary organic aerosol (SOA) remains a poorly understood area of aerosol science. Current theory on SOA formation suggests that volatile organic carbon compounds (VOC's) in the gas phase undergo oxidation in the atmosphere to form gaseous products that are less volatile than the parent compounds (i.e., the vapor pressures of the product compounds are lower than those of the parent compounds). The oxidation products can, if equilibrium conditions exist, partition to the particle phase through a sorption process. SOA volatility is important because it may provide insight into the chemical nature of SOA, as well as information about the formation mechanisms and precursors. In this study, using water-soluble organic compounds (WSOC) in fine particles as a measure of SOA, the volatile nature of SOA has been investigated in two different urban environments. VOC emissions in the Mexico City Metropolitan Area (MCMA) are dominated by local anthropogenic sources (predominantly mobile sources) while VOC emissions in Atlanta, GA are a mix of anthropogenic emissions and a regional biogenic source. Using a combination of aerosol composition measurements (both organic and inorganic), the ISORROPIA aerosol thermodynamic equilibrium model, and the application of a thermal denuder, we investigate the volatility of SOA in two urban environments with predominantly different sources.

14A.1

Measurements and Interpretation of the Effect of Soluble Organic Surfactants on the Density, Shape and Water Uptake of Hygroscopic Particles. ALLA ZELENYUK, Pacific Northwest National Laboratory; Dan Imre, Imre Consulting; Luis A. Cuadra-Rodriguez, Barney Ellison, University of Colorado at Boulder.

A large fraction of atmospheric particles are composed of hygroscopic salts that are mixed with variety of organic molecules, of which surfactants represent an important class. Because of the tendency of surfactant molecules to coat the particles' surfaces, a monolayer might be sufficient to drastically alter particle hygroscopic properties, their CCN activity, and reactivity. Moreover, because the aliphatic chains are exposed to the oxidizing atmosphere they are expected to be transformed through heterogeneous chemistry, yielding complex products with mixed properties. Given the important role that is played by the interaction of particles with the ambient relative humidity it is critical to develop an understanding of the impact surfactants may exert on particle hygroscopic properties. We will report the results from a series of observations on ammonium sulfate, sodium nitrate, sodium chloride and sea salt particles coated with two types of soluble surfactant molecules: sodium dodecyl sulfate and sodium oleate. We have been able to measure the effective densities and hygroscopic growth factors of internally mixed particles with a range of surfactant concentrations that start below a monolayer and extend all the way to particles composed of pure surfactant. For many of the measurements the data reveal a rather complex picture that cannot be simply interpreted in terms of the known pure-compound densities and growth factors. We show that the observed particle density provides evidence that the density of the surfactant fraction changes with concentration and that once this is properly taken into account the water uptake data can be quantitatively understood. For unsaturated hydrocarbons we observed and quantified the effect of oxidation by ozone on particle size, effective density, hygroscopic growth factor and individual particle mass spectral signatures.

14A.2

Evolution of SOA Mass Spectra from Photo-oxidation of Diesel Exhaust. AMY M. SAGE, Emily A Weitkamp, Allen L. Robinson, Neil M. Donahue, Carnegie Mellon University.

Regional chemistry models predicated on laboratory yield curves significantly underpredict the particle-forming capacity of aging urban air masses. The high-flux, volatile organic compounds included in these models cannot account for the large quantities of organic material that condense downwind of anthropogenic sources. Furthermore, the mass spectra of laboratory-generated SOA from traditional precursors do not agree with those observed in aged air masses. Atmospheric abundance is not the sole criterion for identifying SOA precursors. We have suggested that precursor vapor pressure also plays an important role, and we have used the large suite of semi-volatile compounds emitted by combustion sources to test this hypothesis.

UV-initiated oxidation chemistry of diesel exhaust carried out in our environmental chamber results in significant particle growth after illumination. We calculate that the mass formed exceeds that expected from known precursors by a factor of ten. Here we wish to explicitly consider the chemical nature of the SOA that is formed. To that end, the composition of suspended particulate matter was monitored throughout several experiments using a Q-AMS

Using the known mass spectrum of the primary emissions recorded prior to illumination, we can confidently subtract the primary contribution from the total spectrum. The resulting residual spectrum reveals the chemical transformations occurring in the condensed phase as SOA is formed. Our analyses show that the chemical composition of the SOA that is formed is not constant over time. As SOA continues to form, signal in the residual mass spectrum shifts from larger masses ($m/z < 70$) to smaller, oxygen-containing fragments, suggesting that later-forming SOA must be more functionalized before it can condense. After four to five hours of oxidation, we produce aged organic aerosol whose spectrum matches well with ambient observations.

14A.3

HR-ToF-AMS Study of the Yield and Chemical Composition of alpha-Pinene SOA as a Function of Organic Particulate Loading. JOHN SHILLING, Qi Chen, Stephanie King, Thomas Rosenoern, Scot Martin, Harvard University; Jesse Kroll, Douglas Worsnop; Aerodyne Research Inc.; Peter DeCarlo, Allison C. Aiken, Donna Sueper, Jose L. Jimenez, University of Colorado and CIRES.

Recent reports in the literature indicate that models invoking equilibrium partitioning of semivolatile VOC oxidation products into the organic phase are unable to reproduce measured SOA concentrations. This discrepancy between the modeled and measured data demonstrates that the chemical pathways responsible for SOA formation are poorly understood. In an effort to elucidate these pathways, the Harvard Environmental Chamber has been used to generate secondary organic aerosol (SOA) from the ozonolysis of alpha-pinene. The total organic loading was varied by changing the alpha-pinene concentration from 1 - 100 ppbv while holding all other reaction conditions constant. An Aerodyne HR-ToF-AMS was employed to determine the yield and chemical composition of the alpha-pinene SOA as a function of particulate loading.

The yield of SOA from this reaction agrees with previous measurements at the highest particulate loadings studied. However, at low particulate loading, yields were higher than previously reported. Revised yield measurements can help interpret the discrepancy between measured and modeled atmospheric SOA levels.

HR-ToF-AMS results indicate that the chemical composition of the aerosol is a strong function of the organic particulate loading. The spectra show that SOA produced from alpha-pinene ozonolysis is significantly more oxygenated under atmospherically relevant organic loadings than previously reported. Analysis of the high-resolution data shows that the fraction of oxygenated organic compounds ($C_xH_yO_z$) in the SOA increased at the expense of hydrocarbon-like compounds (C_xH_y) as the total loading decreased. The carbon-to-oxygen ratio of the organic material was also determined and decreased with loading. Oligomeric material was observed in the SOA, even at the lowest organic loadings. Furthermore, oligomers composed an increasing fraction of the total organic material as loading decreased. A mechanism for the polymerization of organic material was developed based on the mass spectra. These results significantly advance the understanding of SOA formation and partitioning.

14A.4

Incorporating GCxGC-TOFMS Information on Compositional Complexity of Chamber-Derived Aerosol in Models of Secondary Organic Aerosol (SOA) Formation and Aging. KELLEY BARSANTI, James Smith, National Center for Atmospheric Research; James Pankow, Oregon Health & Science University.

Achieving a quantitative understanding of the formation and aging of secondary organic aerosol (SOA) remains a considerable challenge for the accurate prediction of organic particulate matter (OPM) levels in the atmosphere. Currently, most large scale SOA models assume two products (2p) per parent hydrocarbon (HC); when N parent HCs are present, this is denoted here as the N-2p approach. Recent studies have shown that the N-2p approach leads to significant underprediction of atmospheric OPM levels. At least some portion of this problem is due to failure of the N-2p approach to adequately represent the complex mixture of condensable products that can form from a given parent HC, and the aging processes affecting those products. SOA models are needed that consider: a) the time dependence in the number of products that form from a particular parent HC; b) the time-dependent properties of the products (e. g., increasing polarity due to continued oxidation and/or fragmentation); and c) the formation of essentially non-volatile polymeric material by accretion reactions. Chamber experiments have been conducted using atmospherically relevant levels of parent HCs from live trees under a range of conditions. OPM was analyzed using a Pegasus 4D two-dimensional gas chromatograph/time-of-flight mass spectrometer (GCxGC-TOFMS). GCxGC-TOFMS is well-suited for determining polarity and composition (on a functional-group level) of complex mixtures. Approaches for and implications from porting composition data from chamber-based GCxGC-TOFMS analyses to higher-order, time-dependent SOA models will be discussed.

14A.5

Oxygenated Organic Aerosols: Bridging Field and Smog Chamber Observations Using an Aerodyne Aerosol Mass Spectrometer. M.RAMI ALFARRA, Andre S.H. Prevot, Jonathan Duplissy, Axel Metzger, Josef Dommen, Ernest Weingartner, Urs Baltensperger, Laboratory of Atmospheric Chemistry, Paul Scherrer Institut; Valentin A. Lanz, Christoph Hueglin, Empa, Swiss Federal Laboratories for Materials Testing and Research.

Two types of oxygenated organic aerosols (OOA I and OOA II) have recently been identified at urban locations in Europe and North America using the Aerodyne Mass Spectrometer (Q-AMS) based on multivariate statistical analysis methods. During a summer study in Zurich, Switzerland, OOA I was characterised by a relatively high m/z 44 to total organic ratio and it had a mass spectral signature similar to that of fulvic acid. It was also found to have a similar temporal behaviour to the sulphate component of the aerosols. On the other hand, OOA II was found to be less aged than OOA I and it was characterised by a relatively high m/z 43 to total organic ratio. It also had a similar temporal behaviour to the nitrate component of the aerosol and it was sensitive to ambient temperature (i.e. more volatile than OOA I). In this paper, we investigate the chemical composition of secondary organic aerosol (SOA) generated in a smog chamber from the photooxidation of the biogenic precursor (alpha-pinene) and compare it to the ambient spectra of OOA I and OOA II. In particular, we present results showing the effect of the initial precursor concentration on the mass spectral signature of the SOA produced and on its chemical and physical properties. This work represents a direct application attempt of the AMS to bridge the gap between field measurements and smog chamber experiments with the aim of achieving an improved understanding of SOA formation and transformation in the atmosphere.

14A.6

TBA

16A.1

Emissions and Secondary Formation of Organic Aerosols in the Polluted Atmosphere: New Results from the Northeastern U.S. in 2004 and Texas in 2006. JOOST DE GOUW, Charles Brock, Ann Middlebrook, NOAA Earth System Research Laboratory and CIRES, University of Colorado; Rodney Weber, Georgia Institute of Technology; Tim Bates, NOAA Pacific Marine Environmental Laboratory.

We analyzed airborne measurements of water-soluble organic carbon (WSOC) and ship-based measurements of organic aerosols (OA) in urban plumes in the northeastern U.S. in 2004. A strong growth in secondary organic aerosols (SOA) was observed in urban plumes in the first 24 hour after emission that cannot be explained from the measured volatile organic compound (VOC) precursors, in agreement with the findings from multiple recent studies. The reasons for this discrepancy are discussed and include (i) formation of SOA from lesser-volatile precursors that are not captured by current VOC measurements, (ii) higher SOA yields than smog-chamber studies indicate, and (iii) enhanced formation of biogenic VOCs in urban plumes. A parameterization is derived that explains a large part of the observed variability in WSOC and OA based on measured mixing ratios of carbon monoxide (CO) and the transport or photochemical age of the sampled air masses. Results from the Texas Air Quality Study (TexAQS) in the summer of 2006 provide an interesting test case for these concepts, because the VOC-NO_x-CO composition of industrial plumes in Texas is markedly different from that of an urban plume. Some initial results from organic aerosol measurements during TexAQS will be presented and discussed in the framework of the findings from the northeastern U.S.

16A.2

Assessing Secondary Organic Aerosol Using Online Aerosol Mass Spectrometry. James Allan, Keith Bower, Gerard Capes, HUGH COE, Jonathan Crosier, Paul Williams, University of Manchester, UK.

The talk will utilise recent measurements made using the Aerodyne Aerosol Mass Spectrometer to provide evidence for the behaviour of secondary aerosol in a range of environments. Several major field campaigns have taken place in the last few years around Europe: in the UK, in the Adriatic region and the Po Valley; and also in West Africa during AMMA. Oxygenated organic aerosol is a major component of the submicron mass of aerosols in all these regions and in the polluted northern hemisphere its mass has been shown to be greatly underpredicted by models compared to recent measurements.

During the African Monsoon Multidimensional Analysis (AMMA) project, the UK BAe 146 aircraft flew a series of missions across the West African region in both the dry season and the summertime monsoon. In the dry season biomass burning aerosol were ubiquitous throughout the region, at times mixing with the dust layers observed. Evidence is presented for the spatial extent of the biomass burning aerosol and it is shown that there does not appear to be significant formation of secondary organic mass with age, unlike the situation in continental polluted environments. However, there is evidence for a change in the chemical functionality of the organic biomass burning aerosols with marker compounds such as levoglucosan being preferentially removed and more oxygenated multi-functional moieties increasing with time. In the summertime, the measured organic aerosol loading is close to the detection limit of the instrument. However, the concentrations observed appear to be consistent with model estimates of secondary organic aerosol mass in these regions. This contrasts markedly with polluted northern hemispheres where similar models, based on adsorptive partitioning schemes, greatly underpredict the SOA. The contrast between northern continental mid-latitudes and tropical forests will be highlighted and discussed.

16A.3

Measurements of the Composition of 6 - 30 nm Diameter Biogenic Secondary Organic Aerosols using Thermal Desorption Chemical Ionization Mass Spectrometry.

JAMES SMITH, Jeff Rathbone, National Center for Atmospheric Research; Markku Kulmala, University of Helsinki; Peter McMurry, University of Minnesota.

We report measurements of the molecular composition of 6 - 30 nm diameter atmospheric aerosols performed using the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) at two sites that are dominated by biogenic emissions. The first of these measurements was performed in July 2006 during the CELTIC-Niwot Ridge study, in a subalpine forest located 35 km west of Boulder, Colorado. The second set of measurements was performed during the EUCAARI07 campaign in the Boreal forest in Hyytiala, Finland from 15 April - 30 June 2007. Both sets of measurements indicate a dominant role played by organic species in the formation of atmospheric nanoparticles. Positive ion TDCIMS measurements at both sites show the presence of methyl and dimethyl amines in particles as small as 8 nm. Other oxidized organics detected in positive ion TDCIMS measurements are presumed to be alcohols, aldehydes, or ketones with molecular weights as high as 400 amu. Negative ion TDCIMS measurements show the presence of multifunctional organics with carboxylic acid moieties, with molecular weights as high as 400 amu. The evolution of chemical composition of 6 - 30 nm diameter particles will also be presented in the transition from Spring to Summer in Hyytiala. Changes in composition during early particle growth will also be explored.

16A.4

The search for marine organic aerosols. JAMES ALLAN, Jonathan Crosier, Paul Williams, Keith Bower, Nick Good, Martin Irwin, Gordon McFiggans, Michael Flynn, David Topping, Hugh Coe, University of Manchester, UK.

Understanding the composition of marine aerosols is vitally important, as oceans cover the majority of the earth's surface and are known to be a large source of particles, representing a large but relatively poorly understood factor in radiation budgets through the direct and indirect radiative effects. There is currently mounting evidence for the presence of an organic component of the submicron aerosol, linked with phytoplankton activity, in addition to the known sea salt and sulphate components. The effect of this fraction is potentially hugely significant, as organic matter is known to drastically perturb the cloud activation behaviour of particles, through the reduction of solubility and surface tension, although this is highly dependent on the precise concentrations and mixing states of the components and the size of the particles. Developments in the field of in situ aerosol instrumentation are currently helping to address these issues through the online measurement of composition, size and hygroscopic behaviour in both sub- and super-saturated conditions. Aerosol measurements using instruments such as Aerosol Mass Spectrometers, CCN counters and Hygroscopicity Tandem DMAs from four recent field campaigns in various remote Atlantic locations (on both ground- and ship-based platforms) will be presented, and ongoing work to model the potential implications this fraction will have on cloud formation will be discussed.

16A.5

Exploring the Magnitude and Formation Mechanism of Above-Cloud Organic Layers. SHANE MURPHY, Armin Sorooshian, Harmony Gates, Richard C. Flagan, John H. Seinfeld, California Institute of Technology; Graham Feingold, National Oceanic and Atmospheric Administration; Hafliði Jonsson, Naval Postgraduate School.

Recent field measurements indicate that there is more organic aerosol in the free troposphere than previously thought. Because of the potential impacts on global climate, both through direct and indirect radiative effects, it is important to determine the source and prevalence of this organic aerosol. Cloud processing is one potential pathway that could lead to the formation of organic aerosol in the troposphere above the boundary layer. However, few in situ, chemically-resolved measurements of cloud-processed aerosol are available.

A compact time of flight Aerodyne aerosol mass spectrometer (cToF-AMS) was deployed for the first time on an airborne platform (CIRPAS Twin Otter) off the coast of California near Monterey in July of 2005 and then again in Houston, TX during August, 2006. The high sensitivity of the cToF-AMS enables us to obtain size resolved aerosol mass spectra on a 15 second timescale and non-size resolved spectra on a 2 second timescale. These fast chemical data, in conjunction with the use of a counterflow virtual impactor (CVI), allow us to track the chemical transformation of aerosol particles within a cloud.

We have observed organic aerosol layers above marine stratocumulus clouds off the coast of California and above continental cumulus near Houston. Measurements of the size distribution and chemical composition of below cloud aerosol together with in-cloud measurements of droplet residual chemistry indicate that most of the above-cloud organic aerosol is distinctly different from aerosol that has been transported through the clouds. By monitoring the chemical evolution of aerosol traveling through the clouds, we conclude that there must be another mechanism other than cloud processing acting to form the observed organic layers.

16A.6

A Study on the Sources and Chemical Processes of Organic Aerosol at the Whistler Summit with a High-Resolution Time-of-Flight Aerosol Mass Spectrometer. QI ZHANG, Yele Sun, State University of New York, University at Albany, NY; Richard Leaitch, Anne Marie Macdonald, Kathy Hayden, Shao-Meng Li, John Liggio, Peter Liu, Environment Canada; Aaron van Donkelaar, Randall Martin, Dalhousie University; Douglas Worsnop, Aerodyne Research, Inc.; Michael Cubison, University of Colorado-Boulder, Colorado,

A new Time-of-Flight Aerosol Mass Spectrometer with a high mass resolution of ~ 5000 (HR-ToF-AMS; DeCarlo et al., *Anal. Chem.*, 2006) was deployed at the summit of the Whistler Mountain, British Columbia, from April 20 to May 17, 2006. With this instrument, we determined the concentration, composition, and chemically speciated size distributions of submicron particles (approximately PM₁) every 5 minutes. We also obtained the highly m/z -resolved mass spectra, based on which the elemental composition of most small ion fragments ($m/z < 100$ amu) was quantitatively determined. This improved chemical characterization of organic aerosol mass spectra significantly enhances our ability to address the sources and processes of organic aerosol. Organic aerosol (OA) prevailed at the Whistler summit (elev. ~ 2200 m), accounting for $\sim 50\%$ of the total PM₁ mass. The OA appeared to be highly aged and was composed almost completely of oxygenated organic aerosol (OOA). Sulfate aerosol was usually less abundant than the OA but episodes of strongly enhanced sulfate aerosol were observed. A major sulfate episode occurred on May 15, 2006, during which ammonium sulfate contributed $> 90\%$ of the total PM₁ mass. This episode lasted for ~ 0.5 day and was followed by a high organic aerosol episode. The mass spectra reveal that the organic aerosol is more highly oxidized during the sulfate period. Also, the high resolution mass spectra indicate significant structure difference in organic species between these two episodes. Simulations from a global model of oxidant-aerosol chemistry (GEOS-Chem), backtrajectory analysis, evolution of the size distribution of aerosol species, and correlation of the Whistler aerosol spectrum with previous AMS measurements in rural British Columbia, and in Asia provides supporting evidence of Asian influence during the high sulfate period, in contrast with regional influence during the high organic period.