A21E-1032 0830h POSTER

Photoacoustic Spectroscopic Measurements on Super-saturated Water Vapor

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During the intense debate that followed the discovery, a few year ago, that the atmosphere was absorbing more of the short wave solar radiation than originally allowed in the models, a suggestion was made that the shortwave absorption of water vapor be examined under thermodynamic conditions of saturation and super-saturation. In order to address this concern we devised a photoacoustic absorption chamber in which super-saturated water vapor could be carefully controlled and its short-wave spectrum recorded using photo-acoustic spectroscopy. We present the final results of our experimental study, which was conducted at levels S of super-saturation as high as 1.3, and discuss its implications on the atmospheric application.

A21E-1033 0830h POSTER

Black carbon in snow from the Tian Shan Mountains, Northwest China

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Black carbon aerosols, produced solely by combustion processes, may have a larger associated climate forcing than methane gas and have been implicated in changes to precipitation over China. Yet very little is known regarding the atmospheric distribution or deposition of black carbon, particularly over remote Central Asia. During 2002, snow pit and preindustrial ice samples were collected from Glacier no. 1 and Glacier no. 51 in the Tian Shan Mountains of Northwest China and analyzed for black carbon particles by thermal-optical analysis. Snow concentrations of black carbon at Glacier no.1 were found to be significantly greater than that of Glacier no. 51 and varied at both sites on a seasonal basis. The levels of black carbon in snow from Glacier no. 51 are believed to reflect regional atmospheric concentrations of carbonaceous aerosol, while snow from Glacier no. 1 appears to be impacted by local emissions. Preliminary results from preindustrial ice collected at Glacier no.1 suggest that carbonaceous p

A21E-1034 0830h POSTER

Scale Invariance of Precipitable Water Vapor in the Arctic From Ground-Based Radiometric Measurements

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This study gives a first assessment of the usefulness of Millimeter-wave Radiometer (MIR) brightness temperature measurements for studying the scale invariance in atmospheric Precipitable Water Vapor (PWV) and Liquid Water Path (LWP) distributions in the Arctic. It is shown that MIR data display well defined scaling properties at frequencies close to 183.3 and 89 GHz during both clear-sky and cloudy conditions for horizontal scales between 350 m and 350 km. The turbulent variability of PWV and LWP, in the extremely dry arctic environment, is characterized using three mathematical techniques involving increasingly higher statistical moments. The first technique is the Detrended Fluctuation Analysis from which one can determine the existence of long-range correlations and the Hurst exponent H for the time series. Then, spectral analysis, that is a second order statistics and relies on the assumption of a Gaussian distribution, is performed on the time series data to explore scaling properties through the spectral exponent b. Lastly, a multiplicative cascade model is applied to millimeter-wave measurements to describe intermittency features characteristic of non-homogeneous turbulent fields. The results for LWP during cloudy days are in excellent agreement with previous studies conducted in different environmental conditions giving H = 0.33 and b = 1.61. PWV data during clear sky days have a slightly higher average Hurst exponent and spectral exponent (H=0.57, b = 1.89). Both PWV and LWP have similar intermittency parameter: C1 0.1 and C1 0.06 respectively. The analysis shows that intermittency is an important feature of arctic water vapor variability that can not be captured by a second order statistics such as spectral analysis. Therefore water vapor should not be regarded as a passive scalar subject to homogeneous turbulence. Instead, it should be treated as a randomly advected tracer that presents a multifractal (anomalous) scaling. In the present experiment the data could be well fitted using a universal log-Levy cascade generator. These experimental results can be used to validate theoretical models describing the transport of water vapor at higher latitudes.

A21F MCC: 3016 Tuesday 1020h

Biogenic Reactive Trace Compounds and Their Role in Atmospheric Chemistry and Climate II *(joint with B, OS)*

Presiding: **R Koppmann,** Institut für Chemie und Dynamik der Geosphare Juelich**; P S Stevens,** Indiana University

A21F-01 1020h

Forest Thinning Dramatically Enhances Ozone Flux due to Reactions With Elevated Emissions of Biogenic Hydrocarbons

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Forests are routinely managed for timber production and fire suppression by thinning and harvesting. The impact of these activities on biosphere-atmosphere exchange of reactive trace gases is profound, but has rarely been studied in the field. Here we present simultaneous observations of ozone and terpene fluxes before, during, and after pre-commercial thinning of a ponderosa pine plantation at Blodgett Forest (1300 m elevation on the western slope of the Sierra Nevada Mountains, CA). We previously reported that monoterpene emissions increased by an order of magnitude during and following forest thinning (Schade and Goldstein, GRL 2003). We also previously reported that half the daytime ozone flux to this ecosystem under normal summertime conditions (no disturbance) was due to gas-phase chemical loss, and we suggested that this ozone loss was occurring by reactions with biogenically emitted terpenes whose lifetime was short enough that they reacted before escaping the forest canopy (Kurpius and Goldstein, GRL 2003). Here we report that ozone loss was also dramatically enhanced during and following thinning, and we link these observations to confirm that the chemical ozone loss in the canopy was indeed due to reaction with biogenically emitted compounds whose emission was enhanced by disturbance. Based on the magnitudes of ozone flux due to chemical loss and the measured terpene fluxes, we infer that the emissions of previously undetected short-lived terpenes are approximately 15-20 times those of a-pinene during thinning, and 30-50 times those of a-pinene during summer and fall. Since a-pinene accounts for approximately 25% of the total monoterpenes we routinely measure with our automated in-situ GC instrumentation, we conclude that emissions of highly reactive terpenoid compounds could have been drastically under measured in previous field campaigns and that emissions of unidentified reactive terpenes could be 5-10 times larger than emissions of total terpenes documented in previous studies.

A21F-02 1035h

Ozone Oxidation of Monoterpenes, Sesquiterpenes, and Oxygenated Terpenes: Product Yields and Relevance to Field Observations and Atmospheric Chemistry

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Measurements conducted in a ponderosa pine plantation in the Sierra Nevada, CA have shown that the reaction of ozone with gas-phase compounds dominates summertime ozone deposition to the ecosystem, with an exponential dependence on temperature that is similar to monoterpene emissions. Monoterpene fluxes measured above the forest canopy represent the monoterpenes that have effectively "escaped" the canopy, whereas measurements of ozone deposition due to chemistry provide an estimate of the compounds "missing" from the ecosystem scale flux due to within-canopy reactions with ozone. To be lost within the canopy, these "missing" compounds must have short lifetimes, on the order of a few minutes, compared to those that escape. Longer-lived, less reactive terpenes are widely measured, and are typically the compounds included in global inventories to assess impacts of biogenic emissions on tropospheric ozone production and secondary organic aerosol formation. The shorter-lived, highly reactive terpenes, however, are more difficult to observe and rarely measured, and thus the impacts of these compounds are likely inadequately represented. To better characterize the ozone-initiated oxidation of a range of terpenes, including those that escape the forest canopy and those oxidized within the canopy, we conducted laboratory measurements at the Caltech Indoor Chamber Facility to characterize the gas and particle phase yields from terpene + ozone reactions. These measurements were made to provide a guide to the oxidation products we expect to observe within a forest canopy, and to expand the knowledge of the impacts of these terpenes (both "missing" and "escaped") on atmospheric chemistry. The terpenes studied included several monoterpenes: α- and β-pinene, α-terpinene, terpinolene, myrcene, and 3-carene, two sesquiterpenes: β-caryophyllene and α-humulene, and two oxygenated terpenes: linalool and methyl chavicol, many of which have been observed at our field site. The terpenes were each reacted singly with ozone, in the dark, in the presence of ammonium sulfate seed aerosol and an OH scavenger. A Proton Transfer Reaction Mass Spectrometer was used to measure the gas-phase yields of many low molecular weight oxidation products, including formaldehyde, acetaldehyde, formic acid, acetic acid, and acetone, as well as yields of larger oxidation products, including nopinone, pinonaldehyde, and many currently unidentified compounds which were observed according to their mass to charge ratios. Secondary organic aerosol yields, and yields of small carbonyls and larger oxidation products varied widely between the different terpene species tested. In general, terpenes with high aerosol yields had low yields of small carbonyls, including the sesquiterpenes and α-terpinene, while terpenes with low aerosol yields had high yields of small carbonyls, including linalool, methyl chavicol, myrcene, and terpinolene.

A21F-03 1050h

Large vertical gradients indicate emission, photochemical production, deposition, or a combination for a wide variety of organic trace gases in a Ponderosa Pine plantation in the Sierra Nevada Mountains of California

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We measured vertical gradients for a wide suite of volatile organic compounds (VOCs) through the forest canopy at the Blodgett Forest Research Station (38.88N, 120.62W, 1315m elevation) during summer 2003 using a PTR-MS. The sampling height was switched between 1.1, 3.1, 4.9, 8.75, and 12.5 m above the ground at 6 minute intervals, and mass to charge ratios ranging from 20 to 205 were recorded. The ability of the PTR-MS to achieve high time resolution, low detection limits (few ppt for averaged data), and whole air measurements without preconcentration allowed us to measure gradients for compounds that cannot be measured easily with other techniques. Significant gradients were observed for many compounds. Monoterpene and sesquiterpene emissions from the plants caused mixing ratios that were typically 2-3 times higher below the canopy than above, and our data did not show evidence for soil deposition of these compounds. Methanol mixing ratios were highest at the lowest level (1.1m) indicating that much of the methanol is released from or near the soil. Gradients with the highest mixing ratio above the forest and lowest near the ground indicated persistent deposition for mass 42 (acetonitrile) and mass 71 (MVK+MACR); compounds that are predominantly transported to the local ecosystem. Mixing ratios of several compounds were highest at levels within the canopy and significantly lower above and below. This pattern is indicative of compounds that are emitted or photochemically produced in the canopy whose photochemical lifetime is so short that they are removed before being mixed down to the ground (few minutes) and/or they are efficiently deposited to the soil. Many of these compounds were so far identified only by their mass to charge ratio and their identity has not been conclusively determined. Concentrations of compounds emitted as a function of light and temperature by Ponderosa Pine tended to be highest at the 3.1m level during the day; thereby showing that the emission rates were highest around this elevation; among those compounds is MBO. For one week every month we measured direct plant emissions with a branch enclosure in order to determine which compounds were emitted directly from the plants and which were photochemically produced.

A21F-04 1105h

An overview of the 2003 Chemical Emission, Loss, Transformation and Interactions within Canopies (CELTIC) study

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The Chemical Emission, Loss, Transformation and Interactions within Canopies (CELTIC) study was conducted from June 30 to July 25, 2003 at the Duke Forest FACTS-1 Site. The primary objective of CELTIC is to improve our ability to predict regional air quality (e.g., particulates and ozone) and climate through a quantitative understanding of the processes controlling the exchange of trace gases and aerosols between the atmosphere and vegetation canopies. CELTIC researchers used an unprecedented array of enclosure and whole canopy trace gas and aerosol measurement systems to compile a unique database that is being used to develop and evaluate models of biosphere-atmosphere chemical exchange. Analytical systems included twelve real-time, fast-response and continuous analyzers capable of quantifying key trace gases (>10 VOC species, NH3, PANs, NOy, CO2) and CCN and total particle numbers and chemical composition. The measurements demonstrate that our current understanding of the controlling biological, chemical and physical factors is limited and that current models are not able to accurately simulate observed biosphere-atmosphere exchange of trace gases and particles. Leaf, branch and soil enclosure systems characterized the response of isoprene, monoterpenes, sesquiterpenes, oxygenated VOC, ozone and NOx emission and uptake to changes in chemical (e.g., ozone and CO2) and physical (e.g., temperature, light, soil moisture) conditions. Major findings include observations that 1) isoprene emission increases with elevated ozone, 2) canopy scale isoprene emission increases with elevated CO2, 3) soil and leaf litter are a net sink of oxygenated VOC, and 4) sesquiterpene emissions may be higher than monoterpene emissions under certain environmental conditions. Above canopy fluxes and within canopy vertical profiling systems characterized variations in trace gases (isoprene, monoterpenes, oxygenated VOC, NOx, ozone, CO2, PANs, NH3), particles (numbers, size distribution, chemical composition, CCN) and physical environment (JNO2, UV-B, PAR, temperature, humidity, winds, turbulence). The results include the first above canopy flux measurements of PANs and the chemical components of particles.

URL: http://www.acd.ucar.edu/celtic

A21F-05 1120h

Field Observations of Increased Isoprene Emissions Under Ozone Fumigation: Implications for Tropospheric Chemistry?

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Isoprene is the most abundant biogenic hydrocarbon released from vegetation and plays a key role in the chemistry of the lower atmosphere. Isoprene is produced and emitted by many plant species, yet the reason plants produce this seemingly wasteful carbon compound is still in debate in the plant physiology community. It has been proposed that isoprene may protect plant leaves from thermal damage or damage from oxidant exposure by stabilizing cellular and chloroplast membranes or by direct reactions between exogenous isoprene and oxidative species. As part of the Chemical Emission, Loss, Transformation and Interactions within Canopies (CELTIC) study held at Duke Forest during the summer of 2003, we used dynamic cuvette systems to fumigate leaves of sweet gum (*Liquidambar styraciflua*) with ozone at partial pressures ranging from 0 to 300 ppbv. During fumigations, the effluent air was monitored using infrared gas analysis, on-line proton-transfer-reaction mass spectrometry (PTR-MS) and gas chromatography to quantify changes in partial pressure of CO_2, water vapor, isoprene and other volatile organics. At fumigations above 100 ppbv ozone, leaf-isoprene emission increased 20-35% compared to pre-fumigation. To our knowledge, this is the first reported observation of increased isoprene emission under ozone fumigation. Over the timescale of our measurements (several hours), isoprene emissions, once elevated, did not decrease even after fumigation levels were reduced. The increase in isoprene emission could potentially be due to upregulation of the isoprene synthase gene or simply an increase in the production (or reallocation) of subcellular isoprene precursor species. However, our measurements did not elucidate or eliminate a particular mechanism. If increases in isoprene emission in response to ozone are common among isoprene emitting species, the feedback implications for the atmosphere could be large. Both a mechanistic understanding of the upregulation process and knowledge of the distribution of the response across plant species are needed for future model parameterization.

A21F-06 1135h

Fine-scale Source Distribution of Biogenic VOCs Measured by Proton-Transfer-Reaction Mass Spectrometry.

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We have recently deployed Proton-Transfer-Reaction Mass Spectrometry for measuring reactive biogenic trace gases at a loblolly pine plantation in North Carolina (Duke Forest) as well as a primary tropical rainforest in Costa Rica. An automated moveable inlet system allowed observations of the finescale source structure of various biogenics, such as isoprene, MVK+MAC, acetaldehyde, acetone, methanol and monoterpenes within the canopy using an inverse lagrangian dispersion model. The distribution of oxygenated compounds in general shows a complex behavior of emission and deposition. Together with eddy covariance measurements at the top of the canopy, which we compare with enclosure measurements, we are able to quantify finescale exchange processes of VOCs within the canopy. Our measurements demonstrate that the treatment of emission and deposition currently used for modeling oxygenated biogenic VOCs can only be seen as a first order approximation.

A21F-07 1150h

PTR-MS and GC-MS Analyses of Sesquiterpenes

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Terpene hydrocarbons are ubiquitous compounds in the atmosphere. Frits Went, in 1960 suggested that the volatile organic emissions from plants especially the monoterpenes were responsible for the formation of the atmosphere's blue haze'. Surveys of plant emissions using a Proton Transfer Reaction - Mass Spectrometer (PTR-MS) have shown that many species emit sesquiterpenes (Ssqt's) independent of emitting monoterpenes or isoprene. It is possible they are a comparable source of the organic micro-aerosols responsible for scattering the blue end of the spectrum , i.e. blue haze' in addition to the monoterpenes as they have more rapid and complete reactions with ozone resulting in particles. Ambient concentrations of the terpenic hydrocarbons are site dependent, but are typically very low from a few to 1000 pptCv, except for isoprene which has summer mid-day median levels of 3 to 6 ppbCv. The sesquiterpenes are very difficult to measure in the atmosphere by conventional means but cubebene, copaene, bourbonene and alpha- and beta-caryophyllene are common foliage emissions. Direct measurements of isoprene, monoterpenes and sesquiterpenes over plant foliages with a PTR-MS were compared with captive samples of the air from the same plant foliages collected in Summa canisters. None of the biogenic organic emissions stored in the Summa canisters showed any significant losses due to wall effects. Neither did we observe that any of the processing steps were responsible for losses or internal molecular rearrangements. The reason for the stability and 100% recovery of these C5 to C15 olefinic compounds at room temperature is believed to be due to the water layer formed on the electropolished stainless steel walls of the canister under pressure at 30 psig. Ozone added to the test systems was observed to have an immediate effect on the sesquiterpenes at ambient levels. Measurements

made this past summer at the Duke and Blodgett Research Forests again confirm that the ambient levels of the Ssqt's were very low and unless made close to the source foliage not measurable. However, Ssqt's were readily measured in branch and leaf enclosures in most of the species surveyed. Some conifer foliages produced Ssqt's at rates comparable to their monoterpenes emission rates, but more typically the rates were 1/50 to 1/100 that of the monoterpenes.

A21F-08 1205h

Towerbased and Airborne VOC Flux Measurements Over the Amazonian Rainforest During LBA-CLAIRE 2001

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Volatile organic compounds (VOC) have a major influence on the atmospheric oxidative capacity, greenhouse gas concentrations, and the formation of aerosols, which implies a crucial role of VOC in climate forcing. Even though tropical vegetation has a major impact on global VOC emission strength, these regions have been the least investigated to date, and flux estimates have high uncertainties. During the LBA-CLAIRE 2001 project (Cooperative LBA Airborne Regional Experiment 2001, as part of the Large Scale Biosphere-Atmosphere Experiment in Amazonia), canopy-scale and landscape-scale VOC fluxes were estimated for a remote tropical rainforest site north of Manaus, using different measurement techniques. Above-canopy fluxes were investigated simultaneously with surface layer gradients and relaxed eddy accumulation measurements from a 52-m tower. Airborne measurements of vertical profiles of VOC mixing ratios from 100m to 3000m were used to estimate flux rates on a regional scale. Chemical processes in the model estimates were constrained with measured values of O3, NOx and VOC. VOC flux rates will be compared with CO2 fluxes, which were determined by similar procedures.

A21G MCC: 3018 Tuesday 1020h

Integrating Aerosol Measurements and Models III *(joint with OS, GC)*

Presiding: **K A Prather,** University of California, San Diego**; G R Carmichael,** University of Iowa

A21G-01 1020h

Integrating Aerosol Measurements and Models

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Advances in aerosol measurements are providing detailed information on the properties of aerosols. Advances in modeling include correspondingly detailed representations of aerosol size, composition, hygroscopic, optical, and cloud activating properties. Here, a number of examples of measurement-model integration will be discussed, including satellite-in situ comparisons, CCN closure, CCN-cloud droplet closure, inverse modeling of aerosols, and hygroscopic closure.

A21G-02 1050h

Black Carbon Measurements in the Marine Boundary Layer

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Black carbon (BC) particles are one of the most ubiquitous yet least understood aerosols in the atmosphere. Light absorption by these particles alters the thermodynamic structure of the atmosphere and contributes to regional and global climate change. The magnitude of this impact, however, is poorly understood since so little is known about the temporal and spatial distribution of BC in the atmosphere. In addition, the residence time of BC in the boundary layer and free troposphere is one of the least known parameters in GCMs. Current estimates vary from hours to days. A major source of these uncertainties is the serious deficiency of accurate and quantitative measurements of BC properties, concentration, mass and optical extinction. Until recently there were no instruments that directly measured BC mass with sufficient accuracy, sensitivity and response time. A new instrument, the single particle soot photometer (SP2) has been developed that measures BC mass of individual particles with an accuracy of 50% or better. The patented technique uses laser induced incandescence to derive the mass of particles that absorb light at a wavelength of 1064 nm. The composition of the particle is determined from the temperature of incandescence using two colour pyrometry. The degree of mixing with non-light absorbing material is determined by comparing the light scattering and incandescence signals. The SP2 was recently flown on the CIRPAS Twin Otter to make BC measurements in the marine boundary layer during the CSTRIPE campaign in July, 2003. The measurements show multiple layers of BC with varying degrees of mixing with other, non-light absorbing material. The fraction of non-absorbing material on the BC is apparently related to the age of the particles as estimated from back trajectory analysis.

A21G-03 1105h

Insights into Particle Characteristics, Sources, Nucleation and Growth in Pittsburgh Based on Aerosol Mass Spectrometry

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An Aerodyne aerosol mass spectrometer (AMS) was deployed at the Pittsburgh EPA Supersite from September 6 to September 22, 2002, as part of the Pittsburgh Air Quality Study (PAQS). The main objectives of this deployment were 2) to characterize the size-resolved chemical composition of non-refractory (NR) components in fine particles (approx. PM1.0) and 2) to investigate the chemistry and mechanism of particle growth during the nucleation events in Pittsburgh. We first compare the AMS data with measurements from a wide variety of collocated aerosol instruments, including TEOM, semi-continuous sulfate and ammonium, 2hr- and 24hr-averaged organic carbon, SMPS, and MOUDI. Good agreement is observed for particle concentrations, compositions, and size distributions. Total NR PM1.0 mass concentration in Pittsburgh accumulates over periods of several days with intermittent cleaning due to rain or air mass change. Different aerosol species show different behavior in time and size. Sulfate and organics are the major components of fine particle mass while nitrate concentrations are lower. Significant amounts of ammonium are also present in particles, which most of the time is consistent with sulfate being present as ammonium sulfate. Size distributions of particulate sulfate, ammonium, organics and nitrate vary from day to day, showing unimodal, bimodal and even trimodal characteristics. The accumulation mode (peaking around 500nm in vacuum aerodynamic diameter for the mass distribution) and the fine mode (peaking around 200nm) are most commonly observed. Periods with high sulfate and organics mass loadings are examined. The possible sources and atmospheric processes that caused the events are suggested based on the AMS results, data of gaseous pollutants and meteorological variables and back trajectory analysis. Significant formation and growth of the nucleation mode particles were observed in three days during this deployment. These events appear to be representative of the climatology of the nucleation events observed in Pittsburgh (100 per year). One of the events is among the 10 most intense nucleation events observed in Pittsburgh over a period of 15 months. All these events showed distinctive growth of sulfate, ammonium, organics and nitrate in the ultrafine mode. During each of these 3 events, sulfate was always the first, and often the fastest, species that grew in the ultrafine particles. Significant increase of ultrafine ammonium was also observed, but usually lagged slightly (5 -10 min) behind that of sulfate. For this reason the ultrafine particles tend to be acidic during the initial stages of the nucleation event. Ultrafine organics also increased significantly during the growth of the nucleation mode particles at a later time, probably from the condensation of photochemically produced secondary organic compounds. Among all these four species, nitrate was always the least important in the growth.

A21G-04 1120h

Integrating High Temporal Resolution Single Particle Data with Atmospheric Models

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Single particle analysis can provide direct insight into the evolution of the mixing state of atmospheric particles. Information at this level can be used to gain insights into particle sources as well as atmospheric processing. There are a number of instruments which have been developed in the past decade which allow one to measure the size and chemical composition of individual particles in real time. This presentation will focus on aerosol time-of-flight mass spectrometry (ATOFMS) measurements made during ACE-Asia and other locations in the United States, focusing on the size-resolved chemical information that can be acquired with single particle mass spectrometers. The ability to use single particle signatures to distinguish between elemental carbon (EC), organic carbon (OC), and various mixtures will be demonstrated. Results will be presented showing how unique mass spectral markers can be used to discriminate between dust, sea salt, fossil fuel, and biomass particles, monitoring their relative contributions and changes in chemistry on short timescales. A discussion of how single particle measurements might be used to refine current atmospheric models by adding unique information will be presented.

A21G-05 1135h

New Techniques For Predicting Optical Properties Of Nonspherical Multicomponent Aerosols Using Single Particle Measurements

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