

2M.1**A Method for Extracting Additional Information on the Organic, Elemental and Pyrolyzed Carbon from Real Time Measurements with the Sunset Carbon Aerosol Analyzer.**

MIN-SUK BAE, James J. Schwab, Kenneth L. Demerjian, University at Albany, State University of New York; Oliver Rattigan, Dirk Felton, New York State Department of Environmental Conservation.

Semi-continuous Organic Carbon and Elemental Carbon (OCEC) instruments are becoming more widely employed to measure the carbonaceous fraction of atmospheric particulate matter. Determining accurate concentrations of atmospheric OC and EC is necessary for identifying their sources and predicting their effects on various atmospheric processes. We have obtained hourly time-resolved measurements of OC and EC at Pinnacle State Park (PSP) in upstate New York and the South Bronx, New York City. OC and EC were determined using a NIOSH-like protocol using a Sunset Real Time ECOC Analyzer - that is, using four temperature steps to a final temperature of 840 degrees C for OC and two steps to 850 degrees C for EC.

There is currently no standard procedure for determining concentrations of the empirical parameters OC and EC in the atmosphere, and there is considerable controversy over measurement methods and parameter designations. In this study, the contour plots of the time series carbonaceous concentrations associated with the analysis temperature steps provide clear evidence that the carbonaceous nature of sources changes significantly. The identification of additional "oethermal fractions" with the Sunset ECOC data are compared with organic chemical species measured by aerosol mass spectrometer (AMS). In addition, time series of split time variation determined by optical laser transmittance could illustrate the behavior of pyrolyzed carbon concentrations and shed light on its sources.

2M.2**Interference of Organic Signals in Highly-time Resolved Nitrate Measurements by Aerosol Mass Spectrometer.**

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Highly time-resolved measurements of nitrate in ambient aerosols were conducted by an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS or simply AMS) and a Particle-into-Liquid Sampler with Ion Chromatography (PILS) from field intensives at two sites; an urban site in New York City (Queens College; QC) for wintertime (January 22 to February 5, 2004) and a rural site in southwestern New York state (Pinnacle State Park; PSP) for summertime (July 20 to August 4, 2004). In this study, the inorganic nitrate signal from Q-AMS may contain significant interferences from organic signals, especially in rural atmospheres. Analysis of the QC data indicates a good agreement between the PILS-nitrate and AMS-nitrate measurements ($R^2 = 0.94$; linear regression slope = 1.05). In addition, the m/z 30 and m/z 46 (two dominant ion fragments in nitrate mass spectrum) signals tightly correlate at QC ($R^2 = 0.98$) and have an average ratio similar to that determined in the laboratory for NH_4NO_3 (m/z 30 / m/z 46 = 2.4). In contrast, at the PSP site the correlation between PILS- and AMS-nitrate was poor ($R^2 = 0.34$), the AMS reported nitrate values were substantially higher, and the m/z 30 to m/z 46 ratios were generally much larger than 2.4. These observations, together with evaluations by aerosol phase ion balance, indicate that the AMS m/z 30 signals at PSP have been strongly influenced by organic compounds that also produce signals at m/z 30, including organic nitrates (NO^+), oxygenated organics (CH_2O^+), hydrocarbon-like organics (C_2H_6^+), and nitrogen-containing organic compounds (CH_4N^+).

2M.3

Single Particle Black Carbon and BC Mixing State Measurements over Mexico City and Seattle: Results from the MILAGRO and INTEX-B Studies. R SUBRAMANIAN, Gregory L Kok, Droplet Measurement Technologies; Darrel Baumgardner, Universidad Nacional Aut

Black carbon (BC) plays an important role in aerosol radiative forcing by absorbing light and warming the atmosphere. Recent studies have shown that the absorption efficiency of coated black carbon particles could be 1.5 times that of uncoated BC (Bond et al. 2006). The DMT single particle soot photometer (SP2) measures single particle black carbon mass using laser incandescence, and can also provide information on the mixing state of BC using scattering measurements. The instrument was used on board the NSF C130 aircraft during the March 2006 MILAGRO and April/May 2006 INTEX-B studies over Mexico City and Seattle respectively, and on the DOE G1 aircraft during MILAGRO. Data are available for all eleven C130 flights during MILAGRO and for thirteen flights during INTEX-B. The flights over Mexico sampled different conditions including brown haze, fresh and aged emissions from Mexico City, and clean areas, often on the same flight. For the flight on March 18, 2006, about 10% of the particles incandesced (i.e. contained BC); BC averaged less than 3% of the particulate mass as estimated by the SP2 (assuming ammonium sulfate as the non-BC mass). Incandescent particles were usually composed of 40-60% BC by volume. For the INTEX-B flight on May 1, 2006, the incandescent particles contained 10-15% BC by volume, which correspond well to AMS-reported measurements of high sulfate and low organic content. Use of either a core-shell or internally mixed model did not make an appreciable difference since the aerosol extinction is dominated by non-incandescing particles. Complete results from both INTEX-B and MILAGRO including an intercomparison test between the G1 and C130 aircrafts will be presented at the conference.

2M.4

Carbonaceous aerosols in the remote free troposphere: A time series from the Mauna Loa Observatory. STEVEN HOWELL, Barry Huebert, John Zhuang, University of Hawaii; Trevor Kaplan, Mauna Loa Observatory.

Since June 2005 we have operated a Sunset Labs semicontinuous Organic Carbon/Elemental Carbon (OCEC) analyzer at the Mauna Loa Observatory (MLO) on Hawaii. At 3397 meters, the site is well above the usual marine boundary layer and nighttime downslope winds usually bring minimally perturbed air from the free troposphere. Concentrations are normally very low, so we opted to forego the usual organic/elemental split and instead maximize sensitivity to total carbon (TC). Monthly averages of nighttime samples (10:00 PM to 8:00 AM local time) range from 0.02 to 0.26 micrograms $C m^{-3}$ with maximum values in the spring, corresponding to the elevated sulfate and calcium associated with transport of Asian pollution and dust to MLO. At these low TC levels, the performance of the denuder that removes organic vapors from the sample stream is critical and dominates the error calculation and hence the detection limit. To improve the detection limit, we installed a second OCEC analyzer in September 2006 so blanks and samples can be simultaneous.

2M.5

Organic functional groups in submicron aerosol by FTIR measurements in the Gulf of Mexico during TEXAQS/GoMACCS 2006. Lynn M Russell, LELIA N HAWKINS, Scripps Institution of Oceanography; Tim S Bates, National Oceanic and Atmospheric Administration Pacific Marine Environmental Laboratory.

To characterize the pollutants created in and transported to the Gulf of Mexico and coastal Texas, a multi-platform campaign was conducted involving ground, air, and shipboard measurements. Organic compounds in primary and secondary aerosol particles are of particular interest due to the complexities associated with CCN activity in organic-containing particles. We present results of FTIR spectral analysis from approximately 100 filters collected over 6 weeks of the 2006 Texas Air Quality Study / Gulf of Mexico Atmospheric Composition and Climate Study (TEXAQS/GoMACCS). Quantified functional group concentrations include 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. Aerosol organic fraction and functional group speciation as measured by FTIR analysis is compared with results from an Aerosol Mass Spectrometer (AMS) operated on board the Ronald H. Brown. Specifically, carbonyl concentration as determined by a peak in the infrared spectrum at 1720 cm^{-1} is compared to the loading of $m/z = 44$ which has been established as a CO_2 fragment in previous AMS studies. Time-resolved total organic concentration as derived from each technique is also compared. The AMS particulate organic matter (POM) 50th percentile and 95th percentile are $1.27\text{ micro-g m}^{-3}$ and $14.53\text{ micro-g m}^{-3}$, respectively.

2M.6

Searching for Evidence of Acid-Catalyzed Enhancement of Secondary Organic Aerosol Formation Using Ambient Aerosol Data. ROGER L. TANNER, Kenneth J. Olszyna, Tennessee Valley Authority; Eric S. Edgerton, ARA, Inc.; Eladio Knipping, EPRI.

Laboratory experiments suggest that strong acids promote formation of significant levels of secondary organic aerosol (SOA), which is problematical since organic aerosols have been implicated in health impacts of fine PM. We report efforts examining hourly speciated fine particle data for evidence of aerosol acidity-catalyzed secondary organic aerosol formation. The assumption is that, if SOA formation can be accelerated by acid catalysis in fine particles, larger increases in the concentrations of organic aerosol mass should occur on days and in locations with more acidic aerosol (lower $\text{NH}_4^+/\text{SO}_4^-$ ratios) compared to neutral aerosol days. The approach used herein is based on examining data sets from which the hourly acidity of $\text{PM}_{2.5}$ aerosols can be estimated, and for which hourly organic carbon content have been measured, then selecting episodes and statistically relating within-day SOA buildup with aerosol acidity. Using this approach we have examined (1) VISTAS Focus Site data from Look Rock, TN, Cape Romain, SC, and Millbrook, April, 2003-December, 2004; (2)SEARCH data from CTR and YRK for 2003 and 2004; and (3)other hourly TVA data from the Tennessee Valley.

VISTAS focus site data from Look Rock, for mid-July to mid-August, 2004, included PILS-IC hourly ammonium, nitrate data (J. Collett, personal communication). Surprisingly, nighttime average imputed acidities generally exceeded daytime values, but data showed no increases in OC with increasing aerosol acidity. Plots of OC changes time-delayed from the observed imputed acidity also show no clear relationship. SEARCH network data (2003-2004) for rural Centreville, AL (CTR) and Yorkville, GA (YRK) sites have also been examined for nitrate-corrected $\text{NH}_4^+/\text{SO}_4^-$ - OC relationships. Warm season acidity levels were higher at CTR than YRK, and daytime levels exceeded those at night. However, no consistent evidence of positive correlation between OC levels and aerosol acidity have yet been found, even with lags of up to 6 hr.

2M.7

Investigating the chemical nature of humic-like substances in atmospheric aerosols using LC-MS/MS. ELIZABETH A. STONE, Curtis J. Hedman, Martin M. Shafer, James J. Schauer, University of Wisconsin-Madison and Wisconsin State Laboratory of Hygiene.

Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) was used to investigate the chemical nature of humic-like substances (HULIS) in the atmospheric particulate matter (PM). HULIS has been observed in the atmosphere and has been suggested to comprise a significant portion of the unresolved organic mass. Presently, HULIS is believed to be of secondary origin, although its chemical structure and formation mechanisms are not fully understood. Ambient PM collected at on quartz fiber filters was extracted with ultra pure water using sonication. Water-soluble organic carbon (WSOC) in the extracts was measured and the HULIS portion of WSOC was isolated using reversed-phase LC. Mass spectra of the HULIS material under low fragmentation conditions were used to characterize the molecular weight range of WSOC and to identify high-molecular weight species. MS/MS was used to generate product ion spectra of these compounds and important functional groups were identified based on comparisons to HULIS-relevant surrogate standard compounds. Spectral signatures of HULIS were compared and contrasted between spatially resolved locations in North America where primary sources were well-understood. Correlations between primary sources and secondary HULIS are discussed.

2M.8

Airborne aerosol measurements over West Africa during the AMMA SOP 1 and 2 field campaign. GERARD CAPES, Hugh Coe, Paul Williams, Jonathon Crosier, University Of Manchester, UK; Jennifer Murphy, Claire Reeves, University Of East Anglia, Norwich, UK; Doug Parker, University Of Leeds, UK.

In July-August 2006, a large field campaign took place in West Africa, forming part of the international AMMA (African Monsoon Multidisciplinary Analyses) project. Several ground based sites and 5 aircraft were involved in the project. This paper presents findings from the aerosol particle measurements made on board the UK Facility for Airborne Atmospheric Measurements (FAAM), a BAe146 research aircraft. The operating region covers a large area of West Africa, and some of the Atlantic Ocean off the coast of Senegal.

A preliminary analysis of the AMS data has been performed in conjunction with data from the other instruments, and a very clean mass loading across the operating region, though examples of biomass burning, dust, urban plumes, and areas dominated by biogenic emissions have been identified. Biomass burning layers were encountered between 6 and 10N. These showed a similar spectral signature to those measured in the same region in the dry season and appear to have originated in the southern hemisphere. Urban plumes from Niamey and Lagos were measured, and were characterised by a significant hydrocarbon signature typical of near-source fossil fuel emissions. Emission ratios relative to CO have been estimated. In regions of biogenic emission, where high levels of isoprene and other VOCs were measured, there was little evidence of enhanced organic aerosol loading, typically observed when secondary organic aerosol (SOA) has been produced. The extent to which observable organic loading is observed has been determined on the basis of statistical comparison as individual data points are rarely above the detection limit of the instrument. This illustrates that the loadings are low and that models of SOA formation may predict similar concentrations to observations in clean, biogenic environments.

2M.9

Evaluation of Influences in Ambient Organic Compounds Levels by the Operations of a Coal-Fired Power Station in Tong Liang, China. STEVEN SAI HANG HO, Judith C. Chow, John G. Watson, Desert Research Institute; Deliang Tang, Frederica Perera, Columbia University.

Non-polar organic compounds, including n-alkanes, polycyclic aromatic hydrocarbons, (PAHs), hopanes, and steranes, in PM_{2.5} were measured in a long-term epidemiological study in Tong Liang, China where coal combustion was a major contributing source to the aerosol. A coal-fired power station in Tong Liang was operated in winter and spring (November to May) but permanently shutdown in March 2003. Integrated 72-hour samples were collected at three sites from 3/2/2002 to 2/26/2003 and 3/1/2005 to 2/26/2006 to evaluate the influences by the operations of the coal-fired power station. In-injection port thermal desorption/mass spectrometry (TD-GC/MS) was applied for the organic speciation. At the site closest to the coal-fired power station, compared with the same period when it was operated, the concentrations of priority PAHs with molecular weight ranging from 252 to 302 decreased 14.2% to 36.9% after the station shutdown. Picene, a known organic tracer for coal burning, was also shown a decrease of 11.7%. No consistent variations were determined for other low molecular weight (<228) PAHs. The concentrations of high molecular weight n-alkanes (C<27) were 8.8% to 33.7% lower than those measured before the closure of coal-fired power station. Hopanes, molecular markers of aerosol emissions from fossil fuel utilization, were shown an averagely decrease of 4.8% but no significant changes were determined for steranes. The concentrations of the organic compounds at other two sites closed to urban areas did not demonstrate influences from the coal-fired power station shutdown. Residential coal combustion and vehicle emissions were major contributions for the sites.

2M.10

Organic Speciation of Detroit Exposure and Aerosol Research Study (DEARS) Samples for Source Apportionment. STEPHEN R. McDOW, John Turlington, Sania W. Tong Argao, Ronald Williams, National Exposure Research Laboratory, U.S. EPA.

The Detroit Exposure and Aerosol Research Study is a major three-year study conducted by the U.S. Environmental Protection Agency (EPA). Its primary objective is to investigate the relationship of select air pollutant concentrations and their sources measured at community air monitoring stations in comparison to those measured in various neighborhoods in Wayne County, Michigan. To accomplish this, residential indoor and outdoor samples were collected daily at 40 locations for 6 seasons at a flow rate of 10 liters/minute.

Analysis of samples for organic species by gas chromatography/mass spectrometry (GC/MS) provides valuable data for determining source contributions from several important sources of particulate matter, including motor vehicle exhaust, diesel exhaust, wood burning, and meat cooking. Application of GCMS analysis to daily low volume samples presents a considerable analytical challenge because of the large amounts of material needed for analysis. One approach to addressing this problem is analysis by selective ion monitoring to achieve substantially lower limits of detection and quantitation. As a part of our research effort to reduce uncertainty in source apportionment, we will report method detection limits for selective ion monitoring of organic markers of well under 100 pg/m³ for low volume 24-hour samples. These levels are sufficient for detection of all compounds in most samples collected. We will also report our initial demonstration of method proficiency, which thoroughly characterizes method detection limits, method precision, and recoveries for organic markers. We will also show results from the first year of sampling that indicate concentrations of all markers are present at concentrations well above detection limits, and markers known to be unique and to originate from the same source exhibit measurably stronger associations at levels well above detection limits.

Results to the first year of DEARS samples collected at the community monitoring station indicate that particulate matter from motor vehicle exhaust is subject to extensive day to day variability. Associations among different hopanes, markers for motor vehicle exhaust, and among different polycyclic aromatic hydrocarbons, markers of general combustion processes, were significantly stronger than associations between hopanes and polycyclic aromatic hydrocarbons, suggesting that other combustion sources besides motor vehicles may be important contributors to particulate mass.

Although this work was reviewed by EPA and approved for publication, it may not reflect official EPA policy.

2M.11

Investigation of Sources of OC and EC at Rural Sites in the Northeast US Using Highly Time-Resolved Data. GEORGE ALLEN, Iyad Kheirbek, John Graham, Gary Kleiman, NESCAUM; Jeff Emery, ME-DEP.

Highly time-resolved speciated aerosol measurements combined with back trajectory analysis can provide enhanced insight into aerosol source attribution. In this presentation, we analyze 2-hour EC and OC data from the Sunset Model 3 field carbon analyzer at two sites in the Northeast US: Acadia National Park in ME, and Mohawk Mt. in CT. These are ongoing intensive rural sites run under the MANE-VU Haze RPO RAIN program. Initial analysis of 10 years of summer IMPROVE EC and OC data from Acadia using incremental probability plots showed the source region on high OC days to be from the WNW for both OC and EC, suggesting the source is long-range transport of wildfire smoke (<http://www.nescaum.org/documents/2006-05-memo8-rain.pdf>).

We expand this analytical approach in this analysis to include all seasons and a second site, and to include both third-day 24-h IMPROVE and the two-hour resolution carbon data from the Sunset method. ATAD hysplit back trajectories for each two-hour period are calculated using EDAS meteorological inputs for 2005 and 2006. The objective of this analysis is to determine to what extent we can enhance this source attribution approach using larger and more highly time-resolved data. For example, at Mohawk Mt. in NW CT, we would expect to see a range of carbon source signatures based on back trajectories, including both wildfire and urban mobile sources (from the New Haven and New York metropolitan areas for example).

2N.1

Application of Anion Exchange Chromatography with Pulsed Amperometric Detection for Measurement of Levoglucosan in Ambient Aerosol Samples. AMANDA S. HOLDEN, Amy P. Sullivan, Sonia Kreidenweis, Jeffrey L. Collett, Jr., Colorado State University; Bret Schichtel, William Malm, National Park Service/CIRA, Colorado State University; Graham Bench, Lawrence Livermore National Laboratory.

Six day integrated fine particle samples were collected during winter and summer seasons at 12 IMPROVE sites throughout the United States using Hi-Vol samplers. The monitoring sites included urban, near-urban, and rural locations. Measurements of $^{14}\text{C}/\text{C}$ were made by accelerator mass spectrometry at Lawrence Livermore National Laboratory and presented by Schichtel et al. [2007]. Results of these analyses indicate a prevalence of modern carbon at many of the measurement locations. In order to examine the aerosol fraction associated with biomass combustion, either from residential wood burning or wildland fires, we measured concentrations of levoglucosan in selected samples. Levoglucosan, a breakdown product of cellulose, is a widely used tracer for biomass combustion. Measurements were made using a new approach involving aqueous filter extraction followed by direct analysis of levoglucosan and other carbohydrates using High Performance Anion Exchange Chromatography. In this method carbohydrates are separated on a Dionex Carbopac PA-10 column, using a sodium hydroxide gradient elution, and detected using pulsed amperometry. A summary of measured levoglucosan concentrations will be provided. Using published source profiles, we will estimate the organic carbon fraction associated with biomass combustion and compare findings to fractions of modern carbon determined using the carbon isotope approach.

Bret A. Schichtel, William C. Malm, Graham Bench, Stewart Fallon, Charles E. McDade, Judy C. Chow (2007). Fossil and Contemporary Fine Carbon Fractions at 12 Rural and Urban Sites in the United States, *J. Geophys. Res.*, in review.

2N.2

Identification of Organic Compounds in Aerosols using GCxGC TOF-MS. AMY LEITHEAD, Shao-Meng Li, Douglas Lane, Yu Cheng, Environment Canada.

GCxGC TOF-MS is a powerful tool for the identification of organic compounds in aerosol samples. Compounds that are difficult to analyze by traditional methods can be easily separated and identified using this instrument. The dual columns, cryofocusing on the 2nd column along with the highly sensitive detector and powerful de-convolution software easily separate and identify compounds that are impossible to analyze by traditional GC-MS. Details of the method development work will be shown for different classes of compounds. Methods were tested for both non-polar compounds such as the alkanes and more polar compounds such as the ketones, amides, fatty acids and sugars. To optimize the separation of each class of compounds, three different column combinations were tested.

Preliminary results of aerosol samples collected by Hi-*vol* at 2 sites, a rural site and a forest site will be presented. The samples were extracted by ASE and separated by silica gel chromatography into fractions of increasing polarity. Even after separation, a large number of unique compounds were found in each fraction. Unknown compounds in the aerosol samples will be identified. This large volume of data provides valuable information that is difficult to obtain by other methods.

2N.3

A Quantitative Protocol for Highly Polar Organic Compounds in PM_{2.5} from the New York City Airshed. HARMONIE HAWLEY, Min Li, Monica A. Mazurek, Rutgers University.

This project focuses on the quantitation of highly polar organic compounds extracted from PM_{2.5} samples collected as part of the Speciation of Organics for Apportionment of PM-2.5 in the New York City Area (SOAP). The SOAP network operated from May 2002 to May 2003 at four sites: Queens, NYC (high density urban residential); Elizabeth, NJ (adjacent to the NJ Turnpike); Westport, CT (downwind NYC); and a regional background site in Chester, NJ (upwind NYC).

A key science question was how much of the carbonaceous PM_{2.5} is primary versus secondary. To address this question, a group of highly polar, low molecular weight organic acids were selected as secondary species. These compounds do not appear as significant species in the chemical profiles of known primary sources such as motor vehicle exhaust and cooking emissions. The target compounds selected were diacids (oxalic acid and malonic acid) and oxo-carboxylic acids (glyoxylic acid, pyruvic acid, 2-oxobutanoic acid, levulinic acid, 5-oxohexanoic acid and oxobutanedioic acid). A quantitative extraction and gas chromatographic/mass spectrometric (GC/MS) chemical analysis procedure was developed and evaluated. Trimethylsilyl (TMS) derivatives were prepared prior to GC/MS analysis and 5-point calibrations and multiple replicates were evaluated to determine method precision.

Good precision and sensitivity were seen based on the statistical analysis of the standard compounds evaluated and in the ambient PM_{2.5} samples. This procedure establishes a new identification and quantitation method for determining highly polar and oxidized secondary molecular markers in regional fine aerosols samples.

2N.4

Extractability and Determination of Different Polarity Organic Species in Air Particulate Matter. Tylor J. Lahren, JOSEF BERANEK, Irina Smoliakova, Steven B. Hawthorne, Alena Kubatova, University of North Dakota; Artur Braun, Empa Switzerland.

Air pollution studies involving characterization of organic particulate matter (PM) typically determine 20 - 50 wt% of total organic carbon (OC). This is due to limitations in extractability by organic solvents and/or elutability through GC typically used for PM analysis. Therefore, we have evaluated the extractability using hot pressurized water and sequential organic solvent (Soxhlet) extraction from three PM samples of different origin, e.g., diesel exhaust PM (SRM 2975), urban PM (SRM 1648), and wood smoke PM. The advantage of sequential extraction is its ability to differentiate different polarity fractions and thus estimate the importance of primary (non-polar) vs. secondary (polar) emissions.

Carbon contents in solid samples and extracts were evaluated using a thermal optical organic/elemental carbon (OC/EC) analyzer in transmittance and reflectance modes and a total organic carbon (TOC) analyzer. The extraction yields of total OC (40 - 70%) were comparable for both extraction techniques. Both methods showed capability to separate organics based on their polarity. Highly polar species (e.g., water-soluble) represented significant portions of wood smoke and urban PM (7 and 20%, respectively). Although water-soluble species were not observed, a significant polar fraction (20 - 30%) was extracted with higher polarity solvents (e.g., 50 - 150 degrees C pressurized water or methanol) from diesel exhaust PM.

The distribution of polar organic compounds with hydroxyl, carbonyl and carboxyl functional groups over different polarity fractions was confirmed with carbon 1s near-edge X-ray absorption fine structure (C 1s NEXAFS) and H1-nuclear magnetic resonance (H1-NMR). Furthermore, using gas chromatography with mass spectrometry carboxylic acids, sugars and aldehydes were determined in all studied PM samples. These chemicals were predominantly found in polar fractions of extracts, which correlated with C 1s NEXAFS and H1-NMR analysis.

2N.5

Characterization of Sugars in Fine Particles Collected at Three Rural and Urban Sites in Texas. YULING JIA, Shagun Bhat, Matthew Fraser, Rice University.

A total of 174 aerosol samples ($<2.5 \mu\text{m}$) were collected at two rural sites (San Augustine and Clarksville) and one urban site (Dallas) in Texas from November 2005 to July 2006 for quantification of sugars. Two extraction methods were applied to identical samples, and the combination of 3-15 ml aliquots of dichloromethane and 3-15 ml of methanol was found to extract sugars with greater efficiency ($>75\%$) than other solvent suites.

Concentrations of total aerosol sugars ranged from 22 to 164 ng/m^3 . Levoglucosan, glucose, mannitol, arabinol and glycerol were the dominant saccharides at all the sites. Levoglucosan contributed most to the total sugars, and its concentration was significantly enhanced during local wildfire periods (Nov 2005 – Apr 2006). Glucose was the second most abundant sugar (5% to 39%), and was most prevalent in the growing season, while sucrose was significant only in spring. In contrast, trehalose and sugar polyols (except glycerol) increased concurrently in summer and early autumn during the period of leaf senescence. A Pearson's test supported this observation by showing a strong correlation among the concentrations of trehalose and major sugar polyols during the period of study.

The seasonal variations in the sugar composition in the aerosol samples, concurrent with the seasonal change of sugar production and utilization by plants and microbiota in the ecosystem, indicate a strong contribution from biogenic sources. Total concentrations of sugars were generally higher at the two rural sites (93 ng/m^3 , on average) than at the urban site (55 ng/m^3 , on average). The seasonal trend of sugar composition was significantly weaker at the urban site compared to the rural sites. One possible explanation is a smaller influence of emissions on sugars in aerosols from local sources at the urban site.

