

suited to characterizing the composition of regional PM-2.5 air quality these sites provide the opportunity to compare filter based speciation data to measurements performed with the newest continuous speciation instrumentation technologies.

PM-2.5 chemical speciation samplers draw from 600 to 1000 liters of air per hour across three filters simultaneously over a 24 hour period. The three filters are subjected to specific lab analyses to determine the concentrations of targeted compounds; including metals, ions such as sulfate, nitrate, and ammonium, and elemental and organic carbon. Data from these sites are collected on a one day in three schedule and are available for a year or more from the various locations.

PM-2.5 speciation data are used to determine a ranking of compounds responsible for particulate pollution in various geographical locations in New York State. This information is useful in the attribution of sources to observed PM-2.5 concentrations and in the identification of the differences and similarities of these contributions in urban versus rural environments. PM-2.5 speciation data were obtained at two rural locations, Pinnacle State Park near Corning, NY and Whiteface Mountain in the Adirondacks; and at two urban locations, Rochester, NY and New York City, NY. Comparisons of the rural and urban measurement data suggest that compounds such as sulfate have distinct contributions from long range transport, while nitrate and organic carbon compounds indicate a pattern of more local generation, consistent with their overall atmospheric lifetimes. Back trajectory analysis has been applied to show the relationship between potential source regions and specific PM-2.5 species concentrations.

#### A52C-0134 1330h POSTER

##### Measurements of Natural Radioactivity in Submicron Aerosols in the Pittsburgh Area.

Nancy A. Marley<sup>1</sup> (630 252 5014; marley@anl.gov)

Jeffrey S. Gaffney<sup>1</sup> (630 252 5178; gaffney@anl.gov)

<sup>1</sup>Argonne National Laboratory, Bldg. 203/ER 9700 S. Cass Ave., Argonne, IL 60439, United States

Natural radionuclides can be useful in evaluating the transport of ozone and aerosols in the troposphere. We have used natural radioactivity to estimate apparent residence times for submicron aerosols in the troposphere by looking at the disequilibrium of lead-210 with its daughters bismuth-210 (5-day half-life) and polonium-210 (138-day half-life). We have also measured the activity of beryllium-7 on fine aerosols to examine potential upper-air transport into the tropospheric boundary layer. Two sites in the Pittsburgh area during the summer of 2001 were sampled for beryllium-7, lead-210, bismuth-210, and polonium-210 on fine aerosols by using a Sierra Impactor (Stage 4) that allowed a nominal 1-micrometer cutoff diameter.

One site was located approximately 5 km east of downtown Pittsburgh, on a rooftop next to Schenley Park (40.4395° N latitude and 79.9405° W longitude, elevation 310 m). A second site was located at the U.S. Department of Energy National Energy Technology Laboratory (NETL) Ambient Air Monitoring Station, approximately 15 km south of downtown Pittsburgh (40.30655 deg N latitude and 79.9794 deg W longitude, elevation 325 m). At both sites, 24-hour samples were collected from July 22 to July 30, 2001. Nine samples were taken at the NETL site, and six were taken at the Schenley Park site. The method for determining the lead-210 and its daughters will be described briefly. Apparent residence times ranged from 10-46 days, with an average of 23 days. Data indicate that little wind-blown soil or dust affected the area during the study. The importance of fine aerosol transport will be emphasized.

The authors wish to thank Donald Martello of the NETL and Natalie J. Anderson of Carnegie Mellon University for sample collection. This work was supported by the United States Department of Energy, Atmospheric Chemistry Program.

#### A52C-0135 1330h POSTER

##### The contribution of secondary organic aerosol to PM2.5 concentrations in Pittsburgh

Juan C Cabada<sup>1</sup> (412 268 3650;

jcc@andrew.cmu.edu); Spyros N Pandis<sup>1</sup> (412 268 3135; spyros@andrew.cmu.edu); Allen L Robinson<sup>1</sup>; R Subramanian<sup>1</sup>; Andrea Polidori<sup>2</sup>; Barbara Turpin<sup>2</sup>

<sup>1</sup>Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, United States

<sup>2</sup>Rutgers University, 14 College Farm Road, New Brunswick, NJ 08901, United States

A major component of PM2.5 in the Eastern US is carbonaceous material. This organic particulate matter results from both direct emissions from sources such as

automobiles, trucks and industries (primary), and from the oxidation of organic gases (secondary). Data from the Pittsburgh Air Quality Study are used to examine the contribution of secondary organic aerosol to the total organic aerosol loading measured in the city during 2001 and 2002. The contribution of secondary organic aerosol is estimated by using elemental carbon as a tracer for primary emissions of organic particulate matter (OC to EC ratio approach). A systematic method for the determination of the primary ratio has been developed based on the correlation of measurements of OC and EC to gaseous tracers of photochemical activity (O3) and primary emissions (CO, NOx). This method is applied to different sets of organic aerosols measurements (using an undenuded sampler, a denuded sampler and an in-situ carbon analyzer) for carbonaceous concentrations. Consistent results for the SOA fraction are obtained when the method is applied to the different sets of measurements for OC and EC. This approach indicates that between 20 and 40% of the organic particulate matter in Pittsburgh during the summer and fall of 2001 is secondary in origin while negligible contributions of SOA are estimated for the winter of 2001 and the spring of 2002.

#### A52C-0136 1330h POSTER

##### Measurement of Ambient Elemental Carbon Using the Thermal-Optical Transmittance Technique: Effect of Sample Volume and Refractory Loading on the OC/EC Split

R Subramanian<sup>1</sup> (1-412-268-8540; rs3@andrew.cmu.edu)

Andrey Y Khlstov<sup>2</sup> (andrey@andrew.cmu.edu)

Barbara J Turpin<sup>3</sup> (turpin@aesop.rutgers.edu)

Allen L Robinson<sup>1</sup> (alr@andrew.cmu.edu)

<sup>1</sup>Carnegie Mellon University, Mechanical Engineering, 5000 Forbes Ave, Pittsburgh, PA 15213, United States

<sup>2</sup>Carnegie Mellon University, Chemical Engineering, 5000 Forbes Ave, Pittsburgh, PA 15213, United States

<sup>3</sup>Rutgers University, Environmental Sciences, 14 College Farm Rd, New Brunswick, NJ 08901, United States

Ambient carbonaceous aerosols have been measured on a daily basis in Pittsburgh, PA for over a year. A discrepancy is observed when comparing ambient elemental carbon (EC) levels from samples collected over a 24-hour period to those measured at a higher frequency. For example, the 24-hr average EC calculated from 5 high frequency samples of 4 to 6 hour duration is on average a factor of 2 higher than the value determined from a simultaneous 24-hour sample.

It is well known that EC is operationally defined based on the analysis method, and that the results from different analytical methods do not agree. However, this is not an explanation for the observed discrepancy because all the samples were analyzed with a Sunset Labs Thermal-Optical Transmittance (TOT) analyzer. The TOT method corrects for the pyrolysis of organic carbon (OC) that occurs during analysis by measuring the transmittance of the filter. The ambient EC is taken as the mass of carbon that evolves after the transmittance returns to its original, pre-analysis value. The underlying assumption of the method is that either (a) the pyrolyzed carbon (PC) and ambient EC have similar optical properties, or (b) the PC comes off completely before the EC.

To better understand the cause of the observed discrepancy, experiments were performed involving washing of ambient samples with organic solvents (to reduce OC and minimize pyrolysis) followed by OC/EC analysis, and use of sucrose standards on filters with different refractory levels. Comparing the washed and unwashed filters shows that PC evolves at the same time as ambient EC, and further, that the optical transmittance of these two types of carbon are different. The refractory appears to have two effects on the thermal evolution of the aerosol carbon: (1) higher refractory content increases pyrolysis of the OC, and (2) the refractory causes light absorbing carbon (PC and EC) to come off earlier (at lower temperatures) in the analysis cycle. The net effect of the refractory is to alter the relative rate at which PC and EC evolve from the filter changing the OC/EC split assigned by the TOT technique.

#### A52C-0137 1330h POSTER

##### Monitoring of Water Content of Ambient Aerosol During the Pittsburgh Air Quality Study

Andrey Y Khlstov<sup>1</sup> (412-268-5778; andrey@andrew.cmu.edu)

Charles O Stanier<sup>1</sup> (cos@andrew.cmu.edu)

Dimitris Vayenas<sup>2</sup> (vay@terpsi.iceht.forth.gr)

Spyros N Pandis<sup>1</sup> (spyros@andrew.cmu.edu)

<sup>1</sup>Dept. of Chemical Engineering, Carnegie Mellon University, 5000 Forbes Ave., Pittsburgh, PA 15213, United States

<sup>2</sup>Dept. of Environmental and Natural Resources Management, University of Ioannina, Agrinio 45110, Greece

The absorption of water by atmospheric particles affects air quality, visibility, climate, particle lifetime, and interactions with semi-volatile compounds. Often, the water content of aerosols is calculated by a thermodynamic equilibrium approach. Due to a lack of knowledge about hysteresis effects, aerosol homogeneity, and chemical interactions, there is significant uncertainty in estimates of water concentrations for continental tropospheric aerosols. To address this, aerosol size distributions measured at both dried and ambient relative humidities are being monitored at a sampling site in the Northeastern United States dominated by regional transport of sulfate- and organic-containing aerosols. Four ambient and four dry size distributions are measured each hour, along with a suite of gas-phase, particle-phase, and meteorological parameters. Here we report hourly observations of aerosol water content for over 3500 different hours spanning a wide range of relative humidities, temperatures, and aerosol compositions during a period of several months. The observations are compared with thermodynamic equilibrium calculations based on the simultaneously measured chemical composition data. The effects of organic compounds are evaluated by analyzing changes in water uptake with the fraction of organic compounds. The aerosol size distributions were measured by an automated in-situ system which conditioned aerosols at ambient and dry conditions using computer controlled valves and Nafion dryers. The system included two Scanning Mobility Particle Sizers (SMPS) and an Aerodynamic Particle Sizer (APS) which measured the aerosol size distribution between 5 nm and 10 μm in diameter.

URL: <http://homer.cheme.cmu.edu>

#### A52D MCC: 125 Friday 1330h Oxygenated VOCs I: From Emission to Abundance

Presiding: G W Schade, University of California, Berkeley; J de Gouw, NOAA Aeronomy Laboratory

#### A52D-01 1340h INVITED

##### OVOC Emissions and Atmospheric Transformations.

Robert J Yokelson<sup>1</sup> (4063294812;

byok@selway.umt.edu); Ted J Christian<sup>1</sup> (theo@selway.umt.edu); Isaac T Bertschi<sup>1</sup>; Darold E Ward<sup>2</sup>; Richard J Field<sup>1</sup>; Peter V Hobbs<sup>3</sup>; Jon Goode<sup>1</sup>; Sherri Mason<sup>1</sup>; Ron Susott<sup>2</sup>; Ron Babbitt<sup>2</sup>; Wei Min Hao<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Montana, Missoula, MT 59812, United States

<sup>2</sup>USDA Forest Service, Fire Laboratory, PO Box 8089, Missoula, MT 59807, United States

<sup>3</sup>Department of Atmospheric Sciences, University of Washington, Seattle, WA 98195, United States

We quantified the main emissions from a few vegetation samples and many biomass fires using ground-based, open-path FTIR and airborne, closed-cell FTIR. The two instruments have been rigorously compared to each other and to PTR-MS and canister sampling. OVOC are major emissions from plants. OVOC account for about 70 percent of NMOC from savanna fires (the largest type of biomass burning) and 70-80 percent of NMOC from production and use of domestic biofuels (the second largest type of biomass burning). A table of average biofuel emissions is presented. Data from laboratory and free-burning fires, obtained from Alaska to South Africa, is used to develop equations that predict OVOC emissions from a wide variety of global fires. The impact of OVOC on smoke plume chemistry and the post-emission transformations of OVOC were investigated with two models. Addition of HCHO alone to the simple chemistry used in some global models dramatically reduces NOx lifetime and speeds up O3 formation rates in plumes. A detailed model verifies these effects and shows that OVOC profoundly affect formation of HOx, peroxide, and nitrogen reservoir species. The modeled photochemical transformations of OVOC are diverse, but some key pathways are unknown. We observed rapid production of both O3 and additional OVOC and OH of 1.7E7 in smoke plumes in Alaska and Africa; all reasonably consistent with model predictions. In addition, we found that cloud processing caused large post-emission changes in smoke trace gases

including removal of nearly all methanol, a decrease in acetic acid, and a large increase in HCHO. These observations suggest that OVOC could react in cloud droplets and lead to production of modified aerosol. In addition, transport of OVOC by deep convection may be associated with large effects not explained by solubility alone.

#### A52D-02 1410h INVITED

##### Leaf-Level Controls Over Emissions of Methanol and 2-Methyl-3-buten-2-ol, Oxygenated VOC With Different Production Mechanisms and Solubilities.

Peter C. Harley<sup>1</sup> (303-497-1863; harley@ucar.edu)

James P. Greenberg<sup>1</sup> (greenber@ucar.edu)

Alex B. Guenther<sup>1</sup> (guenther@ucar.edu)

<sup>1</sup>Atmospheric Chemistry Division National Center for Atmospheric Research, 1850 Table Mesa Drive, Boulder, CO 80307, United States

Oxygenated VOC fluxes were investigated in leaves of deciduous trees and grasses, and needles of conifers, using a temperature-controlled leaf cuvette and a proton transfer reaction mass spectrometer. Two alcohols, 2-methyl-3-buten-2-ol (MBO) and methanol, emitted by these plants, illustrate two contrasting patterns of oxygenated VOC emissions. MBO is restricted to a small section of the genus *Pinus*, and is maximal in mature needles. Methanol production appears to be ubiquitous among higher plants, associated with demethylation of pectin during cell wall maturation, and emissions are therefore maximal during rapid leaf growth, decreasing in mature leaves. Although emissions of both compounds respond to variation in leaf temperature and incident light, the nature of the control is quite different. Production and emission of MBO are tightly coupled, and leaf pools are small. Light and temperature affect emissions directly through their effect on production which ceases rapidly in the dark. Effects of light and temperature on production of methanol are unknown, although emissions, and presumably production, continue through the night at reduced rates. Effects of light and temperature on methanol emission are indirect, through their effects on stomatal conductance and evapotranspiration. Data will be presented to justify a conceptual model in which methanol released in the demethylation of pectin partitions into the gas and liquid phase according to Henry's Law. Gas phase methanol is then emitted through the stomata. However, methanol emissions correlate more strongly with rates of evapotranspiration than with stomatal conductance, suggesting that much of the methanol is released from the dissolved pool along with the transpiration stream. At night, when stomatal conductance is low, and assuming constant production, gas phase concentrations increase, and the size of the aqueous pool increases in response. This aqueous pool then empties rapidly upon stomatal opening, correlating strongly with rates of transpiration. Following depletion of the pool, lower methanol emissions reflect a dynamic balance between rates of production, phase partitioning, stomatal conductance and transpiration.

#### A52D-03 1435h INVITED

##### Eddy Covariance Measurements of Biogenic Oxygenated VOC Fluxes using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

Thomas Karl (tomkarl@ucar.edu)

NCAR, PO 3000, Boulder, CO 80307, United States

As indicated by model calculations, 1150 Tg of carbon is emitted into the atmosphere every year in the form of biogenic VOCs from vegetation. However there are still large uncertainties in estimates of the magnitude of VOC fluxes in various ecosystems and oxygenated VOC (oxyVOC) fluxes are particularly uncertain. We have explored the possibility of using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) for measuring canopy scale oxyVOC fluxes by the eddy covariance method. Results from various field sites with a variety of collaborators (Tirol, Austria, 1999/2000; Biosphere 2, Az, 2000; Niwot Ridge, CO, 2001; Prophet, MI, 2001/2002) show that oxygenated compounds can be released in substantial amounts, influencing the HO reactivity and possibly the carbon budget. A detailed knowledge of oxyVOC distribution is needed for regional air quality assessments. Reactive carbon released in form of VOCs is also put in the context of net ecosystem carbon exchange (NEE) and shown to account for as much as several per cent of the NEE. A quantitative understanding of the processes governing the release of oxyVOCs (e.g. diurnal, seasonal changes) remains a major challenge, and future leaf and canopy level studies will be needed for realistic parameterisations/predictions that can readily be incorporated in existing emission models.

#### A52D-04 1520h

##### About the Complexity of the Exchange of Oxygenated Volatile Organic Compounds Between Vegetation and the Atmosphere

Juergen Kesselmeier<sup>1</sup> (jks@mpch-mainz.mpg.de)

Uwe Kuhn<sup>1</sup> (kuhn@mpch-mainz.mpg.de)

Stefanie Rottenberger<sup>1</sup> (rottenbe@mpch-mainz.mpg.de)

Tamara Dindorf<sup>1</sup> (dindorf@mpch-mainz.mpg.de)

<sup>1</sup>Max Planck Institute for Chemistry, POB 3060, Mainz, RP 55128, Germany

Field and laboratory investigations of the exchange of the short-chain organic acids formic acid and acetic acid as well as their homologous aldehydes and ethanol are discussed. These compounds are released from and deposited to crop and tree species as found in several field experiments. Laboratory investigations under purified air conditions showed emission rates with significant differences under light and dark conditions, and a deposition was observed under certain conditions. The bi-directional exchange is significantly triggered by the ambient mixing ratios of both aldehydes and acids and exhibits a compensation point. Under field conditions emission and deposition was found. Acetaldehyde and ethanol are strongly emitted under root anoxia, as it occurs in flooded areas, especially in the tropics. Further studies are needed for generalization of the exchange of these compounds.

#### A52D-05 1540h INVITED

##### Source and Latitudinal Distributions of Select Oxygenated VOCs

Aaron L Swanson<sup>1</sup> (949-824-5457; aswanson@ea.oac.uci.edu)

Simone Meinardi<sup>1</sup> (949-824-5457; smeinard@uci.edu)

Donald R Blake<sup>1</sup> (949-824-4195; drblake@uci.edu)

Eric Apel<sup>2</sup> (apel@ucar.edu)

Rowland Sherwood F.<sup>1</sup> (949-824-6016; rowland@uci.edu)

<sup>1</sup>University of California Irvine, Dept. of Chemistry UC Irvine, Irvine, CA 92697, United States

<sup>2</sup>National Center for Atmospheric Research, Atmospheric Chemistry Division National Center for Atmospheric Research, Boulder, CO 80303

Oxygenated volatile organic hydrocarbons (OVOCs) are emitted to the atmosphere from many sources; biomass burning, fossil fuel combustion, and biogenic emissions are a few of the primary sources. Photochemical production is another major source of atmospheric OVOCs, however, the major sources for most OVOCs in the atmosphere are not well defined and even the atmospheric concentrations are only now becoming understood. Recent work in our laboratory suggests the potential for performing quantitative analyses of select OVOCs in whole air stainless steel canisters after collection and storage from between 5-30 days. An intercomparison with established OVOC measurement groups during the NASA GTE TRACE-P campaign demonstrated reasonable canister analysis capabilities for C3-C4 ketones and C2-C4 aldehydes [Swanson et al., IGAC 2002]. Methyl tert-butyl ether (MTBE) has also been identified as a stable analyte for inclusion in OVOC analysis. Using data from several airborne and surface projects a pseudo-global picture of latitudinal distributions for the select OVOCs can be defined. Source regions are also suggested within these latitudinal distributions.

URL: <http://fsr10.ps.uci.edu/GROUP/group.html>

#### A52D-06 1600h

##### Oxygenated Organic Chemicals in the Pacific Troposphere: Sources and Chemical Consequences

Robert B Chatfield<sup>1</sup> (650-604-5490;

chatfield@clio.arc.nasa.gov); Hanwant B Singh<sup>1</sup>

(650-604-6769; hsingh@mail.arc.nasa.gov); Alan

Fried<sup>2</sup> (303-497-1475; fried@ucar.edu); Mat J

Evans<sup>3</sup> (617-495-1591; mje@io.harvard.edu);

Daniel J Jacob<sup>3</sup> (617-495-1794;

djj@io.harvard.edu); Donald Blake<sup>4</sup>

(949-824-4195; drblake@uci.edu); Brian Heikes<sup>5</sup>

(zagar@notos.gso.uri.edu); Robert W Talbot<sup>6</sup>

(603-682-0322; robert.talbot@unh.edu); Glenn W

Sachse<sup>7</sup> (757-864-1566; G.W.Sachse@larc.nasa.gov)

<sup>1</sup>NASA Ames Research Center, MS 245 5, Moffett Field, CA 94035, United States

<sup>2</sup>NCAR, ACD Box 3000, Boulder, CO 80307, United States

<sup>3</sup>Harvard University, Pierce Hall, 29 Oxford Street, Cambridge, MA 02138, United States

<sup>4</sup>Univ. of California, Irvine, 570 Rowland Hall, Irvine, CA 92697

<sup>5</sup>Univ of Rhode Island, GSO South Ferry Road, Narragansett, RI 02882, United States

<sup>6</sup>Univ. of New Hampshire, ISEOS 39 College Road, Durham, NH 03824, United States

<sup>7</sup>NASA Langley Research Center, Mail Stop 468 100 NASA Road, Hampton, VA 23681

Airborne measurements of a large number of oxygenated organics were carried out in the Pacific troposphere (to 12 km) in the Spring of 2001 (Feb. 24-April 10). Gas chromatography measurements include acetaldehyde, propionaldehyde, acetone, methylethyl ketone, methanol, ethanol, PANs, and organic nitrates. Independent measurements of formaldehyde, peroxides, and tracers were simultaneously recorded. Highly polluted as well as surprisingly clean air masses were sampled. Oxygenated organics were abundant in the clean troposphere and were also greatly enhanced in the outflow regions from Asia. Carbonyls sequester NOx throughout the troposphere and are a reactive intermediate responsible for a large amount of formaldehyde.

It is difficult to explain the large abundances of aldehydes in the background troposphere, and we examine the chemical repercussions of these high concentrations. In clean air, the reaction pathways from acetaldehyde to formaldehyde take more time, and this is reflected in a smaller sampled correlation of their concentrations. The atmospheric behavior of acetone, methylethyl ketone, and methanol is generally indicative of their common terrestrial sources. Including these observed high concentrations of aldehydes somewhat improve simulated HOx chemistry. These data are being analyzed statistically and with photochemical models and results will be presented, particularly as they describe source of the ubiquitous acetaldehyde.

#### A52D-07 1620h

##### World Calibration Center for VOC (WCC-VOC), a new Facility for the WMO-GAW-Programme

Bernhard - Rappenglueck (+49 8821-183-230; Bernhard.Rappenglueck@imk.fzk.de)

Institute of Meteorology and Climate Research, Atmospheric Environmental Division (IMK-IFU), Forschungszentrum Karlsruhe, Kreuzackbahnstr. 19, Garmisch-Partenkirchen D-82467, Germany

Volatile organic compounds (VOC) are recognized to be important precursors of tropospheric ozone as well as other oxidants and organic aerosols. In order to design effective control measures for the reduction of photooxidants, photochemical processes have to be understood and the sources of the precursors known. Reliable and representative measurements of VOCs are necessary to describe the anthropogenic and biogenic sources, to follow the photochemical degradation of VOCs in the troposphere. Measurement of VOCs is of key importance for the understanding of tropospheric chemistry.

Tropospheric VOCs have been one of the recommended measurements to be made within the GAW programme. The purpose will be to monitor their atmospheric abundance, to characterize the various compounds with regard to anthropogenic and biogenic sources and to evaluate their role in the tropospheric ozone formation process. An international WMO/GAW panel of experts for VOC measurements developed the rational and objectives for this GAW activity and recommended the configuration and required activities of the WCC-VOC. In reflection of the complexity of VOC measurements and the current status of measurement technology, a staged approach was adopted.

Stage 1 measurements: C2-C9 hydrocarbons, including alkanes, alkenes, alkynes, dienes and monocyclics. (The WCC-VOC operates currently under this mode). Stage 2 measurements: C10-C14 hydrocarbons, including higher homologs of the Stage 1 set as well as biogenic hydrocarbon compounds. Stage 3 measurements: Oxygenated VOCs, including alcohols, carbonyls, carboxylic acids.

The Quality Assurance/Science Activity Centre (QA/SAC) Germany currently has established the World Calibration Centre for VOC (WCC-VOC). The WCC-VOC has operated in the research mode and has become operational recently. From now on, the WCC-VOC conducts one round-robin calibration audit per year at all global stations that measure VOCs and assists other stations in setting up VOC measurement capabilities. Furthermore, the WCC-VOC will promote inter-comparison experiments with networks related to other programmes, notably EMEP and IGAC.

## A52D-08 1635h

## Advances in Measurement of Carbonyls in Aerosols.

M. Judith Charles<sup>1</sup> (mjcharles@ucdavis.edu); Chris Jakober<sup>1</sup> (cajakober@ucdavis.edu); Reggie Spaulding<sup>1</sup> (rspauldo@selway.umd.edu); Peter Green<sup>2</sup> (pggreen@ucdavis.edu); Hugo Destaillets<sup>2</sup> (hugodest@hotmail.com); John M. Hughes<sup>3</sup> (johnmhughes@agilent.com)

<sup>1</sup>Department of Environmental Toxicology, University of California, Davis, Davis, CA, CA 95616, United States

<sup>2</sup>Department of Civil and Environmental Engineering, University of California, Davis, One Shields Avenue University of California, Davis, Davis, CA 95616, United States

<sup>3</sup>Agilent Technologies, 4847 Hopyard Road, Ste 4, PMB388, Pleasanton, CA 94588, United States

Chamber studies establish the formation of highly polar oxygenated species from the reaction of anthropogenic and biogenic hydrocarbons with hydroxyl radicals or ozone. A paucity of data exists however on the generation and fate of these organics in the ambient atmospheric environment. This is primarily due to the absence of suitable analytical methods. To address limitations of existing methods, we developed methods that rely on O-(2,3,4,5,6)-pentafluorobenzylhydroxylamine (PFBHA), and bis(trimethylsilyl) trifluoroacetamide (BSTFA) in concert with GC/ion trap mass spectrometry (GC/ITMS) to identify and quantify carbonyl, dicarbonyl and hydroxy carbonyl photooxidation products in aerosols at part-per-trillion (pptv) levels. We also optimized and evaluated a mist chamber to sample carbonyls and multi-functional carbonyls with 10 minute sampling times. We applied the method to identify and quantify 2-hydroxy-2-methyl propanal (2-HMPR), a proposed photooxidation product of 2-methyl-3-buten-2-ol (MBO) in the Blodgett Forest, CA. The average 2-HMPR/MBO mixing ratio was 0.33 0.25, which is reasonable since the expected yield of 2-HMPR from the hydroxyl radical oxidation of MBO is 0.19-0.35. Further method development in our laboratory is exploring the employment of HPLC/atmospheric pressure chemical ionization (APCI) mass spectra to identify model aliphatic and aromatic carbonyls (the major classes were aldehydes, ketones, dicarbonyls, and quinones) in aerosols. The data indicate the potential for pentafluorobenzyl derivatization in concert with GC/ITMS and HPLC/ITMS to measure a broad range of carbonyls.

## A52E MCC: 102 Friday 1330h

## Transport and Effects of Anthropogenic Pollutants: ITCT

## 2K2, Including PEACE I (joint with GC)

Presiding: Y Kondo, The University of Tokyo; D Parrish, NOAA Aeronomy Laboratory

## A52E-01 1330h INVITED

## Chemical air mass characteristics along the West Coast of the United States during April 2002, Results from ITCT 2002

M. Trainer<sup>1</sup> (303-497-5295; trainer@al.noaa.gov); E. Atlas<sup>2</sup>; O. Cooper<sup>1,3</sup>; J. deGouw<sup>1,3</sup>; S. Donnelly<sup>2</sup>; E. Dunlea<sup>1,3</sup>; F. Fehsenfeld<sup>1,3</sup>; F. Flocke<sup>2</sup>; J. Holloway<sup>1,3</sup>; G. Huebler<sup>1,3</sup>; D. Nicks<sup>1,3</sup>; A. Neuman<sup>1,3</sup>; J. Nowak<sup>1,3</sup>; D. Parrish<sup>1</sup>; J. Roberts<sup>1</sup>; T. Ryerson<sup>1</sup>; S. Schaffner<sup>2</sup>; V. Stroud<sup>2</sup>; C. Warneke<sup>1,3</sup>

<sup>1</sup>NOAA Aeronomy Laboratory, 325 Broadway R/AL4, Boulder, CO 80305, United States

<sup>2</sup>National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307, United States

<sup>3</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309-0216, United States

In April-May of 2002 the concentration of ozone, ozone precursors, and other photochemical products were measured during 13 flights on board of the NOAA WP3 aircraft over the Eastern Pacific Ocean and the Western United States as part of the Intercontinental Transport and Chemical Transformation (ITCT) experiment. The experiment characterized the long range transport across the Pacific and the addition of fresh emissions along the west coast of the United States.

Extensive pollution layers were observed on several of the flights and allow the study of the chemical transformations during distinct transport regimes.

## A52E-02 1350h INVITED

## Impact of Asian Outflow on O3 and its Precursors Over Japan in January 2002

Nobuyuki Takegawa<sup>1</sup> (81-3-5452-5144; takegawa@atmos.rcast.u-tokyo.ac.jp); Yutaka Kondo<sup>1</sup> (81-3-5452-5145; kondo@atmos.rcast.u-tokyo.ac.jp); Makoto Koike<sup>2</sup> (81-3-5841-4595; koike@eps.s.u-tokyo.ac.jp); Kazuyuki Kita<sup>3</sup> (81-29-228-8400; kita@env.sci.ibaraki.ac.jp); Donald R Blake<sup>4</sup> (1-949-824-4195; dblake@orion.oac.uci.edu); Tomonori Watai<sup>5</sup> (81-298-50-2969; watai.tomonori@nies.go.jp); Shuji Kawakami<sup>6</sup> (81-3-6221-9000; kawakami@eorc.nasda.go.jp); Tomoko Shirai<sup>6</sup> (81-3-6221-9000; shirai@eorc.nasda.go.jp); Toshihiro Ogawa<sup>6</sup> (81-3-6221-9000; togawa@eorc.nasda.go.jp)

<sup>1</sup>Research Center for Advanced Science and Technology, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan

<sup>2</sup>Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

<sup>3</sup>Department of Environmental Sciences, Ibaraki University, 2-1-1 Bunkyo, Mito 310-8512, Japan

<sup>4</sup>Department of Chemistry, University of California, Irvine, 516 Rowland Hall, Irvine, CA 92697-2025, United States

<sup>5</sup>National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-8506, Japan

<sup>6</sup>Earth Observing Research Center, National Space Development Agency of Japan, 1-8-10 Harumi, Tokyo 104-6023, Japan

The Pacific Exploration of Asian Continental Emission Phase A (PEACE-A) aircraft measurement campaign was conducted over Japan in January 2002. In situ aircraft measurements of ozone (O<sub>3</sub>), carbon monoxide (CO), reactive nitrogen (NO and NO<sub>y</sub>), carbon dioxide (CO<sub>2</sub>) non-methane hydrocarbons (NMHCs), and other species were made during PEACE-A. The flights were conducted over the Japan Sea (35-45 N) and East China Sea (20-35 N), providing useful data set to investigate the horizontal and vertical distributions of trace gases in these regions during wintertime. Large enhancements of CO, CO<sub>2</sub>, NO<sub>y</sub>, and NMHCs were frequently observed in the boundary layer (< 4 km), while the mixing ratios of these species in the free troposphere were fairly constant. The origins of air masses sampled in the boundary layer are roughly estimated using backward trajectories. In addition, we use dCO/dCO<sub>2</sub> ratios in the observed air masses (linear regression slope of CO-CO<sub>2</sub> correlation) as a diagnostics of combustion types of emission sources. The air masses sampled at 0-2 km over the Japan Sea were mostly transported from northern China and dominated by relatively high combustion efficiency sources (dCO/dCO<sub>2</sub> = 0.02-0.04). By contrast, the air masses sampled at 2-4 km over the East China Sea were mostly transported from southern China and significantly affected by lower combustion efficiency sources (dCO/dCO<sub>2</sub> ratios = 0.04-0.15). Correlations among CO, NO<sub>x</sub>, NO<sub>y</sub>, and O<sub>3</sub> are discussed in terms of the difference in the dCO/dCO<sub>2</sub> ratios to evaluate the contribution from each type of emission source to the regional budgets of reactive nitrogen and O<sub>3</sub> during the PEACE-A period.

## A52E-03 1410h INVITED

## Forecasting and Modeling Trans-Pacific Transport of Asian Pollution in ITCT2K2

Qinbin Li<sup>1</sup> (617-496-9428; qli@io.harvard.edu)  
Daniel Jacob<sup>1</sup> (617-495-1794; dj@io.harvard.edu)

Robert Yantosca<sup>1</sup> (617-496-9424; bmy@io.harvard.edu)

Rynda Hudman<sup>1</sup> (617-495-8455; hudman@fas.harvard.edu)

Lyatt Jaegle<sup>2</sup> (206-685-2679; jaegle@atmos.washington.edu)

<sup>1</sup>Harvard University, 29 Oxford St., Cambridge, MA 02138

<sup>2</sup>University of Washington, Department of Atmospheric Sciences, University of Washington, Box 351640, Seattle, WA 98195

We used the GEOS-CHEM global 3-D model of tropospheric chemistry driven by forecast meteorological fields from the Goddard Earth Observing System (GEOS) to forecast transpacific transport events

during the ITCT2K2 aircraft mission over the west coast in April-May 2001. ITCT2K2 focused on characterizing Asian inflow to North America. The forecast simulations transported five tagged CO tracers from different source regions. The model successfully predicted several transpacific transport events that were confirmed by in situ observations. We further investigate the performance of the model forecasts by comparing forecast results to the observations and to the post-mission full-chemistry simulations driven by re-analysis meteorological fields. The model is evaluated with the in situ aircraft and ground measurements from both ITCT2K2 and the PEACE-B aircraft mission. The chemical evolution of Asian pollution during transport and the seasonal variations of transpacific transport are investigated.

## A52E-04 1430h INVITED

## Measurements at Trinidad Head, California during ITCT 2K2: Were Asian emissions observed?

Allen H Goldstein<sup>1</sup> (510-643-2451; ahg@nature.berkeley.edu)

Dylan B Millet<sup>1</sup> (510-643-2460; dylan@atmos.berkeley.edu)

Megan McKay<sup>1</sup> (510-642-9732; megan@nature.berkeley.edu)

<sup>1</sup>Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA 94720-3110, United States

Measurements for a wide suite of trace gases and aerosols were made at Trinidad Head, California, from 19 April through 22 May 2002 as part of the NOAA ITCT research program. This talk will provide an introduction to the ITCT ground site, and will address one of the major scientific questions for the measurement campaign: What is the influence of Asian emissions on air masses entering North America in springtime? CO has been identified as one of the most useful tracers to look for Asian emission plumes because of its relatively long atmospheric lifetime and its emission from all combustion sources. Before assessing the influence of long range transport on the observations, local/regional influences must be filtered out of the data set. Methyl Tertiary Butyl Ether (MTBE) serves as a useful tracer because its emissions are associated with use as a fossil fuel additive in North America and its atmospheric lifetime is a few days. CO<sub>2</sub> and radon also serve as useful tracers of regional continental influences, particularly at night when their concentrations are enhanced due to emissions under stable atmospheric conditions. Filtering out local influences removed 25 to 50% of the observations, depending on the constraints applied, and it decreased the mean CO mixing ratio by 4% to 147 ppb. After filtering the data to remove local influences, the variability and the absolute concentration in the remaining CO data can be examined for Asian influence by comparison with forecast models run as part of the ITCT campaign such as GEOS-CHEM (Harvard), MOZART (NCAR), and CFORS (IOWA). The observed variability in the filtered CO data is in general well simulated by the models, showing a dominant influence from North American fossil fuel emissions. Distinct Asian pollution plumes could not be identified in these ground based observations, because the magnitude of CO variability due to Asian emissions was small relative to the total observed variability. However, the relative contributions of emission sources to the total observed CO could be approximated through comparison of the measurements and model results. Comparison of all the ground based trace gas and aerosol measurements with the model results should utilize similar techniques to remove local influences that are unlikely to be captured by the models. Filtering out local influences decreases mean concentrations of aerosols and ozone precursors such as volatile organic compounds and oxides of nitrogen, but it increases the mean concentration of ozone.