to the rural location of the AIRMAP sites, it appears that the depletion is mainly due to dry deposition with an occasional contribution of titration by NO. The relative enhancements of CO_2 and VOCs relative to urban tracers such as C_2HCl_3 and C_2Cl_4, which have minimal local sources, provides information on the magnitude and nature of natural and anthropogenic sources.

A41A-06 0915h

Regional Relationship between CO and O_3 in New England

Huiting Mao[1] (6038620121; hmao@typhoon.sr.unh.edu)

Robert Talbot[1] (6038621546; robert.talbot@unh.edu)

[1]University of New Hampshire, Morse Hall, 39 College Road, Durham, NH 03824, United States

The seasonality and interannual variability in the mixing ratios of ozone (O_3) and carbon monoxide (CO) and their inter-relationship were investigated at the rural low elevation site Thompson Farm (TF) and the hill site Castle Springs (400 m above ground level) in southern New Hampshire using continuous observations (2001-2003) from the Atmospheric Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) program at University of New Hampshire (UNH). Our results show distinct site-dependent characteristics in temporal variations on various time scales in O_3 and CO and particularly large interannual variability in fall and winter at both sites. The grouped O_3 and CO data, based on wind speed and direction over different time periods of the day, showed largely varying probability distribution functions (PDF). It was found that only 10% of the seasonal observations formed a positive O_3-CO linear correlation, leading to an estimate of 370 M moles d^{-1} for O_3 export from the northeastern U.S. This estimate is three times smaller than previous studies. We used a ratio analysis (NO/NO_y and NO_y/CO) to show that the linear O_3-CO relationships were a result of multiple processes rather than simply either photochemical or depositonal loss processes as proposed by previous work. One of the most important features of the O_3-CO relationship is the lower CO boundary, for which we attempeted to provide physical and chemical interpretations.

A41A-07 0930h

Propane and Light Alkene Enhancements at Thompson Farm: Impact on Local and Regional Ozone Production

Barkley C. Sive[1] (603-862-3132; bcs@ccrc.sr.unh.edu)

Yong Zhou[1]

Rachel S. Russo[1]

Robert W. Talbot[1]

[1]Climate Change Research Center, Institute for the Study of Earth, Oceans and Space, University of New Hampshire, Durham, NH 03824, United States

Continuous measurements of nonmethane hydrocarbons (NMHCs) at Thompson Farm in Durham, NH have revealed that large enhancements of propane (approximately 10-30 ppbv) are observed regularly at this sampling site. The large propane enhancements are associated with unique boundary layer dynamics causing an extremely low-level nocturnal inversion allowing for nighttime pollutant buildup. During these events, propane is the dominant NMHC with mixing ratios reaching levels that are at least 2-3 times larger than ethane. Further investigation has revealed that the propane events are not only occurring at Thompson Farm, but throughout the NH seacoast region; spanning an area from Brentwood, NH to Kittery, ME, yet is likely to be much more widespread. In addition, substantial increases in other reactive gases such as NO, CO, ethene, propene and the butanes are observed during these episodes, all of which largely impact daytime ozone production. Currently, the main source of the propane in this region remains unidentified. The local and regional impact on ozone production in New England from the large-scale propane and reactive alkene enhancements will be discussed.

A41A-08 0945h

Aerosol Mass Spectrometer measurements on board the DOE G1 during NEAQS

Tim Onasch[1] (978-663-9500; onasch@aerodyne.com)

John Jayne[1] (jayne@aerodyne.com)

Manjula Canagaratna[1] (mrcana@aerodyne.com)

Doug Worsnop[1] (worsnop@aerodyne.com)

Alex Laskin[2] (alexander.laskin@pnl.gov)

[1]Aerodyne Research Inc., 45 Manning Road, Billerica, MA 02155, United States

[2]Pacific Northwest National Laboratory, P.O.Box 999, MSIN K8-88, Richland, WA 99352, United States

An Aerosol Mass Spectrometer (AMS) was successfully deployed on board the DOE G1 research aircraft during the New England Air Quality Study (NEAQS), a multi agency campaign designed to characterize gas and aerosol pollutants passing through the northeastern U.S. and the outflow over the Atlantic Ocean. The addition of the AMS to the G1 instrument payload added the capability to collect real-time (seconds timescale) data on size and chemically speciated aerosol mass loadings for aerosol containing nitrate, sulfate, ammonium, chloride and organic species. Flight tracks were chosen to provide reasonable lateral coverage of the North Eastern region and important vertical profiles of ambient aerosol. Comparisons between the aerosol chemical properties measured from the G1 platform and similar aerosol properties measured at several ground sites, including on the Ron Brown research vessel, illustrate the layering of air masses and the varying sources and transportation pathways for particulate pollution. Ground level particulate measurements appear significantly influenced by regional sources. For example, bimodal organic carbon dominated size distributions consistent with freshly generated (automobile) emission were observed on flights that passed over NY city metropolitan area. In contrast, vertical profiles identify layers of high mass loadings of monomodal particulate sulfate aerosol accompanied by low SO2 levels that are consistent with aged/transported air. Back trajectory analyses correlate these observations with source emitters outside of the North Eastern region.

A41B MCC: 3016 Thursday 0800h

The Organic Aerosol Component: Impact on Reactivity, Optical Properties, Hygroscopicity, and Cloud-Condensation Properties I

(joint with AE)

Presiding: **G D Smith,** University of Georgia**; T Mentel,** Institut für Chemie und Dynamik der Geosphäre Juelich

A41B-01 0800h INVITED

New Mass Spectrometric Tools and Their Application to Organic Aerosol Studies

Murray V Johnston[1] (302-831-8014; mvj@udel.edu)

Michael P Tolocka[1] (302-831-4265; mpt@udel.edu)

Berk Oktem[1] (302-831-4265; oktem@udel.edu)

[1]University of Delaware, Chemistry and Biochemistry Department, Newark, DE 19716, United States

The organic fraction of airborne particulate matter is a complex mixture of compounds with a combined concentration on the order of 1 to 10 micrograms per cubic meter. Thousands of compounds may be present in a sample, with individual concentrations between about 0.1 and 10 nanograms per cubic meter. The complexity and low concentration levels associated with ambient samples carry over into laboratory investigations and present a significant analytical challenge. We have been exploring the use of new methods for off-line and on-line analysis of organic matter in particles to study aerosol reactions. Off-line analysis is performed with electrospray ionization and matrix-assisted laser desorption ionization in combination with exact mass measurements and tandem mass spectrometry. These methods have allowed us to characterize hundreds of high molecular weight compounds formed by secondary polymerization of the primary products of alpha-pinene ozonolysis. Polymerization provides a reasonable explanation of how the volatile primary products are able to partition to the particle phase. On-line measurements are made with an aerosol mass spectrometer that provides "soft" ionization (i.e. very little fragmentation) of organic compounds. Soft ionization is needed to reduce the spectral congestion that is normally observed from complex samples. On-line measurements permit reaction kinetics to be studied. Experiments currently underway that will discussed include the kinetics of acid-catalyzed polymerization in particles and the effect of surface organic layers on the reactive uptake of nitric acid into aqueous sodium chloride particles.

URL: http://www.udel.edu/chem/johnston/

A41B-02 0823h INVITED

Reactive Heterogeneous Chemistry on Organic Aerosols: Two Case Studies

Jonathan Abbatt[1] (416-946-7358; jabbatt@chem.utoronto.ca)

Christine Braban[1] (cbraban@chem.utoronto.ca)

Keith Broekhuizen[1] (kbroekhu@chem.utoronto.ca)

Troy Thornberry[1] (tthornbe@chem.utoronto.ca)

Joel Thornton[1] (jthornto@chem.utoronto.ca)

[1]University of Toronto, Department of Chemistry 80 St. George St., Toronto, ON M5S 3H6, Canada

Two sets of laboratory studies will be discussed to illustrate the impact that heterogeneous chemistry involving tropospheric organic aerosols may have on both the gas-phase composition of the atmosphere and the chemical nature of the particles themselves. In the first case, the reactive uptake coefficient for the hydrolysis of dinitrogen pentoxide (N2O5) on organic aerosols has been measured in an entrained aerosol flow tube coupled to a Chemical-Ionization Mass Spectrometer (CIMS). The general observation is that the reaction on aqueous malonic acid aerosols behaves in an analogous manner to that on aqueous inorganic salts, i.e. the uptake coefficient shows a linear dependence on the particle water content up to 50% relative humidity (RH), at which point the effect saturates. In addition, there is evidence for the kinetics being dependent on both the size of the particles and the levels of dissolved nitrate. By contrast, the N2O5 hydrolysis kinetics on solid azelaic acid particles are too slow to be atmospherically significant, even at 85% RH. In the second case, the kinetics and product yields from the oxidation of liquid oleic acid by ozone have been studied in considerable detail, with emphasis on the quantification of gas-phase products (nonanal) by CIMS and water-soluble species by HPLC/Electrospray-Ionization Mass Spectrometry (azelaic acid, nonanoic acid). The atmospheric importance of these results will be discussed, in particular with respect to the role of organic aerosol oxidation as a source of cloud condensation nuclei.

A41B-03 0845h

Preparation And Characterization Of Organic Coatings Of Variable Thickness On Inert Cores And Their Chemical Reactions With Ozone

Yasmine Katrib-Kouchnir[1] (ykatrib@deas.harvard.edu); Scot T. Martin[1] (smartin@deas.harvard.edu); Yinon Rudich[2] (Yinon.Rudich@weizmann.ac.il); Haizheng Zhang[3] (zhanghd@bc.edu); Paul Davidovits[3] (paul.davidovits@bc.edu); John T. Jayne[4] (jayne@aerodyne.com); Douglas R. Worsnop[4] (worsnop@aerodyne.com)

[1]Harvard University, 29 Oxford Street, Cambridge, MA 02138, United States

[2]Weizmann Institute, Dept.of Environmental Sciences, Rehovot 76100, Israel

[3]Boston College, Dept.of Chemistry, Chestnut Hill, MA 02467, United States

[4]Aerodyne Research, Inc, 45 Manning Road, Billerica, MA 08121-3976, United States

Recent studies have emphasized the role of organic atmospheric particles in cloud formation, radiative forcing, and health effects. Quantification of these effects is limited because the compositions, morphologies, and chemical reactivities of organic particles are poorly understood. Laboratory studies are motivated to understand and quantify complex particles and their processes. A critical unknown is the heterogeneous chemistry that depends upon and leads to changes in the morphological and chemical complexity of the particles. Our work is focused on ozone heterogeneous chemistry as a general proxy for understanding the role of layer thickness and diffusivity in chemical transformations of surface and interior layers of complex particles. Our approach for preparing the particles is as follows. Polystyrene latex (PSL) particles are atomized into an aerosol flow. Oleic acid particles are formed by vapor condensation from a separate flow through a heated liquid reservoir. When the flows are mixed, the PSL and oleic acid particles are externally mixed. An oven having a linear hot-to-cold temperature gradient is employed to first evaporate the oleic acid particles in the hot region, which is followed by condensation in the cold region onto the surface of the PSL particles acting as heterogeneous nuclei. Internally mixed particles result. The apparatus capability is the controlled and reproducible generation of particles having 2 to 30 nm surface layers of oleic acid and 100 nm polystyrene latex (PSL) cores. The temperature of the reservoir,

the gradient of the furnace, and the adjustable flow are the levers controlling the layer thickness of oleic acid. The particles are characterized in parallel by their electric mobility in a TSI Scanning Mobility Particle Sizer (SMPS) and their aerodynamic diameter in an Aerodyne Aerosol Mass Spectrometer (AMS). Diameter and oleic acid coating mass agree well by the two methods. The particle shape factor is approximately unity, indicating spherical particles. Chemical reactivity of the particles with ozone at 0 and 85% relative humidity (RH) is studied. Changes in particle diameter are studied by SMPS and AMS. Loss of parent oleic acid is observed in the mass spectrum collected by the AMS. These factors are studied as a function of oleic acid layer thickness. Results of these measurements will be presented.

A41B-04 0900h

Direct Observation of the Kinetics of an Atmospherically Important Reaction at the Air-Aqueous Interface

Baagi Mmereki[1] (bmmereki@chem.utoronto.ca)

D. James Donaldson[1] (jdonalds@chem.utoronto.ca)

[1]Department of Chemistry University of Toronto, 80 St. George St., Toronto, Ont M5S 3H6, Canada

Many atmospherically important chemical processes are believed to occur at the interface between the air and aqueous phases. We report direct measurements of the kinetics of a reaction between gas phase ozone and anthracene adsorbed at the air-aqueous interface by monitoring the laser-induced fluorescence of the adsorbed anthracene. The reactions at the "clean" air-water interface and at an interface consisting of one monolayer of 1-octanol were studied. For both cases, the reaction follows a Langmuir-Hinshelwood mechanism, in which ozone first adsorbs to the air-aqueous interface, and then reacts with adsorbed anthracene. The estimated reactive uptake coefficient at the clean air-water interface is about 6 x 10-8 for typical atmospheric ozone concentrations; this value increases by about a factor of 5 when the water surface is coated with a monolayer of 1-octanol.

A41B-05 0915h

The importance of the organic aerosol component for the passivation of aqueous atmospheric particles

Astrid W Kiendler-Scharr[1] (011 49 2461 61 4185; a.kiendler-scharr@fz-juelich.de)

Mareike Folkers[1] (011 49 2461 61 4185; m.folkers@fz-juelich.de)

Thomas F Mentel[1] (011 49 2461 61 6921; t.mentel@fz-juelich.de)

Andreas Wahner[1] (011 49 2461 61 5932; a.wahner@fz-juelich.de)

[1]ICG-II: Troposphäre, Forschungszentrum Jülich, Jülich 52425, Germany

Secondary tropospheric particles are often mixtures of aqueous electrolytes and soluble organic components or surfactants. The uptake kinetics of e.g. N_2O_5 and the thermodynamics of binary and higher mixtures of aqueous electrolytes are quite well understood. In contrast, not much is known on a quantitative basis about the modification of these properties by organic aerosol components. The hydrolysis of N_2O_5 on aqueous aerosol surfaces of mixed inorganic and organic aerosols was used to probe the surface reactivity/water availability. The experiments were performed in the large Aerosol Chamber at the FZ-Jülich at room temperature and 60 - 70 % relative humidity. The ozonolysis of α-pinene, myrcene, limonene and isoprene was utilized to condense organic components on NH_4HSO_4 particles. The build up of the organic component was monitored by Aerosol Mass Spectrometry (Aerodyne AMS). In the terpene experiments the hydrolysis of N_2O_5 on the particle surface was diminished by factors of 2 to 30 compared to the pure inorganic salt (reaction probability $\gamma_{N2O5} = 0.02$). The degree of passivation depends on the organic load and the specific terpene. For purely organic particles from α-pinene ozonolysis, which are not hygroscopic, the reaction probabilty γ_{N2O5} is 0.00045. In the isoprene experiment the main known ozonolysis products in the particulate phase are water soluble α-dicarbonyls. Despite the low organic mass fraction of only 6% the hydrolysis on this mixed organic/inorganic aerosol is significantly retarded by a factor of 2 ($\gamma_{N2O5} = 0.01$). We were able to identify mass fragments of methyl glyoxal and pyruvic acid in the particles. Moreover, there is indication by the AMS that higher molecular components are also present in the particles, possibly formed in the particulate phase. Specific addition even of high loads of the single component methyl glyoxal to $(NH_4)_2SO_4$ particles did only show a smaller effect ($\gamma_{N2O5} = 0.014$) compared to the "real" and complex ozonolysis products of isoprene. Our findings demonstrate the importance of oxidized large biogenic organics for passivation (reduced water availability at the surface) of mixed particles. But also small molecules can contribute to passivation if condensation reactions takes place which form larger (ampholytic) molecules (M. Jang et al., Science, 298, 814-817, 2002) The studies are part of the EC CASOMIO project.

A41B-06 0930h

Fatty Acids as Surfactants on Aerosol Particles

Heikki Tervahattu[1] (+1-303-786-0398; heikki.tervahattu@helsinki.fi)

Jyrki Juhanoja[2] (+358-2-2827782; jyrki.juhanoja@topanalytica.com)

Jarkko Niemi[3] (+358-9-19158841; jarkko.v.niemi@helsinki.fi)

[1]Nordic Envicon Oy, Koetilantie 3, Helsinki FIN-00710, Finland

[2]Top Analytica Ltd, Ruukinkatu 4, Turku FIN-20540, Finland

[3]University of Helsinki, Department of Limnology and Environmental Sciences, P.O.Box 27, Helsinki FIN-00014, Finland

Fatty acids (n-alcanoic acids) are common compounds in numerous anthropogenic and natural emissions. According to Rogge et al. (1993), catalyst-equipped automobiles emitted more than 600 μg km-1 of fatty acids which was over 50% of all identified organics in fine aerosol emissions. Coal burning produces fatty acids ranging from about 1700 mg kg-1 for bituminous coal to over 10000 mg kg-1 for lignite (Oros and Simoneit, 2000). Similarly, biomass burning is an important source for aerosol fatty acids. They are the major identified compound group in deciduous tree smoke, their total emission factor being measured as 1589 mg kg-1 which was 56of all identified organic compounds (Oros and Simoneit, 2001a). Large amounts of fatty acid are also emitted from burning of conifer trees and grass (Oros and Simoneit, 2001a; Simoneit, 2002). Fatty acids have been reported to be major constituents of marine aerosols in many investigations (Barger and Garrett, 1976; Gagosian et. al, 1981; Sicre et al., 1990; Stephanou, 1992). It has been suggested that as the marine aerosol particles form, they acquire a coating of organic surfactants (Blanchard, 1964; Gill et al., 1983; Middlebrook et al., 1998; Ellison et al., 1999). Amphiphilic molecules, including lipids, can be assembled as monomolecular layers at air/water interfaces as well as transported to a solid support. Recently, we could show by time-of-flight secondary ion mass spectrometry that fatty acids are important ingredients of the outermost surface layer of the sea-salt aerosol particles (Tervahattu et al., 2002). In their TOF-SIMS studies on the surface composition of atmospheric aerosols, Peterson and Tyler (2002) found fatty acids on the surface of Montana forest fire particles. In this work we have studied by TOF-SIMS the surface chemical composition of aerosol particles emitted from field fires in the Baltic and other East European countries and transported to Finland as well as aerosol particles transported from Russian forest and peat fires. Fatty acids were commonly observed on the surface layer of these particles. The chain length composition was characteristic to each emission source. In our previous work (Tervahattu et al., 2002), fatty acids on sea-salt particles were originated from dead sea plankton organisms with major peaks ranging from C14 to C18 and maximum at C16 (palmitic acid). Major peaks on the surface of forest fire particles ranged from C16 to C30 with the maximum at C24. This composition indicates the involvement of the smoke from both conifer trees and peat (Oros and Simoneit, 2000; 2001b). On the other hand, TOF-SIMS analysis of the surface of field fire particles showed major peaks from C14 to C30 with two maximums at C16 (highest intensity) and C22. It was concluded that the results indicate emissions from both grass burning and fossil fuels (Simoneit, 2002; Oros and Simoneit, 2000). The presence of surface film on aerosol particles may have an impact on their chemical, physical and optical properties and change their role in light scattering and as cloud condensation nuclei as well as interactions with human tissue.

A41B-07 0945h

A Comparative Study of Organic Aerosol Models Using Molecular Dynamics Simulations

John Silvio Vieceli[1] (949-824-9921; jvieceli@uci.edu)

Douglas Tobias[1] (949-824-4295; dtobias@uci.edu)

[1]University of California, Irvine, Department of Chemistry, Irvine, CA 92697, United States

In order to understand the kinetics and mechanisms of organic aerosol processing by gas phase oxidants, various experimental models for the organic aerosols are used. Despite the progress made using these models, a molecular perspective of the relationship between the model structure and the observed dynamics is difficult to obtain experimentally. Molecular dynamics simulations can be used to study organic aerosol models at a molecular level and complement the experimental work. In particular, this presentation will focus on using simulations to compare the collision dynamics of gas phase ozone with alkenes in three different models of organic aerosols. The three model systems include the organic liquid 1-tetradecene, a self-assembled monolayer composed of 1-octene and a phospholipid monolayer adsorbed at the air/water interface. In each system, the collision rate between ozone and the double bonds is determined by an interplay of structural and dynamic factors. These factors include the density of double bonds in the system, the exposure of double bonds at the surface and the length of time ozone is trapped at the interface. The results also emphasize the importance of determining which model most accurately describes atmospheric organic aerosols.

A

A41C MCC: Level 2 Thursday 0830h

Results From the SOLVE II/VINTERSOL Mission I Posters

(joint with C)

Presiding: **M R Schoeberl,** NASA Goddard Space Flight Center**; L R Poole,** NASA Langley Research Center

A41C-0701 0830h POSTER

SAGE III Measurement System Validation

Michael Pitts[1] (757 864-2693; Michael.C.Pitts@nasa.gov)

Larry Thomason[1] (l.w.thomason@larc.nasa.gov)

Brian Wenny[2] (b.n.wenny@larc.nasa.gov)

Sam Yee[3] (Sam.Yee@jhuapl.edu)

Joseph Zawodny[1] (j.m.zawodny@larc.nasa.gov)

[1]NASA Langley Research Center, Mail Stop 435, Hampton, VA 23681, United States

[2]Science Applications International Corportation, One Enterprise Pkwy, Hampton, VA 23666, United States

[3]Applied Physics Lab, Johns Hopkins University, 11100 Johns Hopkins Rd., Laurel, MD 20723-6099, United States

The Gas and Aerosol Measurement Sensor (GAMS) and the Langley Airborne A-band Spectrometer (LAABS) were flown together aboard the NASA DC-8 aircraft during the Second SAGE III Ozone Loss and Validation Experiment-2 (SOLVE-2) campaign. The instruments were co-aligned using a common pointing system to track the sun through a side-viewing window on the DC-8 and successfully acquired spectra during the sunlit portions of twelve science flights. GAMS is a solar spectrometer that measures line-of-sight transmission at 1024 channels from approximately 430 nm to 1030 nm. LAABS is an 800-channel high-resolution spectrometer that measures the O2 A-band feature centered near 762 nm with 0.029-nm spectral resolution. Utilizing a measurement approach similar to SAGE III, the GAMS/LAABS experiment is focused on the assessment of the SAGE III line-of-sight transmission, ozone, and O4 measurements. This data will also permit thorough testing and intercomparisons of SAGE III solar and lunar retrieval algorithms and the SAGE III O2 A-band forward model. In this paper, we present preliminary results from the GAMS/LAABS experiment for SOLVE-2.

A41C-0702 0830h POSTER

Odin/SMR Limb Observations of Stratospheric Trace Gases During the 2002-03 Northern Hemisphere Winter

Joachim Urban[1] (+33/557/776139; urban@obs.u-bordeaux1.fr); Nicolas Lautié[2]; Eric Le Flochmoën[1]; Eric Dupuy[1]; Patrick Eriksson[2]; Carlos Jimenez[2]; Jérôme de La Noë[1]; Donal Murtagh[2]; Michael Olberg[2]; Philippe Ricaud[1]; Urban Frisk[3]

[1]Observatoire Aquitain des Sciences de l'Univers, L3AB, 2, rue de l'Observatoire, B.P. 89, Floirac 33270, France

[2]Global Environmental Measurements Group, Chalmers University of Technology, Göteborg 412 96, Sweden