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Volatile organic compounds (VOCs) and some of their oxidants (O_3, NO_3) were measured on board the NOAA research ship Ronald H. Brown along the coast of New England, downwind of New York, Boston and Portsmouth and large forested areas in New Hampshire, Maine, and Massachusetts in July and August 2002. The diurnal variations of isoprene, monoterpenes, and aromatics were mainly dependent on the abundance of the oxidants OH and NO_3 and on the emissions. Elevated mixing ratios of short lived VOCs were only encountered at the ship, which was about 1-6 hours downwind of the sources, when the concentrations of the oxidants were low. For the biogenic compounds this was generally the case during morning and evening hours, when the lifetime of the biogenics was long due to low OH and NO_3 concentrations. On the other hand, most anthropogenic VOCs do not react with NO_3 and therefore their mixing ratios remained elevated during the night. The products of isoprene oxidation, methyl vinyl ketone, methacrolein, and peroxymethacrylic nitric anhydride (MPAN) were on average higher than isoprene itself. Only during the transition periods from day to night, when oxidation rates were at a minimum, could isoprene exceed its products. The loss of the biogenic VOCs was dominated by reactions with NO_3, whereas the loss of anthropogenics came mostly from reactions with OH. The oxygenated VOCs are the major contributor to the OH loss, except in close vicinity of emission sources. The total loss of biogenic compounds during the night was so effective that after one night of transport they were in most cases completely reacted away, whereas the mixing ratios of the anthropogenic compounds remained high during the night. The pool of reactive hydrocarbons after one night was thus typically dominated by anthropogenic VOCs.

A41F-07 1150h

Nighttime NOx Loss during NEAQS

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Direct, in situ observations of NO3, N2O5 and HNO3 in the marine boundary layer during NEAQS have provided new insights into the nocturnal budget for NOx. Comparison between the behavior of these compounds in the NEAQS data set and from a continental site in Boulder, CO shows that N2O5 can act as both a reservoir for NOx and an efficient sink that converts it to nitric acid. The total removal of NOx pollution will depend strongly on the efficiency of these processes. Diurnal averages of NO3, N2O5 and HNO3 during NEAQS show that the nitric acid production during the night is comparable to that during the day, and that N2O5 hydrolysis reactions produce a significant quantity of gas phase nitric acid.

A41F-08 1205h

Regional Air Quality Forecasts during NEAQS-2K2: Comparisons with Observations

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The results of two Eulerian-based air quality forecast models (AQFMs) are compared to observations collected during the summer of 2002 North East Air Quality Study (NEAQS-2K2) field campaign. The focus of the comparison is on ozone, and several other key photo-oxidants measured during July and August of 2002 at four AIRMAP surface sites in New Hampshire, the Harvard Forest site in central Massachusetts, and aboard the NOAA Research Vessel Ron Brown that was deployed along the northeast U.S. coastline. The air quality forecast models are NOAA Forecast System Laboratory's MM5-CHEM, and MCNC's Multiscale Air Quality Simulation Platform (MAQSIP). Each model provides forecasts of meteorology and gas-phase oxidants at three horizontal grid resolutions; the coarsest (45 km and 27 km) covering much of the United States, and the finest (5 km and 3 km) covering the Northeast U.S. The modeling systems are completely independent, with different grid structures, precursor emissions estimates, physical parameterizations, and photochemical mechanisms. Two types of model-measurement comparisons are presented; standard statistical measures of variance and model bias, and species-species relationships between key photochemical species. The standard statistical measures allow forecast skill for the six independent AQFMs to be analyzed in terms of model system, horizontal resolution, and lead time of the forecast. In terms of forecast skill, neither model platform is significantly better than the other, and nearly no improvement is seen with increased horizontal resolution. Model biases, however, are noticeably different between model platforms, model horizontal resolution, and distance from coastline. The comparisons between model and measured species-species relationships provide limited information on the reliability of specific model processes such as emissions and O_3 production efficiencies. The models generally reproduce species-species relationships between O_3, nitrogen oxides, and CO with some dependence on model horizontal resolution. Deposition of HNO_3 is shown to be a strong influence on relationships involving nitrogen oxides. These results allow recommendations to be made concerning AQFM formulation, further observations needed to assess individual model components, and provide a statistical base-line for further AQFM development in the Northeast U.S.

A41G MCC: 3016 Thursday 1020h

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

(joint with AE)

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

A41G-01 1020h INVITED

Initial steps of particle formation and growth

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Aerosol particles are ubiquitous in the Earth's atmosphere and influence our quality of life in many different ways. In urban environments, aerosol particles can affect human health through their inhalation (e.g. Wichmann and Peters, 2000). In the global troposphere aerosol particles are thought to contribute to climate change patterns (Stott et al., 2000; Ramanathan et al., 2001). Understanding these effects requires detailed information on how aerosol particles enter the atmosphere and how they are transformed before being removed by dry or wet deposition. Key processes in this respect are the formation of new atmospheric particles and their subsequent growth to larger sizes. Quantitative measurements of aerosol formation and growth rates have required the recent developments in instrumentation for measuring size distributions down to sizes as small as 3 nm in diameter (McMurry, 2000). However, the phase change between vapour and liquid will occur at smaller sizes, typically around 1 nm in diameter. Thus, e.g. DMPS/SMPS systems, which have cut off sizes of 3 nm, are not suitable for direct detection of nucleation and initial steps of the particle growth. Ion spectrometers are one class of experiments that can reach this important size range in which the initial formation is occurring (Hörrak et al., 2000). The ion spectrometers reveal the mobility spectrum, and thus also indirectly the size distribution, of atmospheric ions. Here were report the first field experiments where ion spectrometers (two of them) have been used together with DMPS to study formation and growth of aerosol particles focusing particularly in the initial steps of the growth. In principle the initial steps of the growth can occur via several ways: condensation of nucleating vapours, activation of soluble vapours (multicomponent nano-Köhler theory), heterogeneous nucleation or ion mediated particle formation (Yu and Turco, 2000). In this paper, we demonstrate how the analysis of ion distribution data, together with DMPS data, can result in useful hints concerning the mechanisms of the initial steps of particle formation in Hyytiälä, Finland. The initial analysis supports a hypotheses of formation of thermodynamically stable clusters (Kulmala et al., 2000), their subsequent growth by condensation of sulphuric acid molecules and further activation by soluble organic vapors, resulting in remarkably constant growth rates in the nucleation mode size regime. Much of the work has been done under EU-project CASOMIO. Horrak, U., Salm, J., and Tammet, H. (2000) J. Geophys. research D 105, 9291. Kulmala, M., Pirjola, L., and Mäkelä, J. M. (2000): Nature 404, 66. McMurry, P. H. (2000a): Atmos. Env. 34, 1959. Ramanathan, V., Crutzen, P. J., Kiehl, J. T., and Rosenfeld, D. (2001) Science 294, 2119. Stott, P. A et al.(2000) Science 290, 2133. Wichmann, H.-H., Peters, A. (2000): Phil. Trans. R. Soc. Lond. A. 358, 2751. Yu, F., and Turco, R. P. (2000): Geophys. Res. Lett. 27, 883.

A41G-02 1045h

Evolution of Organic-Carbon/Black-Carbon Nanoparticle Size and Mixing State Near the Point of Emission

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The regional and global radiative effects of fossil-fuel soot (black carbon plus organic matter) are predicted to depend substantially on its mixing state, and the mixing state begins to evolve at the point of emission. One set of field data (1) have shown that, within minutes of emission, the soot particle size distribution can evolve substantially, eliminating a 10-nm nucleation-mode peak, consisting mostly of organic matter, in favor of a larger peak around 40-50 nm, which may merge with the 70 nm emission peak of black carbon. Because the number of small particles in the data set decreased significantly while the number of large particles did not, it was hypothesized in that study that Brownian coagulation played a large role in the evolution of the nanoparticle size distribution. Here, it is found that Brownian coagulation, alone, is insufficiently fast to account for the observed rapid evolution of the size distribution. However, the enhancement of Brownian coagulation due to Van der Waal forces offset by viscous forces together with enhancement due to soot particle fractal geometry can account for a much greater share of the evolution. These processes were represented together with aerosol emissions, nucleation, condensation, dissolution, hydration, and chemistry among 10 aerosol size distributions and gas chemistry in a high-resolution three-dimensional numerical simulation examining the internal mixing of soot among multiple size distributions. Results suggest that coagulation is important, not only for rapidly mixing organic carbon/black carbon nanoparticles, but also for creating new distributions from the interactions of soot with background particles. (1) Zhu, Y., W. C. Hinds, S. Kim, and C. Sioutas, JAWMA, 52, 1032-1042, 2002.

A41G-03 1100h

Organic Aerosol Nucleation From the Oxidation Products of α-pinene

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This laboratory study focuses on new particle formation resulting from the oxidation of α-pinene. Using a Teflon reaction chamber (70 L), ultrafine (>3 nm dia.) particle formation was studied for α-pinene concentrations between $1x10^{-10}$ atm and $2.4x10^{-8}$ atm at ozone concentrations between $1.2x10^{-7}$ atm and $1.4x10^{-6}$ atm. Experimental timescales of 40 minutes allowed appropriate time to investigate particle formation and subsequent growth of nanometer size particles. New information is presented regarding: 1) the effect of oxidizing agent (O_3 or OH) on aerosol mass yield and new particle concentration; 2) measurements performed near atmospherically relevant concentrations; and 3) the dependence of water vapor on the α-pinene gas-phase oxidation mechanism and hygroscopic growth of new particles.

A41G-04 1115h INVITED

Secondary Organic Aerosol Formation: New Insights

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A discussion of some of the important issues related to secondary organic aerosol (SOA) formation is presented, and SOA formation is placed in a context of global fine aerosol sources. Outdoor smog chamber experiments are described for the purposes of exploring the effects of different types of background aerosols on SOA formation from the reaction of α-pinene with NO_x in the presence of natural sunlight. Experiments were carried out by first adding 20 to 200 $\mu g/m^3$ of background aerosols (such as diesel soot, wood smog, and ammonium sulfate seed particles) into $190m^3$, $140m^3$, and $25m^3$ Teflon film outdoor chambers prior to the addition of α-pinene and NO_x. SOA formation was monitored using a scanning mobility particle sizer (TSI-SMPS). Gas and particle phase products were sampled over the course of experiments using denuders and filters. Chamber results indicated that condensed SOA can dramatically alter the chemical composition of primary diesel soot particles as they age in the atmosphere. Since particle phase aldehyde chemistry has recently been implicated as a potentially large source of SOA (Jang and Kamens, et al., *Science* 2002), aerosol growth by the heterogeneous reactions of different organic carbonyls in the presence/absence of acidified seed aerosols was studied in a flow reactor and 500-liter Teflon bag system under dark conditions. The results from unsaturated carbonyl and dicarbonyl experiments indicate large increases in SOA formation in the presence of acidified aerosols. This has implications for both biogenic and aromatic systems that generate SOA.

A41G-05 1135h

Aldol Condensation of Volatile Carbonyl Compounds in Acidic Aerosols

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Reactions of volatile organic compounds in acidic aerosols have been shown recently to be potentially important for organic aerosol formation and growth. Aldol condensation, the acid-catalyzed polymerization of carbonyl compounds, is a likely candidate to enhance the flux of organic matter from the gas phase to the condensed phase in the atmosphere. Until now these reactions have only been characterized for conditions relevant to synthesis (high acidities and liquid phase systems) and remote from atmospheric ones. In this work, the uptake of gas-phase acetone and 2,4pentanedione by sulfuric acid solutions has been measured at room temperature using a Rotated Wetted Wall Reactor coupled to a Mass Spectrometer. The aldol condensation rate constants for 2,4pentanedione measured so far for sulfuric acid solutions between 96 and 70 % wt. display a variation with acidity in agreement with what predicted in the organic chemical literature. The values of these constants, however, are much lower than expected for this compound, and comparable to the ones of acetone. Experiments are underway to complete this study to lower acidities and understand the discrepancies with the predicted reactivity.

A41G-06 1150h

Dissolution and Speciation of Oxygenated Organic Compounds in Sulfate Particles: Acetaldehyde

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The uptake of small organic compounds by sulfate particles is enhanced by the speciation of the compounds in acidic aqueous solution. Acetaldehyde [CH_3CHO] exists in such solutions in several forms: molecular, hydrated, enolized, and protonated acetaldehyde. The contribution of these various dissolution pathways to the heterogeneous interactions of acetaldehyde with upper tropospheric sulfate solutions will be evaluated. The uptake of acetaldehyde by aqueous sulfuric acid has been studied via Knudsen cell experiments over ranges of temperature (210-250 K) and acid composition (40-80 wt. %) representative of the upper troposphere. The Henry's law solubility coefficients for acetaldehyde calculated from these data range from 10^2 to 10^5 M atm^{-1}. Results from the interaction of acetaldehyde with solutions of formaldehyde in sulfuric acid will be presented as well. The physical and chemical processes that affect organic uptake by aqueous aerosols will be explored, with the aim of evaluating organic species not yet studied in low temperature aqueous sulfuric acid.

A41G-07 1205h

Acid-catalyzed Heterogeneous Reactions in SOA Formation

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The importance of heterogeneous reactions in secondary organic aerosol (SOA) formation has recently excited a great deal of interest in the aerosol community. Jang and Kamens (2001) showed enhanced aerosol yield from aldehydes, which can be produced by atmospheric photochemical reactions, in the presence of acidic seed. They suggest that the carbonyl functional groups of the aldehydes further react in the aerosol phase via hydration, polymerization, and hemiacetal/acetal formation with alcohols at an accelerated rate in the presence of acid. Jang et al. (2003) demonstrated similar results using a flow reactor and Czoschke et al. (in press) qualitatively showed increased yields for isoprene and alpha-pinene ozonolysis in the presence of acidic seed. While these findings are intriguing and important, the conditions under which the experiments were carried out were atmospherically unrealistic. A series of SOA formation experiments have been carried out in the Caltech Indoor Chamber Facility, which is comprised of dual 28 m^3 FEP Teflon chambers, with the flexibility to carry out both dark ozonolysis and photochemical OH oxidation reactions. Cycloheptene and alpha-pinene were oxidized in the presence of neutral seed under dry (<10% RH) and humid (50% RH) conditions and in the presence of acidic seed under humid (50% RH) conditions. The SOA yields for these experiments will be presented, and the extent of the influence of acid-catalyzed reactions on SOA yield will be discussed. Reference List 1. Cocker, D. R. III. and R. C. Flagan and J. H. Seinfeld, State-of-the-art chamber facility for studying atmospheric aerosol chemistry, Environmental Science and Technology, 35, 2594-2601, 2001. 2. Czoschke, N. M., M. Jang, and R. M. Kamens, Effect of acid seed on biogenic sceondary organic aerosol growth, Atmospheric Environment, In press. 3. Jang, M., S. Lee, and R. M. Kamens, Organic aerosol growth by acid-catalyzed heterogeneous reactions of octanal in a flow reactor, Atmospheric Environment, 37, 2125-2138, 2003. 4. Jang, M. S. and R. M Kamens, Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst. Environmental Science and Technology, 35, 4758-4766,2001.

A42A MCC: Level 2 Thursday 1330h

Atmospheric Nitrogen Deposition to Critical Estuary Habitats: The Bay Regional Atmospheric Chemistry Experiment (BRACE) I Posters *(joint with B, OS)*

Presiding: **T B Watson,** NOAA Air Resources Laboratory**; N Poor,** College of Public Health, University of South Florida

A42A-0739 1330h POSTER

Partitioning of Nitric Acid to Nitrate by NaCl and $CaCO_3$ and Its Effect on Nitrogen Deposition

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Nitrogen oxides produced by combustion in automobile engines, power plant boilers, and industrial processes are transformed to nitric acid in the atmosphere. This nitric acid then deposits to land or water and may be a significant nitrogen input to sensitive coastal estuaries. The sodium chloride from sea salt spray and calcium carbonate from mineral dust react in the atmosphere with nitric acid to form sodium nitrate or calcium nitrate, respectively. The nitrate particle deposition velocity can be substantially lower than that of nitric acid, which may lower the atmospheric nitrogen deposition rate near the urban sources of nitrogen oxides but raise the deposition rate over the open water. The relative effects of different ambient air concentrations of sodium chloride and calcium carbonate on nitrogen atmospheric deposition rates were examined by using the EQUISOLVII model to estimate the partitioning of nitric acid to nitrate combined with the NOAA buoy model and Williams model to calculate the gas and aerosol deposition velocities.

A42A-0740 1330h POSTER

Nitrate Aerosol Partitioning in the 2003 Bay Regional Atmospheric Chemistry Experiment (BRACE) : Aloft and Surface Comparisons

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The Bay Regional Atmospheric Chemistry Experiment (BRACE) field intensive in May 2003 was designed to help understand nitrogen chemistry and cycling in the airshed of Tampa, FL and included gas-phase and aerosol measurements at two downwind urban locations (Sydney and Tower Dairy) and a bay shoreline location (Gandy) as well as aboard the NOAA Twin Otter aircraft. The Twin Otter made 21 flights in the greater Tampa region over urban, suburban, and rural areas, Tampa Bay, and the Gulf of Mexico. Among these flights were several vertical profiles extending from 60 to 3000 m MSL over the Bay, the Gulf, and the ground sites. Aerosol samples on the Twin Otter were made with high flow rate filter packs followed by IC analysis; surface measurements for aerosols were made with a combination of filter packs, MOUDI samplers, annular denuders, and near-real time wet denuder collection followed by IC analysis. The degree of nitrate partitioning observed with the Twin Otter filter pack samples onto fine (2.5u and smaller) and large aerosols is examined separately for the three flow regimes that predominated during the intensive: strong synoptic, when local effects were overwhelmed; synoptic shift,