Total R is the sum of the individual values. Mixing ratio data for NO, NOy, O3, and CO are collected at 1-minute resolution. Temperature and jNO2 are also measured at 1-minute resolution. However, ten-minute averages of these parameters are used to coincide with ten-minute averages of ROG mixing ratios measured once per hour. Only data that coincide with sufficient sunlight intensity to ensure the photostationary state are used. A zero-dimensional version of a photochemical mechanism is used to estimate mixing ratios of relevant HOx radicals. Results show OPR and R values that are very low compared to other locations. OPR peaks during midday. R peaks earlier and later in the day and tends to be dominated by short-chain hydrocarbons. The low values of OPR indicate that peaks of O3 in this location are likely a result of the mixing of O3-rich air transported from higher levels of the atmosphere or other areas. The relatively high OPE values for this location confirm that the air in southeastern New Hampshire is typically NOx-limited.

A51E-0731 0830h POSTER

Ozone Prediction for the 2002 Air Quality Forecasting Pilot Program Using a Hybrid (Lagrangian-Eulerian) Photochemical Model

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The Hybrid Single-Particle Lagrangian Integrated Trajectories with a generalized non-linear Chemistry Module (HY-SPLIT CheM) model has been developed to calculate the spatial and temporal distribution of different chemical species in the lower troposphere over a regional scale. The simulation relies on a Lagrangian particle approach to compute transport, dispersion and deposition; and uses an Eulerian framework to represent chemical transformations of different air contaminants. HY-SPLIT CheM has been configured to simulate 48-hour ozone mixing ratios for the eastern United States. Air concentrations are computed based upon a 1/2x1/2-degree resolution grid and 10 vertical layers. Emissions of volatile organic compounds (VOCs) and nitrogen oxides (NOx) are based upon the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system. The forecast simulations only include pollutant sources between 25-50 N latitude and 65-100 W longitude. Transport and dispersion is computed using meteorological fields from the Mesoscale Model Version 5 (MM5) model with a horizontal resolution of 45 km, once each day, based upon the 0000 UTC forecasts (to 48 h). The Carbon Bond IV chemical mechanism is used to simulate the photochemical smog formation. Each calculation is started with all the lagrangian particles that are on the domain at the model's initialization time as computed from the previous day's simulation (yesterday's 24 h forecast). Pollutant particles may accumulate for up to 72 h before termination, although most of them are advected off the grid prior to reaching their age limit. The ability of HY-SPLIT CheM to simulate ozone mixing ratios is evaluated by comparing calculated ozone mixing ratios against measured values for a 25-day period (5-29 August 2002). HY-SPLIT CheM is the first operational implementation of the particle-in-grid approach applied to air quality forecasting. This model constitutes a feasible tool for ozone prediction due to its speed and low cost of implementation.

A51E-0732 0830h POSTER

Numerical air quality forecasts made at NOAA/FSL during NEAQS 2002

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The 2002 New England Air Quality Study (NEAQS) was an intensive effort to investigate the chemical and meteorological factors that contribute to poor air quality in the costal New England region. The campaign combined efforts of numerous educational institutions as well as federal, state, and local agencies. Data were collected from an extensive network of ground sites, from the NOAA research vessel Ronald H. Brown, and from the DOE G-1 aircraft. Although many of the ground stations routinely collect data year-round, the period of most intensive measurements was from July 12 through August 10, 2002. This presentation will discuss the configuration and real-time production from numerical guidance in use at NOAA/FSL. The numerical model used during NEAQS is a fully coupled atmospheric and chemistry forecast model (MM5-Chem). The atmospheric model is the Pennsylvania State University/National Center for Atmospheric Research Mesoscale Modeling System Version 5 (MM5). The chemistry model includes the RADM2 chemical mechanism, photolysis, biogenic and anthropogenic emissions and dry deposition. Data analysis is being conducted for three high-ozone events observed along the New England coast, 21 - 22 July 2002, 3-5 August 2002 and 12-15 August 2002. Comparisons are being made between MM5-Chem, observational data and retrospective simulations using other air quality forecast models. The analysis shows that, in general, the various numerical models produce similar results. However, small, but potentially significant, differences in the forecasted boundary layer wind speed and direction, as well as the temperature and moisture profile can result in large differences in regional ozone forecasts. For example, the residual boundary layer originating at the coast of New England and out over the Gulf of Maine was often predicted by MM5 to be warmer, more humid and shallower than what was observed. The resulting temperature and moisture profile is more stable than observed and restricts vertical mixing of pollutants off of the New England coastline.

A51E-0733 0830h POSTER

Evaluations of the Eta, RUC, WRF and MM5 Meteorological Models During NEAQS 2002

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During the summer of 2002 several NOAA Research laboratories (Environmental Technology Laboratory, Aeronomy Laboratory, Forecast Systems Laboratory) collaborated with the National Weather Service, including the National Centers for Environmental Prediction (NECP), on a project to assess and improve forecasts in New England using a regional testbed approach. During this project arrays of special research grade instruments were deployed throughout New England by NOAA Research, including seven 915 MHz wind profilers with RASS, cloud ceilometers, and surface meteorology stations that included solar and net radiation. Measurements from these instruments were compared against predictions made by operational and research forecast models, including the Eta, RUC, WRF and MM5 models. Model/observation comparisons were made on an hourly basis in real-time during the experiment. Results from this project will be presented, focusing on phenomena that most directly affect pollutant transport and mixing, including boundary layer depth, sea-breeze representation, and mesoscale transport.

URL: http://www.etl.noaa.gov/programs/2002/taq/verification/

A51E-0734 0830h POSTER

The Accuracy of Solar Irradiance Calculations Used in Medium Range Forecast Models

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During the 2002 New England Air Quality Study the NOAA Environmental Technology Laboratory (ETL) made radiative transfer observations at the University of New Hampshire, Thompson Farm Air Chemistry Site. We measured upward and downward solar irradiance, upward and downward IR irradiance, and aerosol optical depth at 412, 500, 675 and 862 nm from 18 July through 31 August 2000. We evaluated the solar irradiance forecasts made by both the National Center for Environmental Prediction (NCEP) operational ETA model and the Pennsylvania State University National Center for Atmospheric Research Mesoscale Model 5 (PSU/NCAR/MM5) Air Chemistry Model using the ETL observations. Our observations show that aerosol optical depths exceeding 0.8, accompanied the surface ozone events of 22-23 July and 11-15 August. The comparisons between the solar irradiance observed at Thompson Farm and the ETA and MM5 forecasts for 11-15 August ozone events suggest that the lack of sophisticated aerosol physics in both forecast models can cause the models to produce excessive clear-sky downwelling irradiance. 50-80 W m-2 forecast errors characterize the comparison. Similar comparisons conducted by ETL for Nashville, TN, Houston, TX and the Central Valley of California suggest that the radiative imbalances in models using the Lacis and Hanson solar irradiance parameterization are largest in regions impacted by the aerosols embedded in the East Coast industrial pollution plumes. We will show results that suggest that once the aerosol optical depth exceeds 0.1 the models typically forecast excessive downwelling solar irradiance. We will also present comparisons between JNO2 measured at Thompson farm with the 412 nm sun photometer measurements.

A

A51F MCC: Level 2 Friday 0830h

The Organic Aerosol Component: Impact on Reactivity, Optical Properties, Hygroscopicity, and Cloud-Condensation Properties IV Posters *(joint with AE)*

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

A51F-0735 0830h POSTER

Scanning Transmission X-ray microscopy Imaging of Aerosol Particles

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Scanning transmission x-ray microscopes (STXM) are used to image a diversity of carbon and metal containing items such as biofilms in soils, magnetic materials, polymers and meteorites. Studies on particles collected on SiO2 filters from biomass burns in Flagstaff, Arizona and individual aerosols collected in South Africa on TEM grids are underway at beamlines 5.3.2 and 11.0.2 at the Advanced Light Source of Lawrence Berkeley National Laboratory. Sub micron particles are imaged in the transmission mode over the energy range of 280 - 1900 eV. Spectromicroscopic studies on individual particles using near edge x-ray absorption fine structure (NEXAFS) probe multiple species within or on the same particle. In (STXM) an X-ray beam is focused with a zone plate onto a sample and the transmitted radiation is detected. Since the signal is obtained in the transmission mode, optically thin samples are required. Hence, atmospheric aerosols with submicron thickness and diameter are well suited for this method. Near edge spectra of various elements were scanned in step sizes from 0.1-0.5 eV around characteristic absorption edges, creating 2 dimensional images at each energy. While STXM images are taken with a lower spatial resolution (currently 40 nm) than microscopies such as scanning electron microscopy, transmission electron microscopy, and atomic force microscopy, detailed chemical information with spatial distributions, and oxidation states is obtained. A particular focus of this work is to obtain more detailed information on the type of carbons, multiply, or singly bonded and whether or not carbon is bonded to oxygen. The ultimate goal is discrimination between organic and black carbon within individual aerosol particles and determining if organic carbon, black carbon, and metal species are distributed homogeneously

throughout aerosol particles. Initial scans of the samples from Flagstaff show spectral evidence of aromatic carbon, without distinct C=O signatures. NEXAFS spectra of the boundary haze from South Africa indicate the presence of both metal (Fe in multiple oxidation states) and carbon.

A51F-0736 0830h POSTER

Laboratory Investigations of Aerosol Reactions Using Chemical Ionization Mass Spectrometry

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The technique of chemical ionization mass spectrometry (CIMS) has been used for the direct, real-time analysis of aerosols in the study of gas-particle reactions. The use of multiple reagent ions, both positive and negative, allows detection of a wide range of particle constituents, including organic species, such as aldehydes, ketones, carboxylic acids, alcohols and alkanes, as well as halogenated molecules and nitrates. Thermal vaporization of the particles coupled with CIMS provides a relatively low degree of fragmentation of many condensed-phase organic species thereby enhancing identification and quantification. Recent results using this technique in laboratory studies of gas-particle reactions of atmospheric significance will be presented.

A51F-0737 0830h POSTER

Interactions of Trace Atmospheric Species With Urban Surface Films

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Understanding and modelling episodes of urban air pollution is of increasing importance as the global population in urban centres approaches 50% and rises to 75% in greater developed regions. Recent field and laboratory measurements have confirmed the existence of organic films on impervious urban surfaces (such as windows, structures and roadways) and aerosol particles. Characterization of these films indicate organic species from both biogenic and anthropogenic emission sources. Despite urban areas being characterized by high concentrations of atmospheric pollutants and impervious surfaces, the potential role of surface films in controlling the fate and distribution of urban contaminants has not been explored experimentally. We have constructed a Knudsen cell apparatus coupled to a quadrupole mass spectrometer to study the reactive and unreactive uptake of trace atmospheric gases onto organic films. Our first study investigates low vapor pressure organic substrates and gas phase species, including smaller polycyclic aromatic hydrocarbons, representative of atmospheric constituents. Preliminary results indicate an appreciable uptake coefficient of naphthalene on oleic acid, on the order of 10-3. The results obtained to date, as well as their atmospheric implications, will be discussed.

A51F-0738 0830h POSTER

Properties of Organic Films on Aqueous Subphases

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Recently, it has been determined that organics represent a significant percentage of the composition of certain atmospheric aerosols. The air/aqueous interface of such an aerosol has the ability to act as a concentrator and selector of organic surfactants. Amphiphilic organics, such as fatty acids and alcohols, have been found to partition to the interface of aerosols thus creating a hydrophobic organic coating on an aqueous core. The selectivity of the interface was studied by monitoring the composition of various films, via GC-MS, as a function of exposure time. A Langmuir-Blodgett trough was used to contain and collect the self-assembled films that were produced from the addition of binary solutions of surfactants to the surface of an aqueous subphase. Surfactants with differing carbon number and head group functionalities were studied. The stability of the films was examined by varying the thickness of the organic films and the pH of the subphase. For a multilayer film containing equimolar stearic acid and lauric acid on a distilled water subphase, it was found that the acid with the longer hydrocarbon tail (stearic acid) remained at the interface much longer that the shorter acid. Films containing 1-octadecanol and stearic acid, both of which have identical carbon numbers, showed similar lifetimes at the air/water interface. Octadecane was found to have a longer lifetime at the interface when dissolved in equimolar stearic acid than when in a homogeneous film. Multilayer films and films formed on acidic subphases were found to be the most stable for both fatty acids studied. The relevance of these findings as they relate to organic aerosol content and structure as well as atmospheric processing and transport will be discussed.

A51F-0739 0830h POSTER

Real Time Measurements of Oxidation of SAMs using ATR-FTIR; Kinetics and Reaction Probabilities

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Most studies of heterogeneous reactions on aerosols have focused on their implications for gas phase species. Less attention, however, has been given to the modification of aerosol surfaces during such reactions. Alteration of aerosol surface species may affect their hygroscopic and radiative properties as well as their reactivity toward other atmospheric trace species. In the present study, we use self-assembled organic monolayers (SAM) as proxies for atmospheric organic aerosols. Detection of even very short carbon chains (i.e., C3) as well as continuous monitoring of the SAMs during the experiments are achieved by depositing the SAMs directly on a silicon attenuated total reflection (ATR) crystal (10 reflections) attached to a FTIR. The oxidation kinetics of unsaturated SAMs by ozone and hydroxyl radicals are studied using this technique, as a function of carbon chain length and surface roughness (using mixed SAMs with different length). Reaction probabilities are calculated based on surface oxidation and compared to probabilities previously calculated by gas phase monitoring. The atmospheric implications will be discussed.

A51F-0740 0830h POSTER

A Prototype Instrument for the Real Time Detection of Semi-Volatile Organic and Inorganic Nitrate Aerosol

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Semi-volatile organic and inorganic nitrate aerosol represents an important reservoir for reactive nitrogen (NOy) in the troposphere, having significant implications for the atmospheric lifetime and regional transport of NOy. We describe a prototype instrument capable of chemically characterizing semi-volatile organic and inorganic nitrate aerosol in parallel with their gas phase precursors. Real time chemical detection of laboratory generated semi-volatile inorganic nitrate aerosol was achieved using Thermal Dissociation Laser Induced Fluorescence (TD-LIF). In this application, laboratory generated particles are thermally repartitioned back to their gas phase precursors for subsequent *in situ* detection via TD-LIF. High detection efficiencies, referenced to total nitrate measurements observed using a commercial flash vaporization instrument (R&P Co. Inc.), were found for semi-volatile inorganic species such as ammonium nitrate, while non-volatile nitrate salt species exhibit low detection efficiency. Application to organic nitrate aerosol and considerations for future field deployment are discussed.

A51F-0741 0830h POSTER

Uptake of Acetic Acid on Ammonium Nitrate

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The interaction of acetic acid with thin ammonium nitrate films has been studied using a Knudsen flow reactor equipped with FTIR-RAS (Reflection Absorption Spectroscopy). Initial sticking coefficients (γ's) and coverages (Θ's) were determined over the temperature range 200 to 240 K. In the absence of water vapor (RH < 1%), the uptake saturated with coverages ranging from Θ = 5.0 x 10^{16} molecules/cm^2 at 200 K to Θ = 1.2 x 10^{14} molecules/cm^2 at 240 K. The initial uptake coefficient varied from $\gamma = 0.069$ to $\gamma = 0.0019$ for temperatures from 200 to 240 K, respectively. The IR spectra show that acetic acid ionized on the surface, despite the fact that the ammonium nitrate film was effloresced. Adding water vapor to the chamber resulted in continuous uptake and dramatically increased coverages. The IR spectra again revealed that acetic acid ionized on the surface. These results suggest that organic acids may be readily adsorbed onto inorganic aerosol particles under tropospheric conditions.

A51F-0742 0830h POSTER

Release of dicarboxlic acids by uptake of nitric acid into mixed inorganic/organic aerosols

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Tropospheric particles contain both organic and inorganic components. Not much is known about the processing of the organic components through heterogeneous reactions and the effects of the latter on the hygroscopicity and surface reactivity of the aerosol. In the Large Juelich Aerosol Chamber we conducted several experiments on mixed aerosols consisting of ammonium sulfate or ammonium bisulfate and the dicarboxylic acids C2 -C7. For these studies we utilized ECN's Steam Jet Aerosol Collector (SJAC). The output of the SJAC is an aqueous solution of the dissolvable particulate matter which is analyzed by ion chromatography. We optimized a set of isocratic conditions to quantitatively determine the dicarboxylic acids in presence sulfate and nitrate in mixed organic-inorganic aerosols. The analysis times range between 10 and 25 minutes and the detection limits are in the order of magnitude of a few μmoles/m^3. The results are compared with measurements of the total organic carbon (TOC) in the aerosol phase, which were conducted by ECN as well as measurements with an Aerosol Mass Spectrometer (Aerodyne AMS). The mixed aerosol was then processed by heterogeneous hydrolysis of N_2O_5, which was produced in situ by oxidation of NO_2 with O_3. The uptake of the hydrolysis product HNO_3 into the particulate was measured. As result of the acidification the organic acid was partially or completely forced out of the particulate phase. An interpretation of these observations based on the thermodynamic modelling of mixed organic/inorganic aerosols will be given. The experiments are part of the EC project CASOMIO.

A51F-0743 0830h POSTER

Mass Accommodation of Gas Phase Species on Octanol as a Function of Relative Humidity; Strange Behavior of Gas Phase Hydrogen Halides

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At this point very little is known about the physical and chemical properties of organic aerosols that have been shown to be abundant in many regions of the troposphere. In the work to be discussed, 1-octanol

was selected as a surrogate for the hydrophobic oxygenated organic compounds found in such aerosols. Using a droplet train apparatus, the uptake of several organic gas phase species and gas phase HCl, HBr and HI was measured to probe the nature of hydrophobic organic surfaces as a function of relative humidity. These measurements yielded the mass accommodation coefficient (alpha) which is the probability that a gas phase molecule striking the liquid surface, enters the bulk liquid. The measured uptake of the organic gas phase species is in accord with expectations. The uptake increases with decreasing temperature and is independent of relative humidity. On the other hand, the observed uptake of the gas phase acids is highly surprising. In the absence of water vapor, alpha for both HBr and HI is unity, however, alpha for HCl is much smaller on the order 0.015. The values of alpha change dramatically as a function of relative humidity (i.e. the density of water vapor). As the relative humidity increases, the alpha values for HBr and HI decrease and alpha for HCl increases. At a relative humidity of about 50%, alpha for all three species reaches values measured earlier on pure water (alpha between 0.15 and 0.3, depending on temperature). These results are discussed in terms of the nucleation model for mass accommodation and a mechanism is proposed to explain the surprising results related to the uptake of the hydrogen halides.

A51F-0744 0830h POSTER

Secondary Organic Aerosol Formation from the Ozonolysis of Cycloalkenes

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Secondary organic aerosol (SOA) is ubiquitous in the atmosphere being present in both urban and remote locations and exerting influence on human health, visibility and climate. Despite its importance, our understanding of SOA formation still lacks essential elements, limiting our understanding of the effect of SOA on climate forcing. While there do exist experimental data on SOA yields from both biogenic and anthropogenic precursor compounds, it is difficult to extend these results to predict the aerosol-forming potential of precursor compounds not yet studied. In response to this, a series of chamber experiments were carried out in the Caltech Indoor Chamber Facility, where compounds from the cycloalkene and methyl-substituted cycloalkene families were oxidized by ozone in the dark. The reactions were carried out in dual 28 m^3 teflon chambers at 20^oC and relative humidity below 5%, in the presence of ammonium sulfate seed aerosol. Cyclohexane was used as a scavenger to prevent side oxidation reactions with OH radicals, generated during ozonolysis of the cycloalkene. While cycloalkenes may not be important precursors for SOA formation in the ambient atmosphere, the system was chosen for its simplicity relative to atmospherically relevant SOA precursors such as the biogenic monoterpenes and sesquiterpenes. Cycloalkenes may be seen as the simplified structures on which these more complicated compounds are based. The compounds reacted included the cycloalkenes: cyclopentene, cyclohexene, cycloheptene and cyclooctene, the methyl-substituted cycloalkenes: 1-methyl-1-cyclohexene, 3-methyl-1-cyclohexene, 1-methy-1-cycloheptene and1-methyl-1-cylopentene, and other related classes of hydrocarbons: methylene cyclohexane and terpinolene. Data collected include aerosol yield, chemical composition and hygroscopic behaviour. The effect of the precursor hydrocarbon structure on these properties of the SOA will be discussed.

A51F-0745 0830h POSTER

Methanol Reaction With Sulfuric Acid: Implications for Organo-Sulfate Aerosol Chemistry in the Middle and Upper Troposphere

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Current estimates of global atmospheric methanol predict higher concentrations than those observed in the middle and upper troposphere over the Atlantic and Pacific oceans suggesting that an unknown sink for methanol exists. One possible explanation is the uptake of methanol by sulfate aerosols. The esterification of methanol by sulfuric acid has been studied since the 1950's, yet there is no complete quantitative or molecular level understanding of the reaction system. Using vibrational broad bandwidth sum frequency generation (BBSFG) the surface structure of methanol-sulfuric acid (SA) solutions using atmospherically relevant SA concentrations was examined. Liquid studies using Raman spectroscopy confirm protonation of methanol and formation of methyl hydrogen sulfate. The presence of water controls the formation of dimethyl sulfate. Surface studies reveal the formation of methyl hydrogen sulfate versus dimethyl sulfate from differing solvation effects at the surface relative to the bulk. These results further elucidate the molecular level picture of methanol-sulfuric acid aerosols and their role in middle and upper tropospheric chemistry.

A51F-0746 0830h POSTER

Partitioning of organic aerosol components between gas phase and particulate phase

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To understand the role of organics in aerosols both the particulate composition and the gas/vapor phase composition must determined simultaneously. Ammonium sulfates and dicarboxylic acids are major components of continental, tropospheric aerosols. We performed two experiments in which we studied the partitioning of organic aerosol components between the gas and the particulate phase. As model systems we chose (NH_4HSO_4 + glutaric acid) aerosol and ($(NH_4)HSO_4$ + methyl glyoxal) aerosol (an oxidation product of isoprene). The experiment were performed in the large Aerosol Chamber at the FZ-Jülich at room temperature. The relative humidity was constantly increased in the course of the experiment (40 → 90% r.h., 60 → 90% r.h.).
The particulate phase was characterized on line by SJAC/IC (Steam Jet Aerosol Collector/ Ion Chromatography, ECN) and an AMS (Aerosol Mass Spectrometer, Aerodyne). Simultaneously we measured the gas phase concentration of the organic component by a rotating wet denuder/TOC (Total Organic Carbon, ECN) and PTR-MS (Proton Transfer MS, Ionicon) and the NH_3/NH_4^+ concentration with an online monitor (AMANDA, ECN). Furthermore, the particle size distribution was measured by both an SMPS (TSI) and an APS (TSI3321). Temperature, pressure, and relative humidity were routinely recorded.
The experimental observations will be interpretated based on results of thermodynamic model calculations. This model utilizes a combination of a Pitzer type model for the inorganic components and a UNIFAC model for the organic components.
The studies are part of the EU project CASOMIO.

A51F-0747 0830h POSTER

Heterogeneous Interactions of Ethanol with Low-Temperature Aqueous Sulfuric Acid

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Tropospheric ethanol has both biogenic and anthropogenic sources. Evaporative emissions of ethanol will increase as its use in gasoline increases. Since ethanol has a sufficiently long lifetime to reach the upper troposphere and it is quite soluble in water, its interactions with tropospheric sulfate particles are of interest. Furthermore, ethanol undergoes two different reactions in acidic media and is therefore a useful molecule to test the ability of tropospheric sulfate to process organic matter. The reactivity ethanol exhibits in sulfuric acid is applicable to other primary alcohols, including biogenic compounds such as 2-methyl-3-buten-2-ol. The solubility of ethanol in low-temperature sulfuric acid + water solutions has been studied in a traditional Knudsen cell. Experimental conditions were representative of the upper troposphere; acid composition ranged from 40 to 80 wt. % sulfuric acid and temperature from 215 to 240 K. The solubility of ethanol increases with decreasing temperature and increasing acidity, with measured Henry's law coefficients ranging from 10^4 to 10^9 M atm^{-1}. Experimental evidence for the heterogeneous reaction of ethanol will be discussed as well.

A51F-0748 0830h POSTER

Studies of the Partitioning of Glyoxal into Atmospheric Particulates

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The organic composition of atmospheric aerosols is an area of very active research. Recent research has tried to elucidate possible mechanisms for incorporation of semi-volatile and volatile carbonyl products in particulates, almost all involving some sort of heterogeneous chemical reaction of carbonyl products to form less volatile species that are stabilized in the particle phase. These mechanisms include organic hydration, formation of hemiacetals and acetals, aldol condensations, and polymerization. In order to study the partitioning behaviour of volatile organic carbonyls, we have designed a 2 m3 teflon reaction chamber that uses a differential mobility analyzer - condensation nuclei counter for monitoring the physical properties of particles, an aerosol mass spectrometer (AMS) for monitoring the chemical composition of the particles and an automated DNPH cartridge/HPLC system for monitoring the gaseous composition inside the chamber. In this paper, we will discuss experiments that explore the physical and chemical characteristics of particles formed from the growth of seed particles ((NH4)2SO4, (NH4)HSO4, H2SO4, NaNO3, and NaCl) in the presence of gaseous glyoxal. The unique highlight of this system is the use of the AMS, which gives us a sensitive probe of changes in the chemical content of the particles as a function of time. The particle growth was rapid and significant and appears to be acid catalyzed, but is otherwise independent of the cationic content of the seed. Evidence is presented for the formation of hydrated glyoxal monomer, dimers, trimers and possibly higher order species. Possible mechanisms and mass spectrometric evidence will be discussed.

A51F-0749 0830h POSTER

Formation of Secondary Particulate Matter by Reactions of Gas Phase Hexanal with Sulfate Aerosol Particles

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The formation of secondary particulate matter from the atmospheric oxidation of organic compounds can significantly contribute to the particulate burden, but the formation of organic secondary particulate matter is poorly understood. One way of producing organic secondary particulate matter is the oxidation of hydrocarbons with seven or more carbon atoms to get products with low vapor pressure. However, several recent reports suggest that relatively low molecular weight carbonyls can enter the particle phase by undergoing heterogeneous reactions. This may be a very important mechanism for the formation of organic secondary particulate matter. Atmospheric aldehydes are important carbonyls in the gas phase, which form via the oxidation of hydrocarbons emitted from anthropogenic and biogenic sources. In this poster, we report the results on particle growth by the heterogeneous reactions of hexanal. A 5 L Continuous Stirred Tank Reactor (CSTR) is set up to conduct the reactions in the presence of seed aerosol particles of deliquesced ammonia bisulfate. Hexanal is added into CSTR by syringe pump, meanwhile the concentrations of hexanal are monitored with High Pressure Liquid Chromatograph (HPLC 1050). A differential Mobility Analyzer (TSI 3071) set to an appropriate voltage is employed to obtain monodisperse aerosols, and another DMA associated with a Condensation Nuclear Counter (TSI 7610)

is used to measure the secondary particle size distribution by the reaction in CSTR. This permits the sensitive determination of particle growth due to the heterogeneous reaction, very little growth occurs when hexanal added alone. Results for the simultaneous addition of hexanal and alcohols will also be presented.

A51F-0750 0830h POSTER

Lidar Measurements Of Aerosols In Taiwan

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Lidar observations have been carried out for the tropospheric aerosols in the height region 1-5 km during 2002-2003. Lidar measurements revealed the occurrence, height distributions and transport processes of aerosols related to Asian dust and biomass burning aerosols that has been conveyed from China and southeast Asia respectively. The properties of these aerosols are investigated by comparisons with meteorological conditions (Radiosonde), ground particulate measurements (PM10), satellite image (NAAPS AOD / TOMS AI Composite plots), and trajectory studies (HYSPLIT). The backscattering ratio of the both Asian dust and biomass burning aerosols exhibit the steepest gradient compared with the relative humidity which also show the sharp gradient. It indicates a possibility of modification of aerosol particles which might be mixed with humid air in the transport process. In addition, both of Asian dust and biomass burning aerosols tend to be trapped by temperature inversion layer. From the analysis of depolarization ratio, we found that the nonspherical particles arrived were predominant below 2.5 km for dust events.

URL: http://lidar.phy.ncu.edu.tw

A51F-0751 0830h POSTER

Chemical and Physical Processes Controlling the Distribution of Aerosols in the Lower Fraser Valley, Canada, During the Pacific 2001 Field Campaign

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High resolution size-resolved mass concentration of organic and inorganic species present in/on submicron particles measured during the PACIFIC 2001 field study in the Lower Fraser Valley (LFV) are presented. The measurements of major particulate species (organic, sulfate, nitrate and ammonium) were made in situ and in real time at three different sites representing urban (Slocan Park), semi-rural (Sumas) and rural (Langley) areas, using two Aerodyne Aerosol Mass Spectrometers (AMS). The total non-refractory PM1.0 mass concentrations at the three sites were found to range from 0.72 to 13.72 μg m^{-3}, with an average concentration of 4.25 μg m^{-3}. A large variability in aerosol composition was observed in the LFV, depending on meteorological conditions. Generally, during southwesterly wind conditions, inorganic species dominated the aerosol composition, while during stagnant conditions, organic species made up the majority of the particle mass. The organic aerosol species exhibit a bimodal size distribution, while the inorganic species are in most cases confined to the accumulation mode centered around 400 nm. Background sulfate levels of about 1 μg m^{-3} were observed in the LFV during the entire campaign. Transport is found to be an important factor controlling the composition of sulfate in the LFV. Several photochemical events leading to the observation of substantial increases of sulfate in the LFV were also identified. Many of these events involve sulfate-dominated growth of small particles and appear to occur on a regional scale within the LFV.

A51F-0752 0830h POSTER

Detection of the mixing state of individual organic carbon and elemental carbon particles from 50 nm up to 3 micrometers

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Current semi-continuous methods for organic carbon and elemental carbon rely on an operational definition when distinguishing between the relative fractions of these species in ambient samples. Aerosol time-of-flight mass spectrometry (ATOFMS) measures the aerodynamic size and chemical composition of individual particles, providing information on elemental carbon and organic carbon in atmospheric particles using unique mass spectral signatures. In ambient and source characterization datasets, organic carbon, elemental carbon, and combinations of these species are detected in multiple locations including the Sea of Japan, California, New York, and Georgia. The temporal variability of these species with 30-60 minute resolution has been examined. Furthermore, ATOFMS can be used to monitor partitioning of polycyclic aromatic hydrocarbons over time as a function of temperature and relative humidity. This presentation will discuss how these single particle mass spectral signatures can be used to understand the transformations as well as origins of carbonaceous particles in the atmosphere. A comparison will be made between carbonaceous particles detected in ultrafine (less than 100 nm) versus fine (100 nm to 3 microns) particles.

A51F-0753 0830h POSTER

Measurement of the Optical Extinction of Aerosol With the Cavity Ring-Down Technique

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Accurate measurement of optical properties of aerosols is crucial to quantify the influence of aerosols on climate. In this work, a laboratory system for the measurement of aerosols has been developed based on the highly sensitive Cavity Ring-Down (CRD) technique. In CRD, a laser pulse is coupled into an optical cavity consisting of high reflectivity mirrors to achieve very long effective path lengths (approx. 20 km). The intensity of the light that leaks from the cavity through the mirrors decays exponentially, and the lifetime is a sensitive extinction measurement. We will present results of calibration and statistical analysis of the system at 532 nm with monodisperse polystyrene latex spheres and dioctyl sebacate particles. The measured extinction agrees to better than 5 % with the extinction calculated from Mie theory.

A51F-0754 0830h POSTER

Phase Diagram and Heat Capacities of the Malonic Acid/Water System

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Malonic acid is one of the more ubiquitous dicarboxylic acids found in the atmosphere and is quite soluble in water. Therefore, its impact on particle/cloud droplet formation needs to be better understood through the study of the thermodynamics of its aqueous solutions. The liquid/solid phase diagram and solution heat capacities of the malonic acid/water binary system have been investigated using differential scanning calorimetry and infrared spectroscopy of thin films. We report here the first measurement of the ice melting envelope as well as the ice/malonic acid eutectic temperature and composition in this binary system. Evidence from both thermal analysis and infrared spectroscopy is shown for a malonic acid hydrate, possibly $C_3H_4O_4 \cdot 6H_2O$. We have observed the formation of this hydrate over a large range of concentrations, and have found it is a major fraction of samples within that region. We have also determined the enthalpy of fusion of malonic acid as well as the constant pressure heat capacities of solutions in the concentration range 5 - 55 wt% malonic acid from 323 K to the freezing point of each solution.

A51F-0755 0830h POSTER

Effect of Dicarboxylic Acids on the Phase Transitions of Model Tropospheric Aerosols

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The phase of tropospheric aerosol is important in determining its physical and chemical properties. Tropospheric aerosol is chemically mixed and contains a significant organic fraction including dicarboxylic acids such as malonic and oxalic acid. Experiments have been performed using an aerosol flow tube - FT-IR system (AFT) to identify particulate phase transitions. The major part of this paper is a detailed study into the deliquescence and efflorescence phase transitions of aerosol composed of ammonium sulfate (AS) and malonic acid (MA) at 283 and 293 K, respectively. When the fraction of MA by dry mass (f_{MA}) was < 0.1, phase transitions occurred at the deliquescence and efflorescence relative humidity (DRH and ERH) of AS. However between $0.1 < f_{MA} < 0.25$ deliquescence occurred at the eutonic DRH for the AS-MA system and the crystallisation RH of AS is lowered. Between $0.25 < f_{MA} < 0.90$, no distinct deliquescence or efflorescence was observed, with particles taking up water at all relative humidities. The crystallization of both MA and AS is suppressed by the presence of the other component. The crystallization RH of MA was $< 1\%$ when any AS was present. When $f_{MA} > 0.25$, AS did not crystallise even when RH $< 1\%$. Thus, the presence of the second component increased the range of conditions under which the particles were in the solution phase. This behaviour, should it be widely applicable, will have a large impact on the phase of chemically mixed aerosol in the atmosphere. We have also studied the phase transitions of AS - oxalic acid, AS - ammonium oxalate and other ammoniated dicarboxylic acids. The results from these studies will be summarised and the atmospheric implications of all of the results discussed.

A51F-0756 0830h POSTER

Field Observations of the Processing of Organic Aerosol Particles and Trace Gases by Fogs and Clouds

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In many environments, organic compounds account for a significant fraction of fine particle mass. Because the lifetimes of accumulation mode aerosol particles are governed largely by interactions with clouds, it is important to understand how organic aerosol particles are processed by clouds and fogs. Recently we have examined the organic composition of clouds and fogs in a variety of environments as well as how these fogs and clouds process organic aerosol particles and soluble organic trace gases. The investigations, conducted in Europe, North America, Central America, and the Pacific region, have included studies of polluted radiation fogs, orographic clouds in clean and polluted environments, and marine stratocumulus. Our results show that organic matter is a significant component of fog and cloud droplets. In polluted California radiation fogs, we observed concentrations of total organic carbon (TOC) ranging from 2 to 40 ppmC, with significantly lower concentrations measured in marine and continental clouds. An average of approximately 80 percent of organic matter was found in solution, while the remainder appears to be suspended material inside cloud and fog drops. Ultrafiltration measurements indicate that as much as half of the dissolved organic carbon is present in very large molecules with molecular weights in excess of 500 Daltons. Field measurements made using a two-stage cloud water collector reveal that organic matter tends to be enriched in

smaller cloud or fog droplets. Consequently, removal of organic compounds by precipitating clouds or by direct cloud/fog drop deposition will be slowed due to the fact that small drops are incorporated less efficiently into precipitation and removed less efficiently by sedimentation or inertial impaction. Despite this trend, we have observed that sedimentation of droplets from long-lived radiation fogs provides a very effective mechanism for cleansing the atmosphere of carbonaceous aerosol particles, with organic carbon removed more efficiently than elemental carbon. Efforts to characterize organic matter in clouds and fogs reveal that the most abundant species are typically low molecular weight carboxylic acids and aldehydes. These species have been observed collectively to account for roughly 20-30 percent of the total organic carbon in some fogs and clouds. Dicarboxylic acids, frequently used as model compounds for organic CCN, typically account for only about 1 percent of the organic carbon, with oxalic acid the most important contributor. Measurements by GC/MS, HPLC, and H-NMR reveal that many other organic compounds are present, including aerosol source markers and compound families frequently detected in aerosol particles including n-alkanes, n-alkanoic acids, and polycyclic aromatic hydrocarbons. These latter compounds were detected in both dissolved and undissolved forms in droplets, with dissolved concentrations often higher than their solubilities in pure aqueous solutions, suggesting a possible role of surface organic films. Although more than 100 organic species have been quantified in many samples, the majority of the organic carbon mass remains unspeciated. Given the importance of high molecular weight material, future efforts will focus in part on further characterization of these compounds, including possible contributions from humic like substances.

A51F-0757 0830h POSTER

Effect of Morphology and Composition on the Hygroscopicity of Soot Aerosols

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Freshly generated soot aerosols are initially hydrophobic and unlikely to act as cloud condensation nuclei (CCN). However, during combustion many low vapor pressure gas products are formed that may then condense on existing soot aerosols. Additionally, soot particles may acquire coatings as they age, such as acids, salts, and oxygenated organics. An understanding of this aging process and its effect on soot hygroscopicity is necessary to address the potential of soot to act as a CCN. The transformation of soot from hydrophobic to hydrophilic is the focus of this work. An aim here is to determine the minimum coating required for hygroscopic growth. Soot particles produced by combustion of mixtures of fuel and air are size selected by a Differential Mobility Analyzer (DMA) and entrained in a laminar flow passing through a flow tube. The size selected soot particles are mixed with a controlled amount of the gas phase precursors to produce the coatings to be studied. Initial studies are focused on coatings of H2SO4, NH4NO3, and selected organics. The number of particles per unit volume of air is counted by a Condensation Particle Counter (CPC) and the particles are isokinetically sampled into an Aerosol Mass Spectrometer (AMS). Two distinct types of soot aerosols have been observed depending on the type of fuel and air mixture. With soot produced by the combustion of propane and air, the AMS shows a polydisperse particle size distribution with aerodynamic diameters ranging from 100 nm to 400 nm. The aerodynamic diameter is linearly related to the DMA-determined mobility diameter with the product density x shape factor = 1.2. The organic molecules in this soot are mostly PAH compounds. However, when kerosene is added to the propane flame, the soot particle morphology and composition is strikingly altered. While the DMA shows an essentially unchanged mobility diameter distribution, in the range 100 nm to 400, aerodynamic particle diameter is constant at about 100 nm, independent of the mobility diameter. This type of constancy of the aerodynamic diameter has been observed for soot particles in diesel engine exhaust and has been interpreted in terms of a size-dependent effective density. The soot chemical composition is also altered. In this soot the organics are mainly linear hydrocarbons. The differences between these two types of soot with respect to hygroscopicity and effective area are being investigated.

A51F-0758 0830h POSTER

Deliquescence and Efflorescence of Organic and Mixed Organic-Inorganic Particles: An FTIR/Optical Microscopy Approach

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Organic aerosols have recently gained attention as a significant component of the atmosphere and as such have been the focus of a number of studies regarding phase transitions. We have focussed on the deliquescence and efflorescence behaviour of dicarboxylic acids using optical microscopy in conjunction with a flow cell containing particles with diameters ranging from 2 - 40 microns. Deliquescence of malonic acid, succinic acid, glutaric acid and adipic acid particles were tested over a range of temperature from 253 K to 293 K. In all cases, we observed deliquescence below the eutectic point, suggesting that these species are not good ice nuclei above 253 K. Our deliquescence data is also in good agreement with calculations based on solubility and the UNIFAC model. Deliquescence and efflorescence data for ammonium sulphate - glutaric acid and sodium chloride - glutaric acid mixtures were also measured at 293 K using both optical and FTIR microscopy techniques. FTIR microscopy allows us to make visual observations, while monitoring the chemical content of a single particle or a collection of particles. Additionally, we have extended the FTIR microscopy technique to study phase transition behaviour of single electrodynamically levitated particles. Some preliminary results from this new technique are also discussed.

A51F-0759 0830h POSTER

Patterns in Hygroscopicity of Ambient Particulate Matter at Urban, Rural and Forested Sites

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Hygroscopicity of ambient particles was measured at four sampling sites, using a Hygroscopic Tandem Differential Mobility Analyzer (HTDMA). Particles were first dried to about 10% relative humidity, monodisperse particles were then selected; these particles were humidified to relative humidities ranging from 50 to 85% and the size distribution measured to determine growth due to water sorption. Data was collected at an urban site, a forested site, and two sites with a mixture of urban and rural influences. A common feature observed at all the sites was the existence of particles that sorbed only small amounts of water even at high relative humidity. These particles showed a small and gradual increase in size with increase in relative humidity; at 80% relative humidity, these less hygroscopic particles typically had growth factor of 1.1. At the urban and mixed sites, these less hygroscopic particles were observed on good air quality days; at the forested site, they constituted almost all the particles. Particles with higher hygroscopicity were observed on more polluted days. These particles had growth factors as high as 1.4 at 80% relative humidity. The more hygroscopic particles took up a significant amount of water at higher relative humidity while still behaving like the less hygroscopic particles at lower relative humidities. The point at which this transition occurred ranged from 70% to 75%, and varied more from site to site than over time. On a number of the polluted days, these more hygroscopic particles were externally mixed with less hygroscopic particles, resulting in both less and more hygroscopic mode in the humidified particle distributions. Compositional data will be used to investigate the role of the organic fraction in the hygroscopic growth of these particles.

A51F-0760 0830h POSTER

Concerning Organic Aerosol Components and Ice Nucleation in the Upper Troposphere

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We have obtained evidence in recent field studies indicating an association of the presence of organic aerosol components with impedance of homogeneous freezing nucleation of ice at upper tropospheric conditions. It is important to understand any direct relation between certain organic compounds and ice nucleation because of implications for affecting the conditions of formation, the ice phase composition and ultimately the radiative properties of upper tropospheric clouds. Laboratory studies are being conducted to examine the impact of certain organic compounds on homogeneous freezing nucleation, either as pure species or in mixture with ammonium sulfate. We will present the field evidence for impacts of organic compounds on ice nucleation, discuss some ways that these substances could affect homogeneous ice nucleation and summarize the results of ongoing studies of ice formation by certain organic acid/ammonium sulfate mixtures.

A

A51G MCC: 3016 Friday 1020h

Contributions to Middle Atmosphere Science by Solar Occultation Instrumentation III *(joint with SA)*

Presiding: **L W Thomason,** NASA Langley Research Center**; P L DeCola,** NASA Headquarters**; R Bevilacqua,** Naval Research Laboratory

A51G-01 1020h INVITED

Satellite Occultation MeasurementsContributions to Middle Atmosphere Science

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Solar occultation measurements from earth-orbit began with two orbits of data from aboard Apollo during the Apollo-Soyuz test project flight in 1975. The instrument was called SAM for the Stratospheric Aerosol Measurement. It was a simple proof-of-principle, one-spectral channel experiment that led to the long-duration occultation measurement series beginning in 1978 with the launch of SAM II aboard Nimbus 7. SAGE I, II, and III followed with increasing instrument complexity and capability. SAGE II and III are presently in orbit providing excellent high vertically-resolved measurements of aerosol, ozone, and other constituents. Other occultation sensors for long-duration measurements were launched in the 1990s including HALOE and POAM. This paper will present a historical overview of satellite occultation missions from 1975 to the present. The fundamentals of the occultation technique will be presented along with its advantages and comparison with other remote sensors. The occultation sensors, to-date, have produced exceedingly important measurements that have contributed to atmospheric and climate science. These have included such measurements as: the naming and characterization of Polar Stratospheric Clouds; aerosol and ozone associated with the wintertime polar vortex phenomena; ozone, HCl and HF trends associated with the effects of CFCs; the impact of volcanic aerosols; and aerosol and cirrus cloud distributions and trends. As the lead-off paper in this session, examples of the above data will be presented. Finally, some “lessons-learned” from these occultation missions will be discussed.