

A52E-11 1640h

A comparison of airstream trace gas signatures upwind and downwind of North America

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Recent studies of trace gas export from North America have demonstrated that the transport is closely associated with the airstream flow through mid-latitude cyclones. These cyclones are composed of four primary airstreams: warm conveyor belt (WCB), cold conveyor belt (CCB), dry airstream (DA), and post cold front airstream (PCF). In general the DA advects stratospheric ozone into the mid- and upper troposphere; the WCB exports surface emissions to the upper troposphere and is the most favorable location for photochemical ozone production; the PCF originates to the northwest, and is associated with rapid low altitude transport of surface emissions to the Atlantic; the CCB is generally cloudy and does not show signs of significant photochemical ozone production. The recent Intercontinental Transport and Chemical Transformation (ITCT) aircraft-based measurement campaign has produced chemical measurements in airstreams just west of North America. This new data set provides an excellent opportunity to compare the trace gas signatures of airstreams upwind and downwind of North America. North American trace gas import during ITCT was associated with the remnants of mid-latitude cyclones that had formed over the western North Pacific Ocean. The aged nature of these airstreams and the contrast of emissions ratios between Asia and North America yield different trace gas relationships upwind and downwind of North America. This study examines the relationships between ozone, CO, NO_y and NO in the airstream remnants impacting western North America and compares the results to similar studies conducted for spring 1996 and autumn 1997 on the North American east coast. Conclusions are drawn on the chemical transformation that occurs in air masses traversing North America.

A61A MCC: Hall D Saturday 0830h

Aerosol, Cloud, and Tropospheric Chemistry II Posters

Presiding: C Wang, Massachusetts

Institute of Technology; **S N Pandis, Carnegie Mellon University**

A61A-0040 0830h POSTER

Preliminary Studies on Comparing the Effect of Cloud Chemistry on Tropospheric Oxidants from Modeling a Polydispersed Cloud Drop Population to Modeling a Monodispersed Cloud Drop Population

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Cloud chemistry, that is, both aqueous phase chemistry and the modification of gas-phase chemistry due to separation of reactants, can affect the production

of important tropospheric oxidants. The influence of cloud chemistry on tropospheric oxidants is dependent on the pH of the drops, the liquid water content, and the chemical environment. Because pH varies across the cloud drop spectrum, the degree that cloud chemistry affects tropospheric oxidants is not obvious. For this study, a cloud parcel model that represents cloud drop activation, condensation and coalescence is coupled with a gas-aqueous chemistry module that represents O₃-NO_x-NMHC chemistry appropriate for the remote troposphere. Results of simulations in which cloud drops activate on a polydispersed CCN distribution are compared to results of a simulation in which a single-sized cloud drop population is assumed.

The following hypothesis is tested and discussed. The hypothesis is that the total concentration of species such as O₃, CH₂O, and peroxides will be smaller when a polydispersed cloud drop population is represented than when a single-sized cloud drop population is assumed because previous studies have shown that these oxidants are depleted more or produced less at high pH compared to low pH. This hypothesis assumes that the high pH drops play an important role in the aqueous chemistry as they have previously been shown to do for aqueous sulfur chemistry.

A61A-0041 0830h POSTER

Influence of Biomass Burning on Particle Size Distributions, Hygroscopic and Cloud-nucleating Properties of the Amazon Rain Forest Aerosol

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In the July 2001 transition period between the wet and dry season, aerosol particle size distribution and hygroscopic growth were measured in central Amazonia, as a part of the LBA-CLAIRE experiment. The sub-micron particle number-size distribution were studied with a Differential Mobility Particle Sizer (DMPS) and a Hygroscopic Tandem Differential Mobility Analyzer (H-TDMA) measured the hygroscopic growth at 90% RH for particle dry sizes in the Aitken and accumulation mode size ranges. Three different time periods were selected; a clean time period, a recently yet moderately polluted time period and an aged pollution time period. The pollution was, in both the latter cases, caused by biomass burning.

During the clean time period the observations showed good agreement with the CLAIRE 1998 wet season experiment. During the polluted time periods particle concentrations were substantially increased from about 500 to 2000 part/cc, with a particle number size distribution peak at around 130-140 nm. The biomass burning aerosol frequently showed a bimodal hygroscopic behavior, with a separation into nearly hydrophobic and moderately hygroscopic particles. Besides the increased presence of nearly hydrophobic particles an increase in the hygroscopicity of the moderately hygroscopic particles was observed, compared to the clean case. The numbers of ions in each individual particle were estimated from the H-TDMA data, and together with the DMPS measurements the number of aerosol particles activating to form cloud drops, as a function of water vapor supersaturation, was predicted with a time resolution of 10min. The predicted CCN concentrations were compared with direct measurements performed with a CCN counter, and showed reasonable good agreement.

A61A-0042 0830h POSTER

Modeling of Cloud Droplet Number Concentrations and Their Link to Aerosol and Cloud Chemistry

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The indirect effect of aerosols on clouds is based upon the links between aerosol number concentrations,

activity of particles as cloud condensation nuclei, and cloud drop number concentrations. Modeling and observations have also shown that aqueous-phase chemistry can modify cloud condensation nuclei number concentrations and affect drop concentrations in subsequent cloud cycles. The feedback of chemistry to cloud drop number concentration can be positive or negative, depending upon the initial aerosol size spectrum, chemical environment, and dynamics of each cloud cycle. In this work we focus on the calculation of cloud drop number concentration from a range of specified aerosol initial conditions and examine the sensitivity of predicted drop number concentrations to environmental conditions, model type, and model assumptions.

A61A-0043 0830h POSTER

In Situ Observations of Both Indirect Aerosol Effects

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Cloud microphysics and sub-cloud cloud condensation nuclei (CCN) measurements in polluted, maritime, and transition air masses demonstrated the effects of anthropogenic particles on clouds known as the indirect aerosol effect (IAE). Near-simultaneous cloud droplet measurements showed the higher concentrations and smaller sizes expected for higher CCN concentrations. The associated lower concentrations of large cloud droplets in polluted air indicated that the higher CCN concentrations were responsible for the 1 to 2 orders of magnitude lower drizzle drop concentrations in the polluted clouds. The similarity of the clean and polluted cloud droplet spectra near cloud base, however, suggested that there were no significant differences in giant nuclei concentrations that may have been responsible for greater precipitation in the more maritime clouds. This suppression of warm rain by higher CCN concentrations (2nd IAE) often occurred hundreds of km from anthropogenic sources. These results were similar in: 1) stratocumulus clouds in the eastern Atlantic (ASTEX); 2) small cumulus clouds in eastern Florida (SCMS); and small trade wind cumuli in the Indian Ocean (INDOEX). Comparisons of CCN and cloud droplet spectra showed that cloud supersaturations were lower in the polluted clouds. Thus a smaller percentage of these higher CCN concentrations actually produced cloud droplets. However, the suppression of cloud supersaturation was smaller than previously thought because cloud droplet sizes were so much reduced that it was obvious that many of the polluted cloud droplets were too small to be detected by the forward scattering spectrometer (FSSP). This probably typical undercounting of cloud droplets suggested that the suppression of supersaturations in polluted clouds has probably been overestimated. This means that anthropogenic CCN may have an even greater effect on clouds than previously thought. Moreover, when the missing droplets were accounted for, the relationship between CCN concentrations and cloud droplet concentrations was closer to linear. This suggests that speculations about anomalous effects of some CCN (especially organic material) may be exaggerated.

A61A-0044 0830h POSTER

Cloud-Sulfate Correlations as a Constraint on Heterogeneous Sulfate Production

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Statistical analysis of observed daily cloud cover (from ISCCP) and sulfate surface concentrations in Europe and North America indicates a significant negative correlation between clouds and sulfate. These anti-correlations are at long time scales (typically 8-64 days) and occur for many months of the 3 years of data. A corresponding analysis of modeled sulfate and cloud cover (from the Goddard Institute for Space Studies GCM) fails to produce significant correlation. However, if we separate heterogeneous (cloud-produced) and gas phase sulfate, there is some significant negative correlation between clouds and gas phase sulfate. If we turn off gas phase sulfate production beneath clouds (as should happen since the oxidant OH is photochemically generated), this negative correlation becomes stronger; however the total sulfate-cloud correlation remains insignificant.

This version ('2-prime', 9-layer) of the GISS model, like most global models, does not have a separate budget for dissolved species. Instead, after each cloud

time-step, the sulfate generated in-cloud is returned to the gridbox rather than retained in the cloud droplets. We perform another simulation which has a dissolved tracer budget for sulfate, so that sulfate generated in a cloud is not released to the gridbox unless the cloud evaporates. The result is that more of this sulfate is rained out and therefore sulfate production decreases (relative to the standard simulation): the in-cloud sulfate production drops from 32 to 10 Tg S/yr and total sulfate burden (including gas and heterogeneous phases) drops from 0.71 to 0.54 Tg S. In this simulation, we do achieve significant negative correlation between clouds and sulfate (although still not as much as observed). This study implies that most sulfate is generated in the gas phase, and that global models have excessive heterogeneous sulfate production. We will also present results from the new ('modelE', 16 layer) version of the GISS model that has dissolved species budgets for precursors H₂O₂ and SO₂ as well as sulfate. Finally we will show how the reduction in the heterogeneous sulfate production affects the indirect radiative forcing.

A61A-0045 0830h POSTER

Distinguishing Biogenic From Anthropogenic Aerosols Over the North Atlantic Ocean Using Stable Sulphur Isotopes

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Atmospheric sulphate aerosols may partially counteract the warming effect of greenhouse gases by increasing Earth's albedo. Fossil fuel combustion is a significant anthropogenic source of such aerosols. Dimethyl sulphide (DMS) emissions from pelagic microalgae are a significant natural source. In order to assess whether marine biological sulphur emissions respond to climate change, it is necessary to differentiate between anthropogenic and natural sources. This can be accomplished by measuring their sulphur isotopic compositions. Sulphur emissions from combustion sources in eastern North America have $\delta^{34}\text{S} \sim 0 - 5\text{‰}$ and aerosols with a measured $\delta^{34}\text{S}$ in this range have likely derived their sulphur from anthropogenic sources. Sulphate dissolved in seawater (the source of DMS-derived sulphate and sea salt sulphate) is 21‰ . Assuming that little isotopic fractionation occurs during DMS emission and subsequent oxidation, aerosol samples with a $\delta^{34}\text{S}$ near 21‰ are likely to have obtained their sulphur either from marine biogenic or sea salt sources. The sea salt component of aerosols can be accounted for mathematically using sodium or magnesium as a conservative tracer, allowing contributions from marine biogenic sources to be calculated by simple mass balance.

During Spring (1998) and Fall (1999) cruises of the Northern Oceans DMS Emissions Model (NODEM) program, atmospheric aerosol samples were collected using a PM-10 Hi-vol sampling system with 5-stage cascade impactor mounted above the bridge of the CCGS Hudson. The soluble portion of the aerosols was ultrasonically extracted and analysed for concentrations of sulphate, nitrate, sodium, magnesium, and methane-sulphonic acid (MSA, an oxidation product of DMS). MSA can be formed only from DMS, and so acts as an unequivocal marker of biological activity. Sulphur isotopic compositions were measured on total soluble sulphur using continuous flow isotope ratio mass spectrometry (CF-IRMS). The data conform to a mixing model involving contributions from the individually discernible sulphur sources described above.

A61A-0046 0830h POSTER

Do Organic Films Influence Cloud Droplet Formation?

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The rate of condensational growth is relevant to a variety of atmospheric processes, in particular the activation of cloud condensation nuclei to form cloud droplets. It has been hypothesized that the presence of organic films on the surface of atmospheric aerosols can strongly inhibit condensational growth, but no observations appear to have been previously reported. A brief review of the literature on the effects of films on the mass transfer of water is presented. A novel experiment based tandem differential mobility analysis for the measurement of the time scale for condensational growth (τ_g) for ambient aerosols is introduced. Measurements were taken during the wet season (25–27 September, 2000) and dry season (16–17 November, 2000) in Mexico City for particles with dry diameters of 50 and 100 nm. The results show that most of the particles exhibit $\tau_g < 2$ to 3 s. However, a small number (between 0 and 2.0% depending on particle size and season) do exhibit time scales larger than this. The condensation coefficient of this minority of particles

is calculated to be approximately in the range of 1 to 2×10^{-5} , which is in the lowest range of observed values for laboratory aerosols. The observations show a strong dependence of the occurrence of such particles on season and time of day. It is hypothesized that these measurements suggest that an even larger concentration of particles exhibiting condensation coefficients in the range of 10^{-5} to 10^{-4} may exist. The existence of such particles would be important to the indirect effect of aerosols on climate.

A61A-0047 0830h POSTER

Uptake of Organic Gas Phase Species by 1-Methylnaphthalene

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Using a droplet train apparatus, the mass accommodation coefficients (α) on 1-methylnaphthalene of gas phase m-xylene, ethylbenzene, butylbenzene, α -pinene, γ -terpinene, and 2-methyl-2-hexanol were measured as a function of temperature (265 K to 296 K). 1-methylnaphthalene was selected as a surrogate for hydrophobic and aromatic hydrocarbons found in tropospheric aerosols. The mass accommodation coefficients (α) of all the molecules obtained from these measurements exhibit negative temperature dependence. The upper and lower values of α at 265 K and 296 K respectively are: for m-xylene 0.44 and 0.26; for ethylbenzene 0.37 and 0.22; for butylbenzene 0.47 and 0.31; for α -pinene 0.47 and 0.096; for γ -terpinene 0.39 and 0.12; for 2-methyl-2-hexanol 0.44 and 0.26. The uptake measurements also yielded values for the product $\text{HD}_j^{1/2}$ for most of the molecules studied ($H = \text{Henry's law constant}$, $D_j = \text{liquid phase diffusion coefficient}$). Using calculated values of D_j the Henry's law constant is obtained, and expressed in the form $\ln(H \text{ (M/atm)}) = -A + B/T$. The A and B values for the molecules studied are listed in Table 1.

Table 1: A and B values for the Henry's law constant H expressed as $\ln(H \text{ (M/atm)}) = -A + B/T$

m-xylene:	$A=7.20$,	$B=4060$
ethylbenzene:	$A=5.81$,	$B=3660$
butylbenzene:	$A=16.95$,	$B=7330$
α -pinene:	$A=15.69$,	$B=6360$
2-methyl-2-hexanol:	$A=9.95$,	$B=4760$

A61A-0048 0830h POSTER

Uptake of Atmospherically Important Trace Gases on Aqueous Sulfuric Acid Droplets

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The uptake of atmospherically important gas-species on sulfuric acid droplets has been studied as a function of temperature (250–295 K) and acid concentration using the droplet train flow reactor. New data on uptake of water on concentrated sulfuric acid solutions will be presented and contrasted to our recent determination of the uptake coefficients of ammonia, HCl and other atmospheric trace gases. The distinct features of uptake governed by interfacial mass accommodation, surface reactivity and solubility constraints will be discussed and the atmospheric implications of our results examined.

A61A-0049 0830h POSTER

Reaction Probabilities for N₂O₅ Hydrolysis on Organic Aerosols at Room Temperature

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The heterogeneous conversion of N₂O₅ to HNO₃ on aerosol surfaces is now recognized as playing a crucial role in controlling the fate of nitrogen oxides in both the stratosphere and troposphere. While a significant portion of tropospheric aerosol consists of organic matter, the kinetics of N₂O₅ hydrolysis on organic aerosols have yet to be studied. For this purpose, we have constructed an aerosol flow tube coupled to a chemical ionization mass spectrometer for monitoring N₂O₅ concentrations in the presence of organic aerosol and a differential mobility analyzer for determining aerosol surface area. The aerosol phase – solid, supersaturated solution, or liquid – and relative humidity are simultaneously characterized using a second aerosol flow tube coupled to a FT-IR spectrometer. We focus our analysis on the reaction of N₂O₅ with malonic acid aerosols and, in particular, on the effect aerosol phase transitions have on the reaction probability. Reaction probabilities measured as a function of aerosol surface area, relative humidity, and aerosol phase are presented and implications for the tropospheric NO_x budget are discussed.

A61A-0050 0830h POSTER

Direct Time-Resolved Second Harmonic Generation and Thermal Desorption Studies of Tropospheric Relevant Heterogeneous NO_x Reactions

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It is now recognized that NO₂ can undergo heterogeneous conversion and sequestration reactions on the surfaces of solid atmospheric particulate matter that originate from natural and anthropogenic sources. These reactions are believed to impact the chemical composition of the troposphere as well as the chemical and optical properties of the particles on which the reactions occur. Thus, they are directly linked to climate and global change. However, not much is known about the time scales and the mechanisms of the heterogeneous reactions.

Using the surface-specific nonlinear laser spectroscopy second harmonic generation (SHG) in conjunction with thermal desorption spectroscopy (TDS), we have studied the interaction of NO₂ and HNO₃ with a variety of substrates relevant to solid atmospheric particulate matter in the absence and presence of water vapor. Surface SHG signals around 400 nm identify adsorbed NO₂ due to a two-photon resonance of our laser with electronic transitions in NO₂ near 400 nm and allow for kinetic studies. TDS is used for characterizing the efficiency of HNO₃ and NO₂ interactions with the substrates. The experiments are carried out using atmospherically relevant reactant partial pressures between 10–9 and 10–7 Torr; substrate temperatures are held between 300 and 150 K.

Room temperature measurements show that NO₂ adsorbs poorly to the surfaces of fused quartz and BK-7 glass substrates, while adsorption is efficient at lower temperatures. In contrast, HF-etched BK-7 glass substrates show efficient NO₂ adsorption at temperatures approaching 300K. SHG polarization measurements from additional experiments show that NO₂ is adsorbed to glass with its dipole oriented mainly along the surface normal. We have further studied the interaction of NO₂ with these substrates using SHG-TDS experiments which circumvent complications common to traditional TDS measurements, i.e. artifactual signal contributions from sample gas adsorption onto surfaces other than the sample surface. In addition to studying the glass substrates, we have also followed the adsorption of NO₂ onto wax and soot samples at room temperature.

We have also monitored the heterogeneous hydrolysis reaction of NO₂ on glass, soot, and wax samples according to NO₂ + H₂O → HNO₃ + HONO in real time. This reaction is quantitative on all substrates studied and occurs with half-lives on the order of minutes. The interaction of the product HNO₃ with various substrates was further investigated via TDS.

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A61A-0051 0830h POSTER

The Regional Atmospheric Chemistry Model, Version 2

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An updated version of the gas-phase Regional Atmospheric Chemistry Mechanism, RACM2, is introduced. The RACM2 mechanism is essentially a "one atmosphere approach"; it is intended for simulating remote as well as polluted conditions from the Earth's surface through the upper troposphere. The mechanism includes 275 reactions. This updated version includes improved mechanisms for the atmospheric chemistry of isoprene and for aromatic compounds, and updated cross-sections and quantum yields for the photolysis reactions. The direct formation of particles from biogenically emitted compounds is included in the mechanism. Environmental chamber data are used to evaluate the new RACM2 mechanism's ability to simulate ozone, NO, NO₂ and volatile organic compounds (VOCs). Model simulations of RACM2 are compared with those made using its predecessor, the RACM1 mechanism. We plan to implement the RACM2 mechanism into 3-dimensional atmospheric chemistry models such as the Community Multiscale Air Quality Modeling System (CMAQ) and the Mesoscale Meteorological Model, version 5 with Chemistry.

A61A-0052 0830h POSTER

A cloud-scale chemical-transport simulation during EULINOX. A case study for July 21 1998.

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The main issues addressed by the European project EULINOX covered mainly the quantification of NO_x production from lightning, the transport of NO_x and surface emissions (e.g. CO) by convective systems, and the lightning distribution around thunderstorms. O₃, CO, CO₂, NO_x, CN concentrations, J(NO₂), meteorological variables and lightning have been observed and measured using ground systems and aircraft platforms during the project. Two aircraft have been operated: the DLR Falcon and the Do-228 providing the distribution of species in the PBL and at higher altitudes across the anvil along the jet tracks. July 21st 1998 was a special day during EULINOX: strong convection system, high electrical activities and a NO pic around 23 ppbv on board Falcon in the anvil. Thunderstorms associated with strong convective systems were encountered and well covered by the network of measurement systems as well as for the meteorology than for the chemistry and lightning localization. This work focuses on two objectives: how to describe the meteorology during EULINOX and to quantify the impact of the cloud scales on tropospheric NO and CO concentration. To reach this target, 2 types of simulation have been performed. The first one uses the MM5 model in a 4 domain-nested version (ratio =3) to simulate the convective cloud system or isolated cell with a 1.5km by 1.5km resolution for the finest grid. The second run uses an off-line chemical transport model (MEDIUM) with a detailed chemistry assimilating in input the MM5 dynamics. On a broader scale, the general synoptic meteorology over Europe is well simulated by MM5. Over the finest domain, the model was able to generate a supercell storm but rather weak (vertical characteristics) and unstable compared to the observations. The cell depth is in a good agreement with observations with a horizontal position lightly shifted spatially. The chemical-transport simulation using MEDIUM including as input the MM5 meteorology output shows a significant contribution of surface pollution to the NO_x, CO and hydrocarbons concentration in and near the anvil. This paper discusses the ability of the model to simulate the vertical and horizontal distribution of tropospheric chemical species (CO, NO_x, VOC, O₃) compared to aircraft measurements under convective conditions when using high resolution emission ground chemical sources. Local NO production from lightning is necessary to explain the high NO level in the anvil measured on-board the Falcon. Sensitivity studies are done to explore the level of this production. Strong downward transport of upper tropospheric air masses is simulated by the model within the convection core implying transport of high ozone and NO_x concentration from upper level. The large scale and synoptic dispersion of species after the storm dissipation is calculated and discussed here in order to better quantify the importance of various source emissions on European level for NO_x, CO, ozone and VOC.

A61A-0053 0830h POSTER

A 2D Model Study of the Vertical Redistribution of Soluble and Non-soluble Trace Gases by a Cumulus Ensemble

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The vertical redistribution of trace gases with different solubilities and initial profiles by a cumulus ensemble is studied using a modified version of the Weather Research and Forecast Model (WRF). 2D simulations are performed for the TOGA-COARE region during 20-26 December 1992 specifying initial trace gas profiles for HNO₃, H₂O₂, CH₂O, CH₃OOH, CO, O₃ and other trace gases based on output from a global CTM. The trace gas concentrations are either reset to their initial values after every 24 hours or a simple nudging technique is applied. Results from sensitivity studies comparing two different advection algorithms and two different Lin-type microphysics parameterizations are presented and for H₂O₂ and HNO₃ these sensitivities are compared to sensitivities for varying assumptions about ice-uptake and retention coefficients.

A61A-0054 0830h POSTER

Modeling the Activation of Externally Mixed Inorganic Aerosol Populations: the Effects of Competition and its Sensitivity to Mixing State

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Modeling studies hint at the large impact of competition between pre-cloud aerosol of varying compositions and sizes on cloud condensation nuclei concentrations (e.g., Ghan et al., J. Atmos. Sci., 55(22), 3340, 1998). In certain situations, the presence of a small number of favorably composed aerosol is as important to aerosol activation as the total aerosol loading. Yet most microphysical models used to investigate aerosol activation resolve too poorly the aerosol mixing state and variation amongst the particles. Also, large-scale investigations into the indirect effects generally parameterize activation as a simple function of sulfate loading, and so miss these dynamics entirely.

We investigate the sensitivity of aerosol activation to mixing state of inorganic aerosol populations using a new aerosol-cloud microphysical model that fully resolves both size and composition. The model incorporates aerosol thermodynamics, aqueous and gas phase chemistry, and a non-equilibrium condensation schemes. We present the results of initial studies into how the activation statistics of aerosol in simple externally mixed inorganic systems change when: a) variations in composition amongst similarly sized particles are increasingly resolved; and b) a small number of favorably composed particles are introduced. We suggest further studies that will lead towards parameterizations of multi-component and externally-mixed aerosol activation. These parameterizations should be suitable for representing the relationship between mixed aerosol populations and cloud condensation nuclei formation necessary for including the indirect effect in larger-scale models.

A61A-0055 0830h POSTER

Total Versus Speciated Monoterpene Concentrations and Fluxes: Do Speciated Measurements Underestimate Emissions?

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Concentrations and fluxes of speciated and total monoterpenes were measured simultaneously above a ponderosa pine plantation at Blodgett Forest, in the Sierra Nevada, CA. Speciated measurements were made using relaxed eddy accumulation (REA) coupled with a gas chromatograph with flame ionization detectors (GC-FID), and total monoterpene measurements were made using eddy covariance coupled with a proton

transfer reaction mass spectrometer (PTR-MS). Ambient, in situ measurements of monoterpene concentrations and fluxes are typically limited to a few monoterpene species. Because simultaneous measurements of both total and speciated monoterpenes have never been made, it is not known whether speciated monoterpene measurements adequately represent the impact of total monoterpene emissions to the atmosphere. We present results from the first field experiments comparing simultaneous measurements of concentrations and fluxes of seven commonly emitted monoterpene species with new measurements of total monoterpene concentrations and fluxes. As all monoterpene species share the same mass, the PTR-MS, coupled with the eddy covariance technique, allowed us to make real time, in situ concentration and flux measurements of the sum of all monoterpene species in the atmosphere. These two flux measurement techniques were in good agreement on the temporal pattern of monoterpene flux, but showed that measurements of speciated monoterpenes underestimated the flux of total monoterpenes to the atmosphere. As our GC-FID system is comparable to other speciated monoterpene concentration measurement systems typically used, the underestimation of emissions made by our speciated measurements suggest that models based on speciated monoterpene flux measurements may be underestimating regional and global monoterpene emissions and their impacts on atmospheric chemistry.

A61A-0056 0830h POSTER

Cloud Droplet Effective Radius Derived from Ground-Based Remote Sensing at the ARM SGP and NSA sites

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Aerosols affect global climate directly, by scattering or absorbing radiation, and indirectly, by altering cloud microphysical and radiative properties. However quantification of these effects has been limited, especially the indirect effect. The U.S. Department of Energy's Atmospheric Radiation Measurement (ARM) program established the Southern Great Plains (SGP, north-central Oklahoma) and North Slope of Alaska (NSA, near Barrow) Cloud and Radiation Testbed sites to conduct multiple continuous in-situ and remote measurements of radiation and cloud and aerosol properties over extended periods. Here we examine remotely sensed microphysical properties of low clouds and relations to aerosol loading at the surface at the SGP and NSA sites for the year 2000. Widespread low-level water cloud layers without interference from higher-level ice clouds are most favorable for testing relations between radiation and microphysical properties. Suitable cases were carefully selected by examination of time series for cloud layers (mainly from cloud radar), liquid water path (LWP, microwave radiometer) in excess of 100 g m⁻², and direct and diffuse solar irradiance (pyranometers). Spectral diffuse-horizontal irradiance relative to top of atmosphere was measured by a Multi-Filter Rotating Shadowband Radiometer (MFRSR); cloud optical depth was obtained using the observed atmospheric transmittance and surface albedo (Min and Harrison, GRL, 1996) for solar zenith angle (SZA) less than 75°. Situations of low-level and thin cloud layer are much less prevalent at SGP than at NSA, which is influenced by marine boundary layer cloud but limited by the SZA requirement. The primary controlling influence on cloud optical depth is LWP, with microphysics exerting a smaller influence that is discernible from differences in slopes graphs of optical depth vs. LWP (Schwartz et al., PNAS, 2002). Continental clouds exhibit low effective radii (typically 6-10 μm) indicative of strong aerosol influence.

A61A-0057 0830h POSTER

Terra Aerosol, Cloud and Tropospheric Chemistry Data Sets Available From the NASA Langley ASDC

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Data from three instruments currently flying aboard the Terra satellite whose measurements include aerosols, clouds, and tropospheric chemistry are available from the NASA Langley Atmospheric Sciences Data Center (ASDC). The Clouds and the Earth's Radiant Energy System (CERES) instrument measures broadband radiative fluxes at the top of the atmosphere along with cloud and aerosol properties. The Multi-angle Imaging SpectroRadiometer (MISR) instrument obtains precisely calibrated images at nine different viewing angles and four wavelengths to provide radiance, aerosol, cloud and land surface data. The Measurement of Pollution in the Troposphere (MOPITT) instrument makes global measurements of methane and carbon dioxide concentrations. The Terra satellite, part of NASA's Earth Observing System (EOS) satellite series, was launched on December 18, 1999.

The NASA Langley Atmospheric Sciences Data Center archives and distributes data from all three of these instruments. Data, tools and information are available at the ASDC web site, <http://eosweb.larc.nasa.gov>.

URL: <http://eosweb.larc.nasa.gov>

A61A-0058 0830h POSTER

Trace Elements in Aerosol over the Grand Canyon and Canyonlands National Parks

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Daily samples of total suspended particulates were collected from two national parks, Grand Canyon National Park, AZ, and Canyonlands National Park, UT, in the summer (July) and winter (December-January) of 2001. Trace element and major ion concentrations were determined for source attribution studies. The concentrations of most elements agreed within a factor of two for the two sites. However, for the summer samples, preliminary results indicate that some pollution-derived elements such as Cu, Ag, Hg, Zn, and Pb had higher concentrations and enrichment factors at the Grand Canyon, suggesting impacts from nonferrous combustion source(s) in the area. Additional information, including meteorological data, will be used to help identify these sources.

A61A-0059 0830h POSTER

The Western States Visibility Assessment Program: Diurnal and Seasonal Measurements of TSP, PM_{2.5}, CO, SO₂, NO_x, and O₃ at Grand Canyon and Canyonlands National Parks

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As a part of the Western Visibility Assessment Program, initiated to assess particle and haze formation associated with Class I sites across the Southwestern United States, criteria pollutants were monitored at sites within Grand Canyon (Arizona) and Canyonlands (Utah) National Parks. Beginning in July of 2001, continuous measurements of CO, SO₂, NO_x, and O₃ were initiated. Additionally, three separate intensive field studies (Summer 2001, Winter 2002, and Summer 2002)

were conducted in which filter-based particulate concentrations (TSP and PM_{2.5}) were also collected. Summertime concentrations of CO, SO₂, NO_x, O₃ and Total Suspended Particulate (TSP) at the Grand Canyon site averaged 0.12 ppm, 0.6 ppb, 3.71 ppb, 48.7 ppb, and 19.9 µg/m³, respectively. Corresponding concentrations at the Canyonlands site averaged 0.18 ppm, 0.5 ppb, 2.47 ppb, 49.0 ppb, and 36.8 µg/m³, respectively. Grand Canyon wintertime average concentrations for the same compounds were 0.05 ppm, 1.2 ppb, 2.16 ppb, 42.7 ppb, and 3.3 µg/m³, respectively. Wintertime Canyonlands concentrations averaged 0.20 ppm, 5.2 ppb, 4.75 ppb, 39.2 ppb, and 4.4 µg/m³, respectively. Diurnal and seasonal variability of these compounds, as well as their relationships with local and long-range meteorology, will be presented.

A61A-0060 0830h POSTER

The Western States Visibility Assessment Program: Diurnal and Seasonal Measurements of Halocarbons, Nonmethane Hydrocarbons and Oxygenated Hydrocarbons at Grand Canyon and Canyonlands National Parks

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Air samples were collected and analyzed for selected halocarbons, nonmethane hydrocarbons, short chain carboxylic acids, and low-molecular-weight carbonyl compounds at Grand Canyon and Canyonlands National Parks during the summer of 2001, winter of 2001-2002 and summer of 2002 to determine seasonal and diurnal variations as well as possible sources of the air masses containing these materials. Acetic acid and formic acid average values were low at both sites (2.6 and 1.5 ppbv at Canyonlands and Grand Canyon respectively for acetic acid and 2.1 and 4.8 ppbv for formic acid at the two sites in winter 2001-2002). The summer, 2002 averages for acetic acid and formic acid at Grand Canyon were 2.9 and 2.3 ppbv respectively. The relatively high formic concentration at Grand Canyon in the winter is consistent for the noon and midnight samples. Formaldehyde concentrations during the summer, 2002 sampling averaged 10.5 ppbv at Canyonlands and 6.5 at Grand Canyon, comparable to values seen in urban environments while acetone values were relatively low at 1.0 and 0.65 ppbv respectively. Total carbonyl compounds measured were 15.8 and 10.3 ppbv at Canyonlands and Grand Canyon respectively. Potential sources will be discussed and comparisons will be made with hydrocarbon analyses on whole air samples collected simultaneously.

A61A-0061 0830h POSTER

Mineral dust impact on tropospheric chemistry: The relative roles of photolysis and heterogeneous uptake

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We investigate the influence of mineral dust on tropospheric chemistry in the present climate at global scales. The analysis examines the effects of dust on photochemistry and heterogeneous uptake, operating independently and together. In numerical experiments the size-resolved, time-varying mineral dust distribution predicted by the global Dust Entrainment and Deposition (DEAD) model perturbs the gas phase species in a global Chemical Transport Model (UCI CTM). We find that the photolysis perturbation dominates low-to-mid latitudes and low-to-mid altitudes, while heterogeneous uptake dominates high latitudes and high altitudes. Feedbacks between the photochemical and heterogeneous effects of dust are weak over vast regions. Ozone and odd-nitrogen concentrations are perturbed in opposite directions by photolysis and heterogeneous chemistry, resulting in a weak net change. However,

both processes decrease the concentrations of OH and OH₂. The global mean change due to dust is -0.4% for tropospheric O₃, -5.6% for OH, -1.7% for HO₂, and -1.6% for HNO₃. Large seasonal signals are present in dust source regions. Over the north African region and tropical Atlantic Ocean downwind, OH decreases by -22.1%, a factor of four more than global mean value. In dusty regions, O₃ change due to heterogeneous reactions on dust is not sensitive to dust vertical structure. O₃ change due to photochemistry is sensitive to dust vertical structure but also depends on the availability of O₃ precursors. In polar regions, O₃ change is dominated by transported O₃ and is not sensitive to local dust concentration or vertical structure.

A61A-0062 0830h POSTER

The Study of Artificial Aerosol Clouds on The Basis of Experimental Examinations

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Antihail rockets with different compositions were exploded at the height of 3-8 km in the free atmosphere under the conditions of the natural field experiments.

The microphysical characteristics of the artificial aerosol cloud were measured from plane-laboratory, with cameras and with electromagnetic waves within the range of the wavelength 10mm-2m. The created cloud has positive charge.

Also, at the same time, while this plane-laboratory was flying through the aerosol formation, the values of electrical field voltage, temperature and the humidity of the atmosphere were registered.

The development of the aerosol clouds depends on main physical parameters, which were single out.

On the basis of these experiments it has been derived the dates, which were characterized the correlation relationship between the aerosol cloud's volume and the mass of explosive substances and their characteristics.

A61A-0063 0830h POSTER

AEROSOL PLUME DURING A POLLUTED EVENT OCCURRING OVER PARIS AREA AND ITS POTENTIAL PHOTOCHEMICAL EFFECT

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As in many big cities, there are several pollution events in Paris area. A thorough understanding of the processes leading on the formation of pollutants and their transport during pollution episodes is necessary. One of the pertinent factors, which contributions on atmospheric chemistry and radiative effect are not yet well known, is the aerosol.

ESQUIF (Etude et Simulation de la Qualité de l'air en Ile de France) is the first program dedicated to study such issues over the Paris area. It was carried out from summer 1998 to winter 2000 (Menut et al., 2000). To characterize all the properties of the urban aerosol, many campaigns were coordinated using both ground and airborne measurements (Chazette et al., 2000). We are focusing on the 31st of July 2000 where a well-defined polluted plume has been observed. Aerosol number concentrations in different size classes were measured and show that urban aerosol in Paris area is mainly submicronic. The absorbent part of the aerosol, mainly associated to the black carbon component, has been observed to be associated to particles with diameter less than 0.1 µm. The single scattering albedo has been assessed to be close to 0.85 leading to a significant influence on the photochemical chemistry. Indeed, a significant decrease of the daily maximum ozone concentration has been calculated using the INCA model and will be presented.

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A61A-0064 0830h POSTER

Elemental Carbon in Highly Polluted Urban Fog in South Asia

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Since 1998 severe winter fogs frequently occurred in Northeastern Pakistan and India. These fogs were closely related to the heavy load of aerosols and gases in the atmosphere due to the increasing emissions by the rapid industrialization in this region. In this study, aerosol data including elemental and organic carbon (EC, OC), sulfate and trace element concentrations were determined during two particularly severe fog periods at Lahore, Pakistan. In the first episode, TSP samples were collected on Whatmann 41 filters with high-volume samplers every 12 hour during and after a heavy fog event from January 1 to 5, 1999. A technique had been developed to transfer EC to quartz filter without loss for analysis with thermal-optical method. High EC concentrations were found up to 25 µg/m³. Extremely high sulfate concentration was found, up to 100 µg/m³. The SO₄/Se ratio and trace element factor analysis suggested sulfate were formed from a distant source of hundreds of kilometers away. In the second episode, TSP samples were collected on quartz filters in 6-hour (daytime) and 12-hour (nighttime) intervals for both EC and OC measurements during December 25-31, 1999 with different fog types (very light, light, medium and heavy) and without fog. High EC and OC concentrations ranging in 10 to 25 µg/m³ and 100 to 300 µg/m³ were observed. EC and OC had a high correlation with stable EC/OC ratios within 8 to 16%, which suggested EC and OC in aerosols were from the same source. High sulfate concentrations were also observed, 25 to 55 µg/m³. The SO₄/Se ratio and trace element factor analysis also suggested sulfate were formed during the fog period. Particularly, SO₄/EC ratios had a very strong relation with fog types and sunlight strength. In daytime, the ratio obviously increased with sunlight strength, and significantly changed with and without fog. In nighttime, the ratio generally increased with fog density. Compared to sulfate profile, SO₄/EC ratio could show photochemical process more clearly and thus be a better indicator. However, the major production mechanism for the very high sulfate concentrations in the two fog events still appeared uncertain yet. Total Sulfur concentrations were frequently 25 to 30 ppb in the fog events. The high concentrations of H₂O₂ and O₃ needed to produce such concentrations of sulfate are not expected to be present, especially during winter months. Due to pH limit, other mechanisms including oxidation by metal catalysts and NO₂ also seemed not enough for high sulfate production. The previous lab experiments showed that soot might play a major role in the catalytic oxidation of SO₂ to sulfate in the polluted air (Novakov et al., 1974, *Science*, 186, 259-261). This mechanism was supported by the recent experiments that SO₂ could be rapidly adsorbed in soot (Koehler et al., 1999, *JGR*, 104, D5, 5507-5514) and oxidize soot to form carbon cluster anions, which play as the open shell radicals (Wallace et al., 2002, ACS Conference, Boston). Therefore the very high EC concentrations during the two fog events appeared this mechanism might be the major although not the only one. On the other hand, this study will help us to understand EC concentration and its influence on aerosol characters and mixing types in this region, and the data are useful on climate modeling.

A61A-0065 0830h POSTER

La Jolla Fog Study

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The Center for Atmospheric Sciences at the Scripps Institution of Oceanography conducted a ground-based experiment to study fog/marine-stratus clouds over the San Diego region during the summer months of 2002. The purpose of the experiment is to understand aerosol/cloud interactions and how they might influence cloud radiative properties and precipitation. We operated several instruments on Mt. Soledad to study aerosol and cloud properties. These instruments include a forward scattering spectrometer probe (FSSP-100) and an aerosol particle sizer (APS) to measure the cloud droplet spectra during fog events, condensation particle counters to determine total aerosol concentrations, cloud condensation nuclei counters to understand aerosol/cloud droplet interactions, a scanning mobility particle sizer (SMPS) to determine dry aerosol number size distributions, and a weather station to relate fog events to local meteorology.

Aerosol concentrations showed a diel variation with high and variable particle concentrations during the day, which often were greater than 10⁴ cm⁻³. Night-time concentrations were lower (i.e., several thousand cm⁻³) and exhibited less variation than daytime values. In general, aerosol concentrations do not appear to be correlated to droplet concentrations indicating that local anthropogenic sources may not have a large influence on the coastal fog.

Two types of events (haze and fog) have been characterized during this study based on the droplet distribution. A haze event was dominated by droplets less than 5 µm diameter and sometimes exceeded droplet concentrations of 1000 cm⁻³. There were virtually no particles larger than 5 micron diameter during these events. A fog event was characterized by larger droplets with droplets greater than 5 µm diameter accounting for a bulk of the number concentration. The average effective radius during these fog events was about 5 µm and the droplet concentration rarely exceeded 100 cm⁻³. On several occasions, a fog event changed to a haze and back to a fog again. It is not sure if this effect is a result of anthropogenic aerosol sources or local meteorology and will be discussed in greater detail.

A61A-0066 0830h POSTER

Sensitivities and Uncertainties of DMS Oxidation Products in the Remote Marine Boundary Layer

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The sensitivities and uncertainties of the products of dimethylsulfide (DMS) oxidation to 56 uncertain model parameters were calculated for a diurnally-varying box model of the remote marine boundary layer (RMBL). The oxidation of DMS is based on a recently reported mechanism that includes new routes for the production of gas-phase methanesulfonic acid (Lucas and Prinn, 2002). Direct integration and probabilistic collocation methods were used to compute the following quantities: first-order local sensitivities as a function of time; global and higher-order sensitivities; probability density functions (PDFs) of the concentrations of important DMS-related species; the first three moments of the concentration PDFs; and the parameter contributions to uncertainties in the sulfur-containing species.

From the sensitivity analysis we found that, at the mean values of the model parameters, the oxidized DMS products are locally sensitive to the DMS + OH abstraction and addition reactions, heterogeneous removal, DMS emissions, and mixing into and out of the RMBL. At 1-σ below the mean parameters, however, the global sensitivities are radically different such that heterogeneous removal and DMS emissions are no longer dominant processes. These variations in the sensitivities to global changes in the uncertain parameters are comparable to the diurnal changes in the local sensitivities. Significant second- and third-order sensitivities were also found, thus highlighting the importance of non-linear dependencies and parameter interactions.

On the basis of the uncertainty analysis, the 1-σ uncertainties for the important DMS-related species concentrations range between 40 and 390%. Though DMS emissions and heterogeneous removal are the main contributors to these uncertainties, many gas-phase reactions also make large contributions. In addition, non-linearities—involving gas-phase chemistry, heterogeneous loss, DMS emissions, and RMBL mixing—lead to skewed PDFs for many of the species. Further, these non-linearities are found to account for 2 to 25% of the total uncertainty in the sulfur-containing concentrations.

A61A-0067 0830h POSTER

Assessment of DMS Photochemistry at Jeju Island During the Asian Dust-Storm Period of Spring 2001: Comparison of Model Simulation with Field Observations

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This study examines the influence of long-range transport of dust particles and air pollutants on both local/regional DMS oxidation chemistry and the distribution of sulfur compounds at Jeju Island (33.17°N, 126.10°E) during the Asian dust-storm (ADS) period in April 2001. The atmospheric concentrations of these sulfur species were measured at a ground station on Jeju Island, Korea as part of the ACE-Asia intensive operation. Three ADS events were observed during the periods of 10-12, 13-14, and 25-26 April, respectively. The concentrations of DMS and CS₂ were higher during the ADS period than during the non-Asian-dust-storm (NADS) period. Conversely, a difference in SO₂ levels during the ADS period was not distinguishable from those measured during the NADS period. The diurnal variation pattern of DMS observed was largely different from that in the remote marine boundary layer. DMS loss by NO₃ in the atmospheric boundary layer was dominant due to significantly high NO_x levels influenced by the long-range transport of pollutants from East Asia to Jeju Island. The DMS maximum during the ADS period was observed in the late afternoon. The oceanic fluxes of DMS during the ADS and NADS periods were estimated to be 5.7 ± 2.3 and 2.9 (+2.8/-1.5) µ mole m⁻² day⁻¹, respectively.

A61A-0068 0830h POSTER

Sulphate in PM 2.5 in the Fraser Valley, Canada: Isotopic Evidence for its Sources and Oxidation Pathways

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The source and oxidation pathways for sulphate formation in PM 2.5 were studied as part of the Pacific 2001 campaign to learn more about the mechanisms of aerosol formation and to evaluate the contribution of biogenic emissions to aerosol formation in the region. Aerosols were sampled at two locations; one site was generally upwind of the bulk of land-based emissions and in the midst of Vancouver traffic in Burnaby, while the second site was located in a rural setting in Langley, downwind of Vancouver and rural and industrial emissions. Aerosol sulphate was collected every 12 hours using high volume samplers. Sulphur isotope analysis of the aerosol sulphate provided information on the source of sulphur. The oxygen isotope composition of sulphate was used to examine SO₂ oxidation pathways. Using the isotope data, an apportionment model for the region was constructed. This model was used to provide an estimate of the proportion of DMS sulphate present in PM 2.5.

A61A-0069 0830h POSTER

Measurement of Total Non-volatile and Semi-volatile Organic Carbon Associated with PM2.5 in Vancouver during Pacific 2001

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The behavior and chemical speciation of organic carbon (OC) is one of the poorest understood aspects of fine particulate matter (i.e., PM_{2.5}). In the Lower Fraser Valley, which was the region studied during Pacific 2001, understanding OC is especially important because it is the dominant fine particle component. Accurate determination of the concentration of OC is difficult due to the lack of appropriate sampling methods. Traditional samplers such as a filter pack (FP) have inherent artifacts during sampling, which leads to underestimates of the actual particle phase OC during some conditions and overestimates in other cases. In our study, a denuder-based integrated organic gas and particle sampler (IOGAPS) was employed. The IOGAPS is able to reduce the sampling artifacts, since the gas phase organics are removed first by the denuder placed upstream of a quartz filter while the semi-volatile organic carbon (SVOC) evaporated from the particles is collected by backup sorbent impregnated filters (SIFs). Both denuder and SIF are coated with XAD resin to retain organics. The quartz filter and the SIF can be analyzed directly for non-volatile OC and SVOC, respectively, using thermal-optical transmission analysis. This sampling and analysis method was tested in Toronto in July 2001 and then applied at the urban site (Slocan Park) on seven days during Pacific 2001. In both locations, samples were collected twice a day to investigate the diurnal pattern of OC, SVOC and EC. Compared with the OC determined by the filter pack sampler, lower OC on the quartz filter of the IOGAPS confirmed that the denuder could efficiently remove positive artifacts. Higher nighttime SVOC levels were observed in both cities, suggesting that more of the SVOC from primary sources and secondary formation condenses onto particles at night due to the decreased ambient temperature. At Slocan Park, the amount of the total particle phase OC found to be SVOC ranged from 0% to 32% during the day and 2% to 27% during the night.

A61B MCC: Hall D Saturday 0830h

Oxygenated VOCs II: New Developments Posters

Presiding: R J Yokelson, University of Montana; S Paulson, University of California, Los Angeles

A61B-0070 0830h POSTER

Direct Emission of Methylvinylketone from Birch (*Betula pendula*)Achim Folkers¹ (x49-(0)2461-618679; a.folkers@fz-juelich.de)Ralf Koppmann² (x49-(0)2461-615118; r.koppmann@fz-juelich.de)Jürgen Wildt¹ (x49-(0)2461-618684; j.wildt@fz-juelich.de)¹ICG-III: Phytospäre, Forschungszentrum Jülich, Jülich 52425, Germany²ICG-II: Troposphäre, Forschungszentrum Jülich, Jülich 52425, Germany

Volatile organic compounds (VOCs) are of central importance for the chemistry of the troposphere. They have a significant impact on photochemical processes that lead to the formation of ozone and other photooxidants in the planetary boundary layer. With estimated global emission rates of 520 Tg yr⁻¹ [Guenther *et al.* 1995], biogenic emissions of short chained oxygenated VOCs (SOVOCs) like methanol, ethanol, acetaldehyde, and acetone cannot be neglected for atmospheric chemistry. In addition to the direct emissions by plants SOVOCs are produced by chemical reactions of VOCs in the atmosphere. For some SOVOCs such as methanol, acetone, or leaf alcohols it is known

that they have a large biogenic source strength. Other SOVOCs are believed to be only produced by atmospheric processes. For example methacrolein, and methylvinylketone (MVK) are believed to be exclusively produced during atmospheric isoprene oxidation. Thus, up to now the only known source of MVK in the atmosphere is the oxidation of VOCs like isoprene.

We analysed SOVOC emissions from different plant species under well defined conditions in our plant chambers and determined the temperature- and light intensity dependence of their emission rates. During these measurements we also observed a direct MVK emission from birch. The emission rates exhibit a temperature and light intensity dependence. Artificial MVK formation was excluded by a series of experiments. Due to the direct emission of MVK probably also from other plant species than birch, measurements of ambient concentrations of this compound have to be carefully investigated. The fact that there may be a primary source for MVK has to be considered in model calculations concerning the photochemistry and the concentrations of OH radicals in the lower troposphere.

References

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klüger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. (1995), A global model of natural volatile organic compound emissions, *J. Geophys. Res.*, **100**, 8873-8892.

A61B-0071 0830h POSTER

Bimolecular Reaction of SO₂ with Thermalized Syn Carbonyl Oxide from Isoprene OzonolysisDan Zhang¹ (979-458-1822; dzhang@ariel.met.tamu.edu)Renyi Zhang¹ (979-845-7656; zhang@ariel.met.tamu.edu)¹Department of Atmospheric Sciences, Texas A&M University, College Station, TX 77843

Cycloaddition of O₃ to isoprene yields carbonyl oxides consisting of chemically activated syn and anti configurations. The excited carbonyl oxides then undergo prompt unimolecular isomerization or collisional stabilization. Prompt reaction of syn or anti carbonyl oxides has been shown to be a source of hydroxyl radical OH. The thermalized syn carbonyl oxides also decompose to form OH or engage in bimolecular reactions with SO₂, H₂O, CO₂, aldehydes, etc. The reaction with SO₂ can contribute to oxidation of SO₂ to H₂SO₄, a crucial step in the formation of sulfate aerosols. In order to assess the role of isoprene ozonolysis in OH formation and SO₂ oxidation, we have performed a theoretical study of the bimolecular reaction between syn carbonyl oxide and SO₂. A mechanism involving the addition of SO₂ to carbonyl oxide, followed by decomposition pathways leading to SO₃ formation is proposed. Rate constant of each reaction step is evaluated based on Transition State Theory and compared with other competing reactions in atmospheric SO₂ oxidation. The results reveal a profound impact of the title reaction on SO₂ oxidation and OH formation yield from isoprene ozonolysis under atmospheric conditions.

A61B-0072 0830h POSTER

Quantification of Carboxylic Acid Formation from the Reaction of Ozone with Alkenes

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This study focuses on identification and quantification of carboxylic acids from the ozonolysis of C₃ to C₁₀ alkenes under dry and humid conditions. Analysis was performed using solid phase microextraction for smaller simple acids, and in-inlet derivatization for larger and multifunctional acids. Both techniques were used in conjunction with GC/FID/MS. Acid yields from 2 to 10 percent were observed. Yields decreased somewhat at higher humidities, indicating that the water reaction with the so-called stabilized Criegee intermediate is not the source of acids from these reactions. A possible mechanism for their formation will be discussed.

A61B-0073 0830h POSTER

Ozonolysis of a series of alkenes in a large simulation chamber

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The simulation chamber SAPHIR on the campus of the Forschungszentrum Jülich provides a volume of 300 m³ in which chemical processes of atmospheric relevance can be studied under conditions of ambient trace gases mixing ratios. In this study we examined the ozonolysis of ethene, propene, and 4 different isomers of butene (iso-, n-, trans-, and cis-butene) at different conditions: dry (p(H₂O)=0.1 hPa) and humid (10 hPa), with and without CO. Experiments with CO (500 ppm) were used to avoid the reaction of OH with the alkene in order to follow the loss of alkene due to the ozone reaction. These experiments provide data for the ozone alkene rate constants which were within the error margin given in the literature. By a specific data analysis of the experiments without CO we have been able to determine the OH and HO₂ yields for these reaction systems. The results show a distinct water dependence of the OH yields for most alkenes, not observed before.

A61B-0074 0830h POSTER

Validation Of VOC Measurements By PTR-MS Using A Gas Chromatographic Pre-Separation Technique

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Proton-transfer-reaction mass spectrometry (PTR-MS) has emerged as a useful tool to measure volatile organic compounds (VOCs), including many oxygenated VOCs, in the atmosphere. In PTR-MS, organic trace gases are ionized by proton-transfer reactions with H₃O⁺ and are detected with a quadrupole mass spectrometer. The technique combines a fast time response (a few seconds or less) with a high sensitivity (10-100 pptv), which enables applications in rapidly changing air masses, such as encountered in airborne measurements or when measuring VOCs close to a source. In PTR-MS, only the mass of the ions produced in the instrument is determined, which is a useful but not a unique indicator of the identity of a VOC. Therefore, the selectivity of PTR-MS for different VOCs needs to be investigated. In this work, we have coupled a gas chromatographic column to a PTR-MS instrument to study the selectivity of PTR-MS in different air masses. Using this so-called GC-PTR-MS combination we have analyzed a large number of urban air samples as well as standard gas mixtures. The database that has emerged from this work is a useful tool in interpreting the mass spectra observed by PTR-MS, and a number of VOCs have been identified that can be uniquely detected by PTR-MS. Secondly, we have quantitatively inter-compared on-line PTR-MS measurements with GC-PTR-MS analyses of samples collected in parallel. The good quantitative agreement between the independent measurements infers generally insignificant interferences from such compounds as organic acids and peroxides in the PTR-MS system while the slightly decreased response for certain OVOC's in the GC-PTR-MS system can be attributed to the more involved sample treatment.

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Comprehensive Laboratory Measurements of the Emissions From Fires in Indonesian and African Fuels Measured by FTIR, PTR-MS, and GC

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