

We employ observations from HALOE and from balloon-borne instruments (on OMS-remote, OMS in-situ, and Triple) to investigate ozone loss in the stratosphere in the vortex in Arctic winter 1999-2000. Using HF and CH₄ as a long-lived tracer, we identify chemical ozone destruction and chlorine activation in the polar vortex. Reference relations, relevant for chemically undisturbed "early vortex" conditions are derived from the OMS-remote and in-situ balloon measurements on 19 November and 3 December 1999. Deviations from this "early vortex" reference are caused by chemical ozone loss and heterogeneous chlorine activation. The observations indicate severe chemical ozone loss, with a maximum loss of over 60% locally in the lower stratosphere (465-415 K) by mid-March 2000. The average loss in column ozone between 380-550 K, (deep) inside the vortex, in mid-March amounts to about 85 ± 10 DU.

The findings for winter 1999-2000 are put into perspective of Arctic ozone loss deduced from HALOE measurements in earlier cold winters (e.g., 1992-1993, 1994-1995, and 1996-1997). These winters have been reanalysed using the most recent HALOE data version. Further, additional observations were taken into account to investigate the validity of the reference relation for chemically unperturbed conditions in the early vortex.

A51E-0091 0830h POSTER

Some Characteristics of the Mesosphere and Lower Thermosphere (MLT) as Observed by the High Resolution Doppler Imager (HRDI) on UARS

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The HRDI instrument measured the winds, temperature, and molecular oxygen A band volume emission rate from November, 1991 until September, 2001. The altitudes examined were typically 65-115 km. The precession rate of UARS allowed complete local time coverage at mid and low latitudes to be sampled in about a month. This paper examines features found in nearly 10 years of MLT data collected by HRDI. This length of time has covered about 20 semi-annual cycles, 10 annual cycles, 4 QBO cycles, and almost an entire solar cycle. The response of the wind and temperature fields to these phenomena are examined

A51E-0092 0830h POSTER

Data Comparison: Satellite and Falling Sphere Temperatures

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Small meteorological rocketsondes providing temperature data have been used for comparison with, and validation of measurements from satellite-borne instruments. A significant number of rocket-borne falling spheres were launched in conjunction with the Upper Atmosphere Research Satellite (UARS) for validation of the Halogen Occultation Experiment (HALOE), High Resolution Doppler Interferometer (HRDI), and the Microwave Limb Sounder (MLS) instruments. Upper stratosphere and mesosphere temperatures measured with these instruments on UARS are compared with inflatable spheres launched from Wallops Island (1992-1998), Brazil (1994), Hawaii (1992), Norway (1992), and Sweden (1993 and 1996). Time and space differences varied between the satellite measurement and the rocketsonde launch, for example HALOE overpasses occurred within 5 days and in some cases there were spatial differences of up to 30 degrees longitude. Validation measurements of the HRDI instrument occurred at Wallops Island when it passed within 20 minutes and 330 kilometers of the launch site. Because of discontinuity in the falling sphere drag coefficients when fall speed neared MACH 1 falling sphere temperatures near 70 kilometers altitude are biased toward lower temperatures. Availability of improved software and a new atmospheric model have helped to reduce this bias. The

validated remote instrument measurements permit a new perspective of atmospheric structure to be formed, not always possible with the limited number of falling sphere measurements. Features of the remote measurement temperature profiles and their possible use to extend the climatological data base at the rocketsonde sites will be discussed.

A51E-0093 0830h POSTER

Longitudinal Variations of Mesospheric Temperature at Middle and High Latitudes - the WINDII Perspective

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Longitudinal variations of mesospheric temperatures observed by the WIND Imaging Interferometer (WINDII) on the Upper Atmosphere Research Satellite will be presented and discussed. The study will examine global day-to-day and year-to-year variability in the height range 65-95 km. Planetary scale perturbations will be analysed employing LMS spectral analysis.

A51F MC: Hall D Friday 0830h

Tropospheric Chemistry and Constituents II

Presiding: P Shepson, Purdue University,

A51F-0094 0830h POSTER

Effect of a Frontal System on Non-Methane Hydrocarbon Distribution over Central Europe

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The distribution of C2-C7 non-methane hydrocarbons (NMHC) has been determined during periods of convective and frontal activity over central Europe. High frequency whole air sampling was carried out on board the UK Meteorological Office C-130 Hercules aircraft during the EXPORT campaign, August 2000 (European eXport of Precursors and Ozone by long-Range Transport). The distribution of NMHC during and after the passage of a WCB (Warm Conveyor Belt) associated with a cold front was investigated. Advection was shown to have occurred over several days but embedded convection within the WCB caused rapid uplift of reactive carbon from the boundary layer to the mid-troposphere. Post-WCB, elevated levels of NMHC in the free troposphere due to convective mixing were observed. High mixing ratios of NMHC were found at altitudes of up to 5 km (propene, $t = 5.28$ hours, 13.8pptV).

The observations indicate that uplift of reactive NMHC during frontal passage may significantly perturb partitioning and abundance of inorganic and organic peroxy radicals and lifetime of hydroxyl radical (OH). The net production rate of ozone (N(O₃)) within the WCB was calculated using the photostationary state expression (PSS), showing net ozone production in the free troposphere.

A51F-0095 0830h POSTER

Mono-aromatic complexity in urban air and gasoline assessed using comprehensive GC and fast GC-TOF/MS.

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Two state-of-the-art analytical techniques have been used to assess mono-aromatic complexity in gasoline, gasoline vapors and polluted urban air. A comparison of comprehensive gas chromatography (GCxGC) and fast gas chromatography - time-of-flight mass spectrometry (GC-TOF-MS) has been made, with emphasis on the ability of each technique to appreciate at high isomeric complexity. The high spectral acquisition rates from TOF-MS gave improved peak deconvolution of overlapping analytes when compared to standard quadrupole configurations, with 89 mono-aromatic isomers isolated in gasoline in a 200 s GC separation. Highest resolution was obtained using GCxGC, isolating 140 mono-aromatics, using combined column retention behavior for analyte identification. Analysis of urban air using GCxGC indicated the presence of 136 mono-aromatic species with up to 7 carbon substituents on the ring. Comparison of 3D GCxGC chromatograms for air and gasoline vapors demonstrated visually the impact of evaporative emission sources in urban environments. The potential contribution of larger mono-aromatic compounds as precursors to both photochemical ozone and secondary organic aerosol is discussed along with the implications on modeling OH chemistry in polluted air.

A51F-0096 0830h POSTER

Modeling Biogenic Emission Sources of Acetone and Other Oxygenated Organic Carbon Compounds

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Acetone is of considerable interest in atmospheric chemistry as a source of HO_x radicals and peroxyacetyl nitrate (PAN) to the upper troposphere. The potential biogenic sources of acetone include terrestrial plant canopies, oxidation of dead plant matter, harvest of cultivated plants, biomass burning, and the oceans. These sources are very poorly constrained at present. Based on laboratory, field, and satellite observations to date, we present a first global modeling approach for estimating daily emissions of acetone from the terrestrial biosphere. Our modeling approach is driven by observed surface climate and estimates of vegetation leaf area index (LAI) generated at 0.5 degree spatial resolution from the NOAA satellite Advanced Very High Resolution Radiometer (AVHRR). Seasonal changes in LAI are estimated using modified MODIS radiative transfer algorithms to identify the probable dates and locations of crop harvest in cultivated areas and litter-fall of newly dead plant matter in non-cultivated areas. Temperature-dependent emission factors are applied to derive global budgets of acetone fluxes from terrestrial plant canopies, oxidation of dead plant matter, and harvest of cultivated plants.

URL: <http://geo.arc.nasa.gov/sge/casa>

A51F-0097 0830h POSTER

Laboratory Studies of Hydrocarbon Oxidation Mechanisms

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The oxidation of hydrocarbon species (alkanes, alkenes, halogenated species, and oxygenates of both natural and anthropogenic origin) in the troposphere leads to the generation of numerous potentially harmful secondary pollutants, such as ozone, organic nitrates and acids, and aerosols. These oxidations proceed via the formation of alkoxy radicals, whose complex chemistry controls the ultimate product distributions obtained. Studies of hydrocarbon oxidation mechanisms are ongoing at NCAR and Ford, using environmental chamber / FTIR absorption systems. The focus of these studies is often on the product distributions obtained at low temperature; these studies not only provide data of direct relevance to the free/upper troposphere, but also allow for a more fundamental understanding of the alkoxy radical chemistry (eg., from the determination of the Arrhenius parameters for unimolecular processes, and the quantification of the extent of the involvement of chemical activation in the alkoxy radical chemistry). In this paper, data will be presented on some or all of the following topics: kinetics/mechanisms for the reactions of OH with the unsaturated species MPAN, acrolein, and crotonaldehyde; the mechanism for the oxidation of ethyl chloride and ethyl bromide; and the mechanism for the reaction of OH with acetone and acetaldehyde at low temperature. The relevance of the data to various aspects of tropospheric chemistry will be discussed.

A51F-0098 0830h POSTER

Subsurface Ectomycorrhizal Fungi: A New Source of Atmospheric Methyl Halides?

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Incomplete source budgets for methyl halides—compounds that release inorganic halogen radicals which, in turn, catalyze atmospheric ozone depletion—limit our abilities to predict the fate of the stratospheric ozone layer. We tested the ability of ectomycorrhizal fungi to produce methyl bromide and methyl iodide. These fungi are abundant in temperate forests, where they colonize tree roots and provide nutrients to their symbiotic plants in exchange for carbon compounds. The observed range of emissions from seven different species in culture is 0.001- to 100- $\mu\text{g g}^{-1}$ fungi d^{-1} for methyl bromide, and 0.5- to 500- $\mu\text{g g}^{-1}$ fungi d^{-1} for methyl iodide. While methyl chloride was not specifically tested, large emissions were observed from several species with little to no emissions observed from others. Further analyses of the effects of substrate concentration, headspace concentration, and temperature were performed on the species *Cenococcum geophilum*, one of the most abundant ectomycorrhizal fungi. Our results suggest that subsurface fungal emissions may be a significant global source of methyl halides.

A51F-0099 0830h POSTER

Hydroxyl Reactivity With a Series of Nine C6-C9 Alkanes From 230-380 K

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Rates of reaction of the hydroxyl radical (OH) with a series of C6-C9 alkanes have been measured from 230 to 380 K using the Harvard High Pressure Flow System. Cyclooctane, methylcycloheptane, propylcyclohexane, isopropylcyclohexane, cyclohexane, methylcyclohexane, methylcyclopentane, 2-methylhexane and 3-methylhexane exhibited reactivities consistent with estimated rate coefficients from OH-hydrocarbon reactivity schemes, and previous experimental measurements for cyclooctane, cyclohexane and methylcyclohexane.

These compounds are present in small percentages in gasoline. Several are found at levels exceeding 100 pptv in rural atmospheres, and their depletion relative to more stable hydrocarbons in the atmosphere is an indicator of atmospheric hydroxyl radical since they do not react with ozone. In this way, they offer an alternative suite of molecules to the aromatics currently used to examine atmospheric OH reactivity. Others with short OH lifetimes have only been detected in urban atmospheres where their presence reveals recent emissions from hydrocarbon sources.

A51F-0100 0830h POSTER

Simulation of Radon transport and comparison with measurements in Europe and in the Indian Ocean

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Radon transport is simulated by a numerical atmospheric model LMDZ, developed at the Laboratoire de Météorologie Dynamique in Paris. This model calculates eulerian large-scale advection based upon finite-volume methods and parameterization of turbulent mixing and convection. Simulations with 192x145 grid cells regularly distributed over the globe and 19 levels vertically, are carried out in a "nudged" mode, where horizontal velocities and temperature are relaxed towards wind analyses ECMWF, available every 6 hours. Transport is based on mass conservation of the tracer in the atmosphere, taking into account the radioactive decay. The Radon source is prescribed as a reservoir diffusing in the soil and a 0 concentration is initialized in the atmosphere. Calculated radon concentrations are compared with measurements at 6 stations in Europe and 1 in the Indian Ocean for the period January-April 1998. We show that our model reproduces with reasonable accuracy the time series of Rn222, which essentially validates the transport away from the continental surface as well as convection in the boundary layer. Sensitivity tests are carried out by varying the spatial resolution of models, the position of receptors and the influence of the convection scheme.

A51F-0101 0830h POSTER

HYSPLIT modeling of Rn-222 Transport During the Year 1998 in Europe and in the Indian Ocean, Comparison with Continuous Measurements

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Radon 222 is used as a tracer to evaluate and to probe atmospheric transport in the model HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory, NOAA Air Resources Laboratory). Rn-222 is a terrigenous radionuclide which is a decay product of Uranium., with a half-life of 3.8 d. Radon is an inert gas, so the only sink process for it is radioactive decay. We have simulated the atmospheric transport of this radionuclide during the year 1998 with a hybrid lagrangian particle code using NCEP reanalysed meteorological files with a $1^\circ \times 1^\circ$ spatial resolution and 6 hours time resolution. Sources of Radon are supposed null over oceans, uniform over continents (1 atom/cm²/s) between latitude 60°S and 60°N. This flux is reduced by a factor 3 between latitude 60N and 70N to take account of a freezing conditions. Synthetic concentrations of Radon are compared to continuous measurements at 6 stations in Northern Europe (Macehead, 9°54'W 59°20'N Ireland; Heidelberg 8°42'E 49°24'N, Schausland 7°55'E 47°55'N Zingst 1 2°44'E 54°26'N Germany; Jungfraujochlon 7°59'E 47°33'N, Switzerland; Tver 32°55'E 56°28'N, Russia) and one in Indian Ocean. We have conducted intercomparison of numerical models HYSPLIT and LMDZ (Laboratoire de Météorologie Dynamique, Paris).

A51F-0102 0830h POSTER

Measurements of NO₂ in Maritime Atmosphere in Japan by Laser-Induced Fluorescence Technique

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NO₂ is one of the most important species in tropospheric photochemistry since it plays a key role as a precursor of ozone. Photostationary-state (PSS) between NO and NO₂ is a critical factor for ozone production. It is essential to measure NO₂ precisely at the level of pptv in the remote, background region.

In this study, a compact and sensitive instrument for direct measurement of NO₂ has been developed utilizing laser-induced fluorescence (LIF) technique. For the purpose of simple, compact and stable measurement, the single wavelength excitation by a powerful Nd:YAG laser (532.1 nm, 6500 mW at 10 kHz) is adopted. As a result of improvement, the sensitivity, background signal, dark current and the limit of detection are 0.07 cps ppbv⁻¹ mW⁻¹, 70 cps and 4 pptv (60-s, S/N=1), respectively. These specifications suggest the LIF-NO₂ instrument can be utilized to measure NO₂ at the level of pptv.

Two field observations have been successfully carried out under maritime conditions in Japan. The measurements were conducted in Okinawa Island for 10 days and in Rishiri Island for 18 days. The stability of the instrument was confirmed through these observations. In intercomparison with a chemiluminescence-based detector, excellent agreement between two instruments were shown. Thus, the LIF instrument is confirmed to be reasonable for measuring atmospheric NO₂.

Finally, PSS of NOx in Rishiri Island is considered. As a result, it is suggested that unidentified species such as halogen oxides can be important in the conversion process of NO to NO₂. This additional conversion of NO to NO₂ can increase the formation rate of nitric acid. In this case, the increase of formation rate can be estimated as 7 %.

Consequently, the high-performance LIF instrument realizes precise consideration about NO₂ in PSS of NOx. This compact, simple method is promising to be applied conveniently in remote regions over the world.

A51F-0103 0830h POSTER

Evidence of European Emissions Perturbation on the Background Tropospheric CO and Ozone in Remote Siberia/East Asia

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We evaluate the possible impact of European pollution export to the remote atmosphere of Siberia/East Asia using ozone and CO data observed at Mondy (100E) in eastern central Siberia. From trajectory analysis, the air masses arriving at Mondy are categorized into three different regions. It is found that the ozone and CO mixing ratios in the air masses transported from Europe are higher than those from Siberia and from high latitude region for most of the year. The residence time analysis of air masses transported from the European continent further indicates that CO mixing ratios show good correlation with the residence times of air masses after leaving Europe. CO mixing ratios significantly decrease with the longer transport times of air mass from Europe to the site while rapid air motion keeps hold of higher CO mixing ratios in every season. Due to the admixture of polluted European air into the continental background air during transport over Eurasia, CO mixing ratios decrease at a rate of 6-7 ppb per day in summer and fall, and 2-4 ppb per day in winter and spring. The similar feature is found for ozone but only in summer at a rate of 2-3 ppb per day. Reexamination of this analysis by limiting only the air masses from Western Europe shows a similar result indicating that European pollutions do have an impact, though not very strong, on the background ozone and CO at Mondy in remote Siberia/East Asia.

A51F-0104 0830h POSTER

Fluxes of NO₃⁻ Between Snow Surfaces and the Atmosphere in the European High Arctic

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Fluxes of NO_x and HONO emissions are sufficient to alter the composition of the overlying atmosphere in polar regions. The mechanisms for the release of NO_x and HONO from photochemical reduction of NO₃⁻ (aq) in snow surfaces have been identified in both laboratory and field experiments. The source of this NO₃⁻ (aq) in snow is, however, still unknown.

We measured during the spring of 2001 at Ny-Ålesund, Svalbard during two intensive campaigns surface fluxes of nitrogen and other atmospheric trace species, detailed aerosol physical and chemical characteristics, as well as snow physics and chemistry. We explore in this work the hypothesis that the deposition of NO₃⁻ (aq) in particulate matter is a significant source of nitrate in Arctic snow surfaces.

A51F-0105 0830h POSTER

Measurement Of Atmospheric CO₂ Trapped In The Ice Core From Siple Dome, Antarctica

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We have measured the CO₂ concentration in air occluded in the newly drilled Siple Dome ice core from Antarctica. We did this so far at moderate depth resolution from the Holocene to the bottom of the core. Higher resolution measurements will follow. The general pattern is similar to the Taylor Dome core and (at less resolution to the Vostok core). The dating of the Siple Dome core is not yet established firmly. However, the deepest CO₂ results indicate values of mid way of termination II, thereafter rising to 270 ppm and then declining. Features of CO₂ variations between 20 and 60 thousand years before present (kyr BP) resemble those by Indermuhle et al.(1999). Higher resolution

data have to be done. Across termination I CO₂ follows temperature. As in the Holocene in Taylor Dome, the Siple Dome CO₂ record shows that the carbon cycle did not reach steady state after the termination I.

Ref. Indermuhle et al (1999) Geophys. Res. Lett., 27-5, 735-738

A51F-0106 0830h POSTER

LIF Detection of NO₂ Using a CW Diode Laser Combined with a Supersonic Jet

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Atmospheric NO₂ is detected by LIF with a sensitivity of 300 pptv/10 sec (S/N = 2) using a cw laser combined with a supersonic expansion. A 16 mW tunable diode laser (840 nm at 1 MHz linewidth) is used to excite a single rotational feature in first excited electronic state of NO₂. A cw supersonic expansion cools the NO₂ to approximately 25 K enhancing the population in the rotational level we excite and increasing the signal by a factor of 20. The supersonic jet is maintained by a compact pumping system utilizing an automobile supercharger backed by a rotary oil pump. The complete system is small and operates autonomously for days to weeks. Data from a ground-based campaign in Granite Bay, California from July 16 through September 15, 2001, including an inter-comparison with our dye laser based LIF instrument operating at 585nm will be described.

A51F-0107 0830h POSTER

Model Study of Ozone Levels Over Snow-Covered Surfaces

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A column gas-aerosol-radiative model is used to simulate chemistry and radiation in and above snowpack at mid-latitudes and over the Arctic. Fifty vertical layers are modeled, the lowest of which represent the upper 15 cm of the snowpack. Snow layers are treated as dense aerosol layers with the physical and optical properties of snow. Aqueous phase and heterogeneous reactions thought to occur in the snowpack are represented as reactions on the aerosol surface. Model simulations include analysis of (1) the spectral UV radiation extinction in the snowpack, (2) chemistry over the snowpack, including snowpack release of NO_x and H₂O₂ and ozone reduction and its susceptibility to the presence of aldehydes and bromine, (3) and the effect of soot in snow on chemistry, UV extinction, and local energy balance. Model predictions are compared to measurements of UV fluxes and ozone over snow.

A51F-0108 0830h POSTER

Cape Grim Baseline Air Pollution Station: Proposed major upgrade!

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A major upgrade of the Australian Cape Grim Baseline Air Pollution Station (CGBAPS - <http://www.bom.gov.au/inside/cgbaps/>) in northwest Tasmania is being planned. CGBAPS is one of the main international Global Atmosphere Watch (GAW - http://www.wmo.ch/web/arep/gaw_home.html) stations and has been operating for 25 years, over 20 of those years with the current facilities. A mid-life refurbishment of the main, 75 metre, telecommunications tower at the station has been proposed by 'Telstra' (Australian telecommunications company) for this Austral summer (November 2001 to March 2002). With Telstra having committed to keep and maintain the existing telecommunications tower, the CGBAPS science community has started planning for significant enhancements to the research and monitoring facilities at Cape Grim. Suggested changes include additions to the existing sampling tower and/or new sampling

tower, relocated air intake lines, an additional building, and/or an expansion to the existing CGBAPS building.

These proposed changes to the CGBAPS facility will impact on present and future research and monitoring studies at Cape Grim. Therefore input and advice is being solicited from all in order to maximize the benefits of the proposed improvements!

URL: <http://www.bom.gov.au/inside/cgbaps/>

A51F-0109 0830h POSTER

OH and HO₂ in Urban Environments. Measurements by Laser-Induced Fluorescence and Comparison With Model Predictions

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In contrast to remote, unpolluted regions, measurements of OH and HO₂ in urban environments are rare. Our understanding of the complex chemical mechanisms in polluted air has not yet been fully evaluated through a comparison of measured HO_x and model predictions. We have made measurements of OH and HO₂ in the polluted boundary layer at two locations in the UK, in both summer and winter. OH is detected directly by laser-induced fluorescence (LIF) at reduced pressure, and HO₂ by titration with NO followed by LIF detection of OH, with noon detection limits of less than 1e5 molecule cm-3 (OH) and 1e6 molecule cm-3 (HO₂). The instrument is equipped with two fluorescence cells and thus is capable of making simultaneous measurements of OH and HO₂. The URGENT PUMA campaigns were located around 2 miles west of Birmingham city centre during June 1999 and January 2000, enabling a seasonal comparison of OH and HO₂ radicals. During the summer campaign, OH and HO₂ displayed distinct diurnal cycles, with maxima occurring at noon in the range (3-8)e6 (OH) and (1-8)e6 (HO₂) molecule cm-3. Unexpectedly high concentrations of both OH and HO₂ were measured during the winter campaign, with OH concentrations on average only a factor of 2-3 lower compared to summer, much less than the corresponding factor for J(O1D). The results suggest that the oxidising capacity of the urban boundary layer in winter may be underestimated. The PRIME campaign was located around 15 miles west of central London in July - August 1999. On four days the site was downwind of the polluted London plume, and very high concentrations of ozone were generated. In the plume OH, HO₂ and O₃ concentrations were highly correlated, and were found to peak several hours after local solar noon. On August 11, 1999, OH measurements were made during the nearly total solar eclipse, displaying a rapid and dramatic modulation with light intensity. For both locations, comparisons of the measured radical concentrations and the predictions of a zero-dimensional photochemical box model are made. The model is constrained using observations of longer lived species and radiative parameters that control the production and loss of OH and HO₂. During PUMA the model provides quantitative agreement with OH and its diurnal profile, although HO₂ is underestimated. During PRIME, the model reproduces the striking diurnal cycle of OH which peaks well after local noon. The explicit mechanism enables a thorough investigation of the budgets of these species to be evaluated, and there is strong evidence for the generation of OH and HO₂ from reactions of O₃ with alkenes.

A51F-0110 0830h POSTER

Role of Anti Carbonyl Oxides in OH Production from Ozone-Alkene Reactions

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It is now well established that the gas-phase ozone-alkene reaction is an important tropospheric source of HO_x radicals, particularly the hydroxyl radical, OH. Experimental and theoretical results suggest that much of the radical generation arises from decomposition of syn carbonyl oxides. However, the role of anti carbonyl oxides, which are formed from the reaction of ozone with virtually all alkenes found in the troposphere, is far less certain. For example, theory predicts no OH should be formed from ozone + ethene, yet yields of 12-20% are consistently observed. In order to better understand this mechanism, we have prepared the partially deuterated alkenes cis- and trans-3-hexene(3,4-d₂). This allows for the products of anti carbonyl oxides to be distinguished from those of syn carbonyl oxides. Using laser-induced fluorescence, we measure yields of both OH and OD from the reaction of ozone with these two species. The production of OD suggests that anti carbonyl oxides do indeed contribute to hydroxyl radical formation, probably via formation of a vibrationally excited organic acid. Pressure-dependent yields, syn/anti branching ratios, and the atmospheric significance of anti carbonyl oxides, are discussed.

A51F-0111 0830h POSTER

Seasonal Cycles of the Stable Carbon Isotopic Composition of Ethane and Benzene in the Arctic Troposphere: Measurements versus Model Results

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Stable carbon isotopic composition of volatile organic compounds (VOC) provides additional information about the photochemical age and source of the studied VOC. This paper uses isotopic composition measurements in the Arctic along with results from a global transport and chemistry model (GISSCTM using the EDGAR Database) to place constraints on the sources, transport, and chemical loss processes for ethane and benzene.

From July 1999 until March 2001 fortnightly samples of background air were collected at Alert (Nunavut, Canada). Concentrations of VOC were higher in the winter than in the summer, in agreement with published results. The model could only account for half the observed ambient concentrations at Alert for ethane and less than half for benzene.

We also analysed the samples for the stable carbon isotope ratios of benzene and ethane. Seasonal variations of the isotopic composition were significant. During the summer the measured isotopic composition for ethane ranged between -14 and -21 ‰, while in the winter the range was -24 to -29 ‰, reflecting the difference in extent of atmospheric processing. The kinetic isotope effect of ethane is not known. Assuming a plausible kinetic isotope effect of 5 ‰ the modelled isotopic composition of ethane agrees with observations. For benzene we measured summer isotopic compositions in the range of -25 to -30 ‰, and in winter -20 to -24 ‰. Using the known kinetic isotope effect of benzene (7.8 ‰), the model agrees with the observations during the winter months, but during the summer the model predicts up to 15 ‰ heavier benzene than observed. This indicates that the model substantially overestimates the age of benzene in the summertime Arctic air mass. The observed isotopic composition is close to the source isotope composition suggesting that emissions are likely to be local. Indeed, model tests introducing a small emission at high latitudes predicts concentrations and isotopic compositions that are close to observations.

A51F-0112 0830h POSTER

Ozone Measurements from Atlantic Tropical Cyclones

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Tropical cyclones (TCs, hurricanes) are episodic mesoscale features of the tropical and subtropical oceans that are likely to have a large impact on the distributions and fluxes of trace gases. The troposphere boundary layer, possibly enriched by enhanced exchange of dissolved gases from the sea surface, is transported upward as high as 15 km and redistributed over a large horizontal area. Measurements of selected trace gases should therefore be useful in understanding hurricane dynamics and structure; for example, to resolve an ongoing controversy about the lifetime of air within the eye and mixing areas of the eye wall boundary (Willoughby, Mon. Wea. Rev. 126, 3053, 1998). However, few systematic measurements of significant trace gases in TCs have been obtained. NOAA-AOML has measured ozone (O₃) in eyewall crossings for a number of Atlantic TCs during the 1998 and 1999 seasons on board NOAA P-3 hurricane research flights. Ozone concentrations showed considerable variation across the eye wall and within the eye; significant changes were also observed as the hurricane aged. These results, related measurements, and their implications for TC structure and marine tropospheric chemistry will be presented.

A51F-0113 0830h POSTER

Rotational Energy Transfer in the A State of Nitric Oxide

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Rotational energy transfer (RET) in the A state of nitric oxide is an important part of atmospheric monitoring of this species. In the airborne, two-photon laser induced fluorescence instrument operated by Georgia Institute of Technology, the A state is pumped in a low set of rotational levels, and the consequent D-A transition employs a higher rotational level. RET is essential to this approach.

We have made measurements of RET in the A state of NO in the laboratory, pumping the A state in the ultraviolet and probing it via the D-A transition in the infrared. The colliders nitrogen and oxygen have been studied. Nitrogen quenches the A state very little, so as the single collider, the rotational population thermalizes before radiating. However, oxygen is a good quencher, so its presence can freeze the rotational distribution. From the data we can extract quantum state specific RET rate coefficients, and use them to model the two-photon process in the airborne instrument.

This work was supported by NASA's Global Tropospheric Experiment and the NSF Research Experience for Undergraduates Program.

A51F-0114 0830h POSTER

The BTEX Family of Pollutants in Automobiles and Ambient Air Measured by Jet-REMPI

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The BTEX group of hazardous air pollutants comprises benzene, toluene, ethyl benzene, and the three xylene isomers, often found together in air mixtures. Each is thought to be carcinogenic. We have used the Jet-REMPI method (resonantly enhanced multiphoton ionization) followed by time of flight mass spectrometry to measure these compounds. Samples were taken from open containers, gasoline tank headspace, automobile exhaust, and ambient air. In ambient air, we collect samples on a filter cartridge for 3.5 hours, to obtain enough sample to use GC/MS as a survey tool. Only toluene shows in the GC/MS scan as a small signal. To use Jet-REMPI, we must dilute the sample a factor of 20,000 to avoid overloading the instrument, and simulate a corresponding sampling time of about 1 sec. All of the BTEX compounds are seen readily in the Jet-REMPI instrument, and the three isomers of xylene show different REMPI patterns even though all are at the same mass. All compounds are present at a few part per billion concentration.

This work was supported by the Environmental Protection Agency and the NSF Research Experience for Undergraduates Program.

A51F-0115 0830h POSTER

Atmospheric Ammonia Emissions From Operational Areas of a Dairy

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Ammonia gas is important in aerosol formation, soil acidification, aquatic eutrophication, acid rain and can damage human and animal respiratory systems. Anthropogenic emissions are approximately two-thirds of the global emissions of NH₃ and agriculture is the dominant anthropogenic source. We are studying NH₃ emissions from the WSU dairy located near Pullman, WA to provide a detailed emission inventory. The dairy has approximately 200 milking cows and 200 replacement heifers. The cows are housed in open air barns and the liquid waste is stored in four open air lagoons until it is applied to grass fields in the late summer. Agricultural emissions of NH₃ have been measured in Europe but very few measurements have been made in the United States. Differences in feed and waste management practices between Europe and the U.S. could have a significant effect on NH₃ emissions. Since NH₃ is an aerosol precursor knowing emission levels is also important for the new U.S. EPA PM_{2.5} standard. NH₃ was measured using an open short-path spectroscopic absorption near 200 nm. The instrument has a time resolution of about a second and a limiting sensitivity of a few ppb. The open path method has the benefit that it is fast, self-calibrating and does not have errors associated with NH₃ adherence to inlet walls. As part of a detailed emission inventory, NH₃ fluxes were determined from the milking cow stalls and of the main slurry lagoon using a SF₆ tracer technique. Emissions from various parts of the dairy will be discussed.

A51F-0116 0830h POSTER

Eddy Covariance Fluxes of NO and NO₂ above a Northeastern U.S. Forest

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Although tropospheric NO, NO₂, and O₃ rapidly interconvert in a fast photochemical cycle, the processes governing their removal rates, interactions with ecosystems, and human interest in their mitigation are distinctly different. Thus a detailed understanding of their behavior at the atmosphere-biosphere interface is crucial. The reactivity of this family of gases has often confounded measurements in the past, and the question of biospheric emission and uptake of NO_x remains open.

In order to address these issues, we present concurrent eddy covariance fluxes of NO and NO₂ at the rural, deciduous, mixed hardwood Harvard Forest in central Massachusetts during the summer and fall of 2000. The independent measurements were conducted above the forest canopy, at similar heights, on two towers within several hundred meters of one another. NO was measured using an existing chemiluminescence detector in the eddy covariance mode, and NO₂ using a new tunable diode laser absorption spectrometer (TD-LAS). The TD-LAS has the advantage of being verifiably species-specific and spectroscopically calibrated. O₃ concentrations, profiles, and fluxes were also measured at the site. At night, NO fluxes were effectively zero while small but persistent downward NO₂ fluxes

were observed. Fluxes of NO_2 during the day were generally upward and coupled with downward NO fluxes of similar magnitude. The opposing NO and NO_2 fluxes confirm the predictions of some canopy exchange models that include the effect of the light gradient within the canopy on photo-reactive species. The results do not show evidence of significant NO_x uptake by the canopy during daylight hours.

A51F-0117 0830h POSTER

Uptake of N_2O_5 on NaCl Powders and Synthetic Sea Salt Using a Knudsen Cell Coupled to an Electron Impact Mass Spectrometer

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The uptake and reaction of dinitrogen pentoxide (N_2O_5) on NaCl and synthetic sea salt were studied using a Knudsen cell coupled to an electron impact quadrupole mass spectrometer. Production of nitryl chloride (ClNO_2) from the N_2O_5 reaction, and production of HCl from the reaction of HNO_3 , N_2O_5 impurity, was observed. The reaction was found to increase with an increase in the number of salt layers, indicating diffusion of the gas into the bulk salt sample. Dinitrogen pentoxide uptake was also found to occur more readily on synthetic sea salt, which holds more water, than on NaCl salt samples. This behavior is consistent with reaction and uptake of N_2O_5 on aqueous salt solutions and water adsorbed on salt surfaces. These experiments show that the uptake and reaction of N_2O_5 on dry NaCl is slow, $\gamma < 10^{-4}$. The effects of water and the atmospheric implications will be discussed.

A51F-0118 0830h POSTER

Observations of NO_2 , ΣPANs , $\Sigma\text{Alkyl Nitrates}$ and HNO_3 During the TEXAQS-2000 Campaign

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We present continuous, high time resolution observations of NO_2 , the sum total peroxyacetylnitrates (ΣPANs), the sum total alkyl nitrates and hydroxyalkyl nitrates (ΣANs), and HNO_3 mixing ratios which were made at La Porte, Texas during the Texas Air Quality Study (TEXAQS 2000) from August 15- September 15,

2000 using Thermal Dissociation-Laser Induced Fluorescence. Typical daytime NO_2 , ΣPANs , ΣANs , and HNO_3 mixing ratios were 6.5, 0.8, 0.9, and 2.5 ppbv respectively. Peak values coincident with O_3 mixing ratios of 200ppb were 12, 5, 2.5, and 6 ppbv respectively. An intercomparison of ΣPANs with gas chromatograph measurements show good agreement. The ΣPANs contributed to 8-15%, the ΣANs between 8 and 14% and HNO_3 contributed between 25-45% of the total NO_x , where NO_x is defined as $\text{NO}_y\text{-NO}_x$. ΣANs , ΣPANs , and HNO_3 are each strongly correlated with CO and O_3 . The ozone- ΣANs correlation indicates approximately 50 O_3 molecules are formed per alkyl nitrate produced and that the $\text{RO}_2 + \text{NO}$ reaction has an average alkyl nitrate yield of about 4% in the Houston plume.

A51F-0119 0830h POSTER

Impact of Asian Megacity Emissions on Regional and Global Tropospheric Chemistry

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Air quality requires serious attention in the megacities. The current trend in urbanization and motorization in the developing countries of Asia are in many ways reproducing the patterns followed in developed countries. Air pollutants such as sulfur dioxide, nitrogen dioxide and ozone are known to cause damage to human health, crop production, and forest cover. Due to their longer lifetimes, these trace gas emissions play a vital role in the long-range transport. The GFDL/Global Chemistry Transport Model (GCTM) and regional chemical transport model STEM-III and RAMS were applied to better understand the chemical nature, transformation and transport of trace gases from the megacities of Asia. During the ACE-Asia and TRACE-P field experiments in the East Asia, some of the mission objectives were designed to understand the aging and transport features of pollutant plumes from East Asian megacities. We conducted GCTM simulations for the present emission levels compared to a reference run excluding Asian megacity air pollution and real-time simulations for the megacities using STEM-III during the campaign period of March-May 2001. The model simulation results included particulates, sulfur dioxide, nitrogen oxides and primary and secondary photochemical products. In this paper, we will present tropospheric chemistry and urban chemistry results from the GCTM and RCTM simulations respectively for the experiment period.

A51F-0120 0830h POSTER

Mercury Depletion Episode Studies in the Canadian High Arctic

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Episodic mercury depletion episodes were first recorded in Alert, Canada in 1995. Since this time, considerable research has been undertaken to further study this phenomenon. It has been found that there is an occurrence of fast photo-chemically induced reactions involving the oxidation of Hg (0) to Hg (II) during the springtime period in the high Arctic. Data from a cold regions pyrolysis unit (CRPU) have confirmed that particle-associated mercury (PM) and reactive gaseous mercury (RGM) are still present in the air during a mercury depletion event when Hg (0) concentration levels are very low. These more reactive species are less

volatile and are more readily removed in the air and/or are deposited on the snow surfaces than Hg (0). In the winter and spring of 2000 in Alert, snow samples collected showed an almost 20 fold increase in mercury concentrations during the springtime period from the dark period. Air profiling measurements undertaken during the same time period have shown that Hg (0) is re-emitted from the snow pack surfaces both over land and the frozen Arctic Ocean near Alert. It is thought that free radical BrO is responsible for the destruction of ozone depletion episodes in the Arctic during springtime and increased concentrations from satellites have been measured during these times. Ground level in situ measurements taken over the frozen ocean during depletion events showed an anti-correlation between Hg (0) and BrO concentrations during MDEs. In February 2001, continuous automated RGM and PM measurements were initiated to further study this phenomenon in parallel with the CRPU to measure total atmospheric mercury concentrations in ambient air in the Canadian Arctic during springtime depletion events. A summary of findings from these studies will be presented.

A51F-0121 0830h POSTER

Summer to Early Fall O_3 and CO Measurements in the North Atlantic Ocean at a Mountaintop Site in the Azores Islands

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A system for the continuous ground-based measurement of ozone (O_3) and carbon monoxide (CO) was recently installed at a mountaintop site in the Portuguese Azores Islands in the central north Atlantic Ocean. The main objective of this site will be the determination of the frequency and impact of transport events bringing O_3 and O_3 precursors from North America and Europe to the central north Atlantic Ocean region.

These measurements are a part of the PICO-NARE study (Pico International atmospheric Chemistry Observatory - North Atlantic Research Experiment). The measurement site is located on the top of Pico mountain at an altitude of 2225 meters, allowing frequent sampling of free tropospheric air. Frequency and magnitude of long-range pollution events to the north Atlantic from continental sources are determined through analysis of correlation between O_3 and CO and the use of back-trajectory data.

Data obtained from July to October, 2001 will be presented here. The measurements will be analyzed to assess ambient levels of O_3 and CO in the remote central north Atlantic region. Additionally, these measurements will be utilized to identify and quantify O_3 import and en route production associated with polluted air masses transported to the north Atlantic region. Meteorological data will also be analyzed and presented, to begin characterization of the PICO-NARE site for determination of the frequency of the free tropospheric observations at the site.

URL: <http://www.cee.mtu.edu/~reh/pico/>

A51F-0122 0830h POSTER

Methyl Chloride Emission from Tropical Plants

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We studied CH_3Cl emissions from tropical plants in Tropical Rainforest Glasshouse (25 m x 20 m x 10-24 m high) in Tsukuba Botanical Gardens, where more than 200 representative species from lowland tropical forests of Southeast Asia grow. CH_3Cl concentrations were always higher in the glasshouse than outside and increased significantly when the windows were closed. The fluxes of CH_3Cl from the tropical rainforest system in the glasshouse were calculated from the averages of their accumulation rates when the windows were closed (average: 142 pptv h^{-1}) with the dimension of the glasshouse. Emission rates per unit area for CH_3Cl was 5.4 mg $\text{m}^{-2} \text{h}^{-1}$. In order to determine which of the plants or whether the soil is responsible for the increase of CH_3Cl , flux measurements were done by using an enclosure method. The soil was found to take up CH_3Cl at a small rate. On the other hand, some plants

from the Marattiaceae, Cyatheaceae (tree fern), Dicksoniaceae, and Dipterocarpaceae families were found to significantly emit CH_3Cl . The first three families are ferns commonly growing in tropical forests, and Dipterocarpaceae species are dominant in the tropical rainforests of Southeast Asia. The average CH_3Cl emission rate from the 9 plants in these families was around $0.5 \text{ mg (g dry leaf)}^{-1} \text{ h}^{-1}$. As for Cyatheaceae, we conducted a flux measurement from *Cyathea lepifera* E. Copel. in a subtropical forest in Okinawa and detected high emissions of CH_3Cl amounting to $1.1 \text{ mg (g dry leaf)}^{-1} \text{ h}^{-1}$. Strong emissions of CH_3Cl from tropical forests raises questions about the trends of chlorine compounds in the future and in the past.

A51F-0123 0830h POSTER

Long-range transport of pollution to the Northeast Pacific: A global 3-D analysis of PHOBEA observations

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The PHOBEA (Photochemical Ozone Budget of the Eastern North Pacific Atmosphere) field studies have provided clear evidence that Asian emissions and their by-products can reach the West Coast of the United States during rapid transport events (Jaffe et al., GRL, 1999; Jaffe et al., JGR, 2001). In this study, I use the GEOS-CHEM global 3-D model driven by assimilated meteorological observations for the time periods of the PHOBEA ground-based missions (March-April 1997 and 1998, at Cheeka Peak Observatory 48°N , 125°W , 480 m) to test the model's ability to simulate long-range transport events and examine the role of these events in influencing the budgets of radon, ozone, CO, and NO_y in the Northeast Pacific. Simulations of radon concentrations compare well with the observations (modeled means and standard deviations are within 10% of observations). The model captures the timing and magnitude of sporadic high radon events when the winds are from the East (U.S. continental emissions), but tends to underestimate the amount of radon reaching Cheeka Peak Observatory during long-range transport events. Transport of Asian emissions contributes to 10% of model calculated radon on average. Five rapid long-range transport events are identified during the spring 1997 and 4 events during the spring 1998. Simulated mean concentrations and standard deviations for CO are within 10% of observed values. I estimate that emissions from Asia, Europe and U.S. contribute about equally to the levels of CO observed at Cheeka Peak Observatory. Observed PAN and ozone concentrations are also well reproduced by the model. I will discuss the role of Asian emissions in affecting the NO_y and O₃ budgets during the PHOBEA experiments, and the role of inter annual variability in emissions and transport.

A51F-0124 0830h POSTER

Assessment of the Export of O₃ and Nitrogen Oxides From North America Over the North Atlantic Ocean During Late Summer Through Fall 1997 Using Measurements From the NARE-Cape Pine Study

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Measurements of CO, O₃, and nitrogen oxides (NO, NO₂, PAN, and NO_y) were made in southern Newfoundland from late August to November, 1997, as part of the North Atlantic Regional Experiment (NARE) 1997 intensive. The NARE-Cape Pine study occurred at a marine boundary layer (MBL) site near the southern-most point in Newfoundland. The resulting data were used to investigate the export of ozone and nitrogen oxides from North America over the North Atlantic Ocean, by analyzing correlations of ozone and nitrogen oxides with CO. These analyses were conducted both for monthly datasets and for specific periods when transport from North America was indicated by either back-trajectories or high correlations among the compounds. The resulting correlations between O₃ and CO

follow a seasonal pattern similar to that observed previously, with the magnitude of estimated O₃ export declining through fall. However, the magnitude of the slope ($d[\text{O}_3]/d[\text{CO}]$) is significantly larger than that derived from earlier observations. This difference is partially attributable to a decline in North American CO emissions during the 1990s, but may also imply increased O₃ export. In contrast to the behavior of O₃, a significant positive correlation between CO and nitrogen oxides (NO_y, (NO_y - NO_x), and PAN) was present during the entire study period, indicating increasing export of nitrogen oxides throughout the period. The estimated export is less than that predicted by numerical models, a finding that may be due to loss of HNO₃ and PAN in the MBL. These results indicate that, while export of ozone is reduced during winter, export of nitrogen oxides and the resulting potential for downwind ozone formation are increased.

A51F-0125 0830h POSTER

Rainfall, Stemflow and Throughfall Chemistry at Declined and Non-Declined Areas of Japanese Red Pine (*Pinus densiflora*)

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Rainfall, stemflow and throughfall were collected from 1996 to 1999 at seaward side, pine declined area, and mountain summit and inland side, non-declined area at Mt. Gokurakuji, western Japan. Rainfall deposition showed small differences among seaward side, mountain summit and inland side. Inorganic N ($\text{NO}_3^- + \text{NH}_4^+$) and S deposition of rainfall were estimated to be $5.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $6.3 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, respectively at the seaward side and $5.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and $5.9 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, respectively at non-declined area (mountain summit and inland side). NO_3^- and SO_4^{2-} concentrations in stemflow were significantly higher at seaward side (34.4 and 25.0 M, respectively) than at inland side (4.8 and 14.4 M, respectively) and were several times higher compared to those of rainfall collected simultaneously. Throughfall deposition of NO_3^- and SO_4^{2-} also significantly higher at seaward side, whereas bulk deposition showed small differences between study sites. Net throughfall (NTF) deposition of NO_3^- and SO_4^{2-} accounted for 80 and 53 % of total deposition at seaward side, respectively, while 47 and 33 % at inland side, respectively. From these results it can be concluded that there are small spatial changes for fluxes of wet deposition, while dry deposition is significantly higher at seaward side compared to at inland side at Mt. Gokurakuji. Inorganic N ($\text{NO}_3^- + \text{NH}_4^+$) deposition was estimated to be more than $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ at seaward side, which was greater than the literature threshold of nitrogen deposition that could cause nitrogen saturation in Europe and United States.

A51F-0126 0830h POSTER

Chlorine-Enhanced Ozone Formation Observed in Urban Air

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Chlorine and other reactive halogen species have been suggested to significantly contribute to the oxidative capacity of the troposphere. Chlorine chemistry, in particular, has been recently implicated in rapid ozone formation above Houston, TX. We report the results of a three-fold approach to confirm and quantify the importance of chlorine radicals in enhancing urban tropospheric ozone formation: 1) The detection of marker species in the urban troposphere that are unique to chlorine radical chemistry, 2) Captive ambient air experiments performed in outdoor environmental chambers exhibit significant enhancement of ozone formation after injection of small quantities of molecular

chlorine, and 3) Significantly enhanced ozone formation is predicted by regional photochemical modeling that incorporates chlorine radical chemistry.

A51F-0127 0830h POSTER

Seasonal Variation in Modeled VOC Emissions from Southern African Vegetation

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Volatile organic carbon (VOC) emissions from vegetation account for approximately 95% of the global VOC budget, with the tropical regions producing the largest amounts. Emission estimates have been modeled for many regions including the tropical regions of Africa, but there are few emissions data for the African region south of the equator. During the SAFARI 2000 project VOC leaf level emission factors were measured for many of the dominant tree species in southern Africa. The main aim of this project was to scale these leaf level fluxes up to the regional level using species composition data and leaf area index (LAI) data from the satellite MODIS. Species composition data for the African region south of the equator were obtained from the National Botanical Institute in Cape Town, South Africa. A monthly average LAI for the tree species was obtained from MODIS data by using field calibrated LAI data and tree cover maps. LAI and specific leaf area (m^2/g) values were used to calculate the leaf foliar density for the various species for each month. VOC emission factors were determined in the field for a variety of species, and remaining species were grouped into plant families and assigned estimated VOC emission factors based on the literature. The temperature data from NOAA NCDC were used, while cloud cover (used in the calculation of photosynthetically active radiation) was estimated from the MODIS cloud mask. All these data was used as input to the GLOBEIS model to calculate an average emission of VOCs (isoprene, monoterpenes and other volatile organic compounds) for each month between June 2000 and June 2001. VOC emissions are highest in the more northern tropical regions and remain high for a longer period than in the drier southern sites. Along the south and southwestern coast of South Africa the vegetation is more productive during winter due to the winter rainfall pattern. This region, known as the Fynbos, is estimated to have maximum emissions during winter, whereas the rest of the region has peak VOC emissions during the hot, wet summer (November to April) period.

A51F-0128 0830h POSTER

The Seasonally Varying Isotopic Composition of CO at Barbados: Observations and Inverse Model Results

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We have collected and analyzed air samples for carbon-13, oxygen-18, and CO concentration from Barbados, West Indies (12N, 60W) for the period July 1996-1999. The stable isotopic composition, coupled with CO concentration, is useful in constraining relative strengths of the dominant sources. As expected, CO concentration is lower at this site than at mid-latitude sites, and carbon and oxygen isotope values are smaller, which reflect a less important anthropogenic source component. The tropical stable isotope data follow a relatively normal seasonal cycle, with an amplitude in $\delta^{13}\text{C}$ of almost 8 per mil and a $\delta^{18}\text{O}$ amplitude of about 7 per mil, both of which are large compared to observations at middle latitude sites. The magnitude of the seasonal cycle is due to varying source strengths and the kinetic isotope effect during the CO-OH reaction, the latter of which is relatively well known.

With respect to varying sources, the methane-derived CO component, which is quite depleted in carbon-13 (-52 per mil, including a 5 per mil kinetic isotope effect), and the hydrocarbon oxidation component, which is depleted in oxygen-18, are both visible. We used a 3-dimensional chemistry-transport inverse model (TM2) to investigate the source strengths of CO at this site, and to test our understanding of CO source strengths in the remote tropical troposphere. This modeling effort represents the most sophisticated approach to date, yet results indicate that existing CO budgets are inconsistent with current knowledge regarding the isotopic constraints at this site.

A51F-0129 0830h POSTER

Isotopic Composition of Marine-Derived Methyl Bromide

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Methyl bromide (CH₃Br) is the largest source of atmospheric ozone 50-60 times more efficiently than chlorine. Despite much attention that has been focused on CH₃Br in recent years, it has proven difficult to constrain its global budget. It is of particular interest to compare the magnitude of the anthropogenic source with that of the largest naturally occurring source, which is believed to be marine-derived. One way to estimate the relative strengths of these sources is to use stable carbon isotopes as a tracer. The viability of this approach relies on the distinctiveness of the isotopic composition of each source and, in the case of marine-derived CH₃Br, on the extent to which isotopic fractionation occurs during chemical degradation in the water column. Once produced in the water column, CH₃Br undergoes ion exchange (CH₃Br + Cl⁻ → CH₃Cl + Br⁻) and hydrolysis (CH₃Br + H₂O → CH₃OH + HBr), which changes the isotopic composition of the remaining CH₃Br. In this study we measured the fractionation factor (k₁₂/k₁₃) for both ion exchange and hydrolysis of CH₃Br in sea water, and then used a simple air-sea exchange model to determine the extent of fractionation that occurs in the water column. Using a range of 20-30 per mil for the isotopic composition of marine biologically produced methyl bromide, the predicted isotopic composition of CH₃Br emitted to the atmosphere is significantly enriched and further distinguished from the average anthropogenic signature of 54.4 per mil. An isotopic study may therefore prove to be a useful tool for constraining the methyl bromide budget.

A51F-0130 0830h POSTER

Intercomparison of NO_y chemiluminescence and TD-LIF measurements at the University of California Blodgett Forest Research Station

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An intercomparison of NO_y (= NO + NO₂ + HNO₃ + PAN + RONO₂ + HNO₄ + ...) measurement techniques was conducted at the University of California - Blodgett Forest Research Station - a rural site in the Sierra Nevada mountains that regularly experiences both clean, continental air and the aged urban plume from the nearby city of Sacramento, CA. The intercomparison involved two instruments: a commercial instrument that converts NO_y to NO with a Mo converter followed by the detection of the NO using O₃ chemiluminescence and a home-built instrument that uses thermal dissociation of NO_y species to NO₂ followed by detection of NO₂ via laser-induced fluorescence. The TD-LIF instrument has four channels measuring NO₂, total peroxy-nitrates, total alkyl-nitrates, and HNO₃. In this poster, we describe the intercomparison of standards of NO₂, n-propyl nitrate, and nitric acid in both dry air and as a standard addition to ambient air. We also compare more than twelve months of concurrent ambient measurements.

A51F-0131 0830h POSTER

A Study of the Atmospheric Oxidation Mechanism of Propylene Using Chemical Ionization Mass Spectrometry

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The oxidation of olefins is known to be of importance in atmospheric chemistry, particularly in the formation of photochemical smog. The rate of reaction of propylene with OH is very well established, but the rate coefficients of most intermediate steps in the oxidation mechanism are not known. Chemical ionization mass spectrometry has been used to verify the rate coefficient of the propylene reaction with OH as well as measure intermediate reaction rates. The measured rate coefficient for propylene + OH at 298 K is $k = (2.7 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value agrees well with current recommendations. The rate coefficient of the hydroxypropylperoxy (C₃H₆(OH)O₂) radical reaction with NO was also measured at 298 K. The measured coefficient is $k = (1.1 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is comparable to other RO₂ + NO rate coefficients. The branching ratio of this reaction to form the peroxy-nitrate (RONO₂) has also been measured. Product yields were also obtained for conversion of propylene into acetaldehyde and formaldehyde. The mass balance $\Delta\text{C}_3\text{H}_6/\Delta\text{Aldehyde}$ was measured to be (1.0 ± 0.1) for both formaldehyde and acetaldehyde.

A51F-0132 0830h POSTER

Deposition of Nitric Acid to a Northeastern U.S. Forest and its Contribution to Total Reactive Nitrogen Flux

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Nitric acid (HNO₃) and total reactive nitrogen (NO_y) were measured at the Harvard Forest Long Term Ecological Research site in central Massachusetts along with micrometeorological and supporting data during the summer and fall of 2000. The concentration of HNO₃ was measured using a tunable diode laser absorption spectrometer (TDLAS) installed on a tower above the forest canopy. The inlet was designed to keep the residence time short, to minimize wall effects, and to exclude aerosols from the sample flow. The TDLAS specifically and quantitatively measured gas-phase HNO₃, eliminating interferences from other reactive nitrogen species such as PAN, hydroxy alkyl nitrates, NO_x, and fine aerosols which are included in the NO_y measurement. The hourly deposition velocity of HNO₃ was estimated using a dry deposition inferential method (DDIM) in which the deposition velocity, V_d, is modeled as a set of resistances in series depending on meteorological and site-specific conditions. The flux was computed as the product of measured HNO₃ concentration and inferred V_d. Diel correlations between HNO₃ concentration and V_d did not introduce a substantial bias in the daily and weekly inferred flux when compared to the hourly values integrated over the same interval.

The measurements confirm that HNO₃ is often the primary NO_y depositor and suggest conditions at Harvard Forest where other species are important. Under unpolluted, background flow conditions when winds are from the Northwest, HNO₃ deposition only falls short of NO_y deposition during morning daytime hours, in late summer and early fall, by approximately 20-30% of FNO_y. During Southwesterly flow when the site is subject to warmer transport from polluted source regions, the deposition flux of HNO₃ accounts for half or less of measured NO_y deposition, leaving as much as 2-5 μmol/m²/hr of the reactive nitrogen flux in the form of species not individually measured.

A51F-0133 0830h POSTER

Stability of Trace Gases in High-Pressure Cylinders

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Long-term observations of atmospheric trace gases require calibration methods that are consistent and reproducible over the duration of the observations. Small trends in calibration can be difficult to detect, and can mask or alter the apparent atmospheric trends. Trace gas standards in high-pressure cylinders are often used for the calibration of gas chromatographic instruments employed for long-term monitoring, as well as for the collection of archive air samples. We have studied the stability of part-per-million-, part-per-billion-, and part-per-trillion-level gas mixtures (in air) in aluminum and stainless steel cylinders. The stability of a particular compound depends on the type and size of the cylinder, the passivation method employed, and the pressure of the gas in the cylinder. We will report on stability studies involving mixtures of methyl halides, chlorinated solvents, nitrous oxide (N₂O), sulfur hexafluoride (SF₆), carbon monoxide (CO), and carbonyl sulfide (COS). Methyl halides (CH₃Cl and CH₃Br) appear to be more stable in stainless steel than in aluminum cylinders. N₂O and SF₆ show good stability in both types of cylinders. CO tends to increase with time in aluminum cylinders. The stability of CO may improve with higher volume to surface area ratio, but further testing is required. Some chlorinated solvents, such as CH₂Cl₂, decrease rapidly in non-passivated aluminum cylinders, but can be stable in passivated aluminum and stainless steel cylinders.

A51F-0134 0830h POSTER

In Situ Measurements of Carbonyl Sulfide and Methyl Chloride

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For the past 3 years, in situ measurements of carbonyl sulfide (COS) and methyl chloride (CH₃Cl) have been made at the NOAA baseline observatories. Four gas chromatographs make air measurements once an hour at Alaska, Hawaii, American Samoa, and the South Pole. Each air measurement is referenced to a pair of calibrated gas standards to calculate the atmospheric mixing ratio. Both COS and CH₃Cl have common sources such as oceans and biomass burning. However both of their budgets are poorly balanced. Current source estimates for CH₃Cl are 20% lower than sink estimates. Continuous in situ measurements can reveal information about the sources and sinks of these compounds. At the coastal station on American Samoa, large rapid enhancements of CH₃Cl of up to 200 parts-per-trillion (ppt) over background levels of about 550 ppt have been observed. Virtually all high mixing ratios of CH₃Cl occur during light or no wind, indicating a local source. However, COS is not enhanced during these episodes. Gradual changes of COS over weeks of nearly 35 ppt above ambient levels of 500 ppt (~7% enhancements) are measured while CH₃Cl remains unchanged. These opposing behaviors point to differences in the oceanic source regions or source strengths of these gases. Observations made at Mauna Loa, Hawaii often show diurnal variations in CH₃Cl of about 50 ppt as well as larger events of about 100 ppt (~10% enhancements). The diurnal cycle is caused by daytime upslope winds that rapidly bring air from coastal areas. At nighttime the air cools and flows down Mauna Loa causing down slope winds that bring air from the free troposphere. COS does not show a diurnal cycle, however there are multi-day enhancements of nearly 100 ppt (~20% enhancements) that are correlated with some of the increased levels of CH₃Cl.

A51F-0135 0830h POSTER

Secondary Atmospheric Photooxidation Products: Evidence for Biogenic and Anthropogenic Sources

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Isoprene, 2-methyl-3-buten-2-ol (MBO), their photooxidation products, and carbon monoxide (CO) were measured above a Ponderosa pine plantation, near Blodgett Forest Research Station, CA, from August 15-19 and September 11-15, 2000. An automated gas chromatograph-flame ionization detector system was used to measure isoprene, its "first-generation" photooxidation products, methyl vinyl ketone and methacrolein, MBO, and the MBO photooxidation product, acetone. A mist chamber was used for collection of the MBO photooxidation product 2-hydroxy-2-methylpropanal (2-HMPR), and the "second-generation" isoprene photooxidation products glycolaldehyde, hydroxyacetone, and methylglyoxal. Carbonyl and hydroxyl groups in these compounds were derivatized with O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBA) and bis(trimethylsilyl)trifluoroacetamide (BSTFA), respectively, and the derivatives were quantified by using gas chromatography with ion trap mass spectrometry. Isoprene, MBO, and their photooxidation products had similar diurnal cycles, with maximum mixing ratios in the afternoon and minimum mixing ratios in the early morning. The highest mean mixing ratios were observed for glycolaldehyde (0.69 ppb), hydroxyacetone (0.42 ppb), and 2-HMPR (0.30 ppb), while methylglyoxal was lower (0.13 ppb), consistent with its shorter lifetime in the atmosphere. Secondary isoprene photooxidation products had diurnal cycles similar to their precursors, while changes in 2-HMPR lagged behind corresponding changes in MBO. These observations are consistent with transport of isoprene and its photochemical products from a source several hours upwind, and a local source of MBO with in situ photochemical production of 2-HMPR. Glycolaldehyde and hydroxyacetone mixing ratios exceeded the mixing ratios of their biogenic precursors on days with high CO. They were also more highly correlated with CO than with their biogenic precursors, suggesting that oxidation of anthropogenic compounds contributed to their production.

A51F-0136 0830h POSTER

Effect of Temperature on the Conversion of DMS to Gaseous H₂SO₄Linda Koch^{1,2,3} (kochlc@colorado.edu)A. R. Ravishankara^{1,2,3} (ravi@al.noaa.gov)¹National Oceanic and Atmospheric Administration, Aeronomy Laboratory, R/AL-2 325 Broadway, Boulder, CO 80305, United States²Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Campus Box 216, Boulder, CO 80309, United States³The Department of Chemistry and Biochemistry, University of Colorado, Boulder, Campus Box 215, Boulder, CO 80309, United States

It has been suggested that Dimethyl sulfide (DMS) is a major source of sulfate particles in the marine troposphere, especially in pre-industrial times. Sulfate particles are formed from the gaseous H₂SO₄ produced by the tropospheric oxidation of DMS. Therefore, the end products of the complex oxidation of DMS were computed using a box model with the goal of understanding the temperature dependence of the conversion efficiency of DMS to SO₃(g) and hence, to H₂SO₄(g). Based on the temperature dependence of DMS oxidation reactions, higher temperatures lead to a larger fraction of DMS becoming SO₃. One of the primary oxidants, OH, is expected to increase in concentration with temperature and lead to an increased rate of DMS oxidation and conversion of SO₂(g) to SO₃(g). These effects are expected to lead to greater particle formation rates at higher temperatures and may be the missing process in the CLAW hypothesis that links temperature increases to higher sulfate particle production from DMS.

A51F-0137 0830h POSTER

Measurements of Dry Deposition of S and N Compounds on Natural Surfaces (leaves) and Their Parameterization

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Measurement of Dry Deposition of S and N Compounds on Natural Surfaces (leaves) and Their Parameterization

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ABSTRACT Promotion of rapid economic growth and urbanization have led to the increasing emissions of acidifying sulphur and nitrogen compounds in the atmosphere which are most potent for injury to vegetation, deterioration of monuments and acidifications of lakes, soils. Dry deposition appears to be an important process by which, air pollutants can be delivered to sensitive surfaces in the form of gases or particulates from the atmosphere as dry conditions prevail for maximum period in this geographical region. The studies reported for deposition of acidifying sulphur and nitrogen compounds on natural surfaces are limited and none from India. Direct measurement of dry deposition on natural surfaces is lacking. This paper deals with measurements of rate of dry deposition of S as sulphate and N as nitrate on natural surfaces (Ashok and Cassia leaves) at Dayalbagh, Agra in India and estimate the total input of S and N compounds. The mean annual dry deposition rate of SO₄ and NO₃ on Ashok leaf was found to be 1.07 0.64 mg m⁻² d⁻¹ and 0.76 0.58 mg m⁻² d⁻¹ while on Cassia leaf values were found to be 1.11 0.75 and 0.81 0.56 mg m⁻² d⁻¹. The deposition of SO₄ includes both the deposition due to gaseous SO₂ and particulate SO₄ while deposition of NO₃ include deposition contributed by HNO₃ vapor and particulate NO₃. The high deposition rates on Cassia leaf may be due to large number of leaf hairs and stomatal pores on leaf surface as compared to Ashok leaf as observed by Scanning Electron Microscopic photographs. The dry deposition rates for SO₄ and NO₃ were highest during the monsoon followed by winter and summer. The annual input of S was found to be 3.89 kg/ha on Ashok leaf and 4.23 kg/ha on Cassia leaf. For N total annual deposition values were 2.67 kg/ha on Ashok leaf and 2.79 kg/ha on Cassia leaf. The total input of S calculated by parameterization method for vegetation in this region is 11.9 kg/ha while N is 2.85 kg/ha.

A51F-0138 0830h POSTER

A new Model for Studies of Tropospheric Ozone and Non-Methane Hydrocarbons: Characteristics, Evaluation, and Budgets of MATCH-MPIC, Version 3

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A new version of the three-dimensional global chemistry-meteorology model MATCH-MPIC (Model of Atmospheric Transport and Chemistry, Max-Planck-Institute for Chemistry Version) has been developed. The model includes a representation of Non-Methane Hydrocarbon Chemistry, surface emissions based on recent emission inventories and an improved treatment of dry deposition, as well as improvements in the model physics. A flexible integration method has now been incorporated allowing for easy modification or extension of the chemical mechanism.

Results from a high resolution (1.9° × 1.9°) simulation are thoroughly evaluated with available observations. Surface and airborne measurements of O₃, CO, NMHCs, and oxygenates are included in the comparison. The model is largely able to capture the main features of the observations, but also some interesting discrepancies are found which provide information on unknown emissions or chemical processes.

Selected budgets of the troposphere and some sub-regions are also discussed. In particular the loss pathways of carbon and the CO₂-yield from different groups of hydrocarbons is considered and the importance of the assumed solubility of intermediates is assessed.

A51F-0139 0830h POSTER

The Fate of Ozone at a Ponderosa Pine Plantation: Partitioning Between Stomatal and Non-stomatal Deposition Using Sap Flow and Eddy Covariance Techniques

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Major advances in quantifying ozone deposition to vegetated ecosystems have been made using above-canopy techniques – such as eddy covariance – that allow for the direct measure of ozone flux into natural systems. However, from above-canopy flux measurements alone, it is impossible to differentiate between deposition through stomatal openings of trees versus non-stomatal surfaces or within canopy chemical loss. Therefore, there is a need to partition ozone fluxes into plant stomatal and non-stomatal components. Sap flow measurements provide a direct measurement of stomatal conductance from which we can infer ozone uptake by trees: this represents a novel way to determine pollutant loading on stomatal surfaces of trees that is inexpensive, reliable, and can be deployed in a multitude of environments. Sap flow measurements were used to determine ozone uptake by ponderosa pine trees in the Sierra Nevada Mountains year-round starting in June 2000 at Blodgett Forest, an Ameriflux site located ~75 miles downwind of Sacramento, CA. Concurrently, total ecosystem ozone flux was measured using eddy covariance. Mean total ozone flux to the ecosystem was 46.6 μmol m⁻² h⁻¹ (±15.1) in summer 2000, 27.6 μmol m⁻² h⁻¹ (±14.2) in fall 2000, 8.2 μmol m⁻² h⁻¹ (±5.1) in winter 2001, and 21.1 μmol m⁻² h⁻¹ (±11.6) in spring 2001. Mean ozone flux through the stomata was 14.6 μmol m⁻² h⁻¹ (±4.1) during summer 2000, 12.9 μmol m⁻² h⁻¹ (±5.8) during fall 2000, 5.6 μmol m⁻² h⁻¹ (±2.8) during winter 2001, and 12.7 μmol m⁻² h⁻¹ (±3.7) during spring 2001. The percentage of total ozone deposition which occurred through the stomata was 31% in summer, 47% in fall, 69% but highly variable in winter, and 60% in spring. The difference between total ozone flux to the ecosystem and stomatal ozone flux to the trees varied exponentially with air temperature, suggesting that much of the non-stomatal deposition was actually due to chemical loss either on surfaces or within the canopy. The influence of biogenic VOC and/or NO_x emissions in controlling the non-stomatal ozone deposition will be further explored.

A51F-0140 0830h POSTER

Theoretical Study of OH Reaction with Toluene

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Aromatic hydrocarbons constitute a major fraction of total volatile organic compounds (VOCs) in the urban and regional atmosphere, and are emitted primarily from anthropogenic sources, i.e. emission from automobiles, fuel-based vehicles, and industry. In addition to their important role in gas-phase chemistry of urban air pollution, oxidation of aromatic hydrocarbons leads to formation of various non-volatile and semi-volatile organic compounds, which are responsible for the formation of secondary organic aerosols. Toluene is the most abundant aromatic hydrocarbon. Reactions of toluene in the atmosphere are mainly initiated by attack from hydroxyl radical OH. In this study, we report a theoretical study of the reaction of toluene with OH.

Density functional theory (DFT) and ab initio calculations have been employed to investigate the OH-toluene adduct isomers. The geometries and energetics of the four isomers of the OH-toluene adduct radicals as well as their corresponding transition states are presented. The DFT and ab initio theories applicable to the OH-toluene reaction system are evaluated. We also present calculations of the rate constants and isomeric branching ratios of the formation of the OH-toluene adduct isomers.

A51F-0141 0830h POSTER

Mechanism and OH Yield of Ozonolysis of Isoprene

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Although ozonolysis of isoprene represents an important nighttime source of tropospheric hydroxyl radicals, its chemical mechanism remains highly uncertain. The O₃-isoprene reaction proceeds through several intermediates, including chemically activated primary ozonides and carbonyl oxides which are critical in determining the final product distribution. We have studied the formation and unimolecular reactions of primary ozonides and carbonyl oxides arising from the O₃-initiated reactions of isoprene using density functional theory (DFT) and ab initio molecular orbital calculations. The structures and energies of these intermediates as well as the transition states and products of their unimolecular reactions were determined. The ab initio energetics were used to determine the reactions and activation enthalpies of formation and cleavage of primary ozonides and unimolecular reactions of carbonyl oxides. We also investigate the reaction pathways of these intermediates using statistical-dynamical master equation and transition state theory. OH yields from both prompt and thermal decomposition of carbonyl oxides are determined.

A51F-0142 0830h POSTER

Two High-Resolution, Quantitative, Infrared Spectral Libraries for Atmospheric Chemistry

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The Pacific Northwest National Laboratory (PNNL) and the National Institute of Standards and Technology (NIST) are independently creating quantitative, 0.10 cm⁻¹ resolution, infrared spectral libraries of vapor phase compounds. Both libraries contain many species of use to the gas-phase spectroscopist, including for atmospheric chemistry. The NIST library will consist of approximately 100 vapor phase spectra primarily associated with volatile hazardous air pollutants (HAPs) and suspected greenhouse gases, whereas the PNNL library will consist of approximately 400 vapor phase spectra associated with DOE remediation mission.

Data are being recorded from 600 to 6500 cm⁻¹ to cover not only the classical fingerprint region, but much of the near-infrared as well. The wavelength axis is calibrated against published standards. To prepare the samples, the two laboratories use significantly different sample preparation and handling techniques: NIST uses gravimetric dilution and a continuous flowing sample while PNNL uses partial pressure dilution and a static sample. The data are validated against one another and agreement on the ordinate axis is generally found to be within the statistical uncertainties (2σ) of the Beers law fit and less than 3% of the total integrated band areas for the 4 chemicals used in this comparison. The nature of the two databases and the rigorous nature used to acquire the data will be briefly discussed.

A51F-0143 0830h POSTER

Detailed Validation of MOPITT Instrument Radiances Using In-situ Profile Data

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Operational retrievals of carbon monoxide profiles using data from the MOPITT (Measurements of Pollution in the Troposphere) instrument are based on a total of 12 calibrated satellite radiances in two spectral bands. To a large extent, the quantitative agreement of the satellite radiances with values calculated by the MOPITT operational forward radiative transfer model determines the ultimate accuracy of the MOPITT CO retrieval results. For example, a radiance bias as small as 1% in one particular signal may produce a retrieval bias in the CO profile larger than 10%.

Validation of both MOPITT Level 1 (calibrated satellite radiances) and Level 2 (CO profile and total column retrievals) products is primarily based on comparisons of MOPITT results with in-situ profiles acquired as part of a program conducted by NOAA's Climate Monitoring and Diagnostics Laboratory. Regular sampling flights have been made at five globally-distributed sites. The goal of the work presented here is to identify and quantify MOPITT radiance biases using the CMDL in-situ data in a manner that accounts for all significant sources of error. These potential error sources include local surface characteristics (e.g. surface emissivity), proximity to CO emission sources, in-situ vertical sampling characteristics, and MOPITT cloud-clearing performance. By minimizing errors associated with each of these effects, we show that the goal of quantifying MOPITT radiance biases to within 1% is realistic.

A51F-0144 0830h POSTER

Recent Global Measurements of Atmospheric COS and Historic Trends Inferred from Firn Air at the South Pole

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Available measurements of carbonyl sulfide provide a picture of atmospheric distributions and seasonal variations that are somewhat inconsistent with our current understanding of COS sources and sinks [see Kjellstrom, *J. Atmos. Chem.*, 1998]. Over the past 1.5 years, we have made measurements of COS at 10 ground-based sampling stations to address some of these concerns. In addition, we have measured COS in firn air from the South Pole in an attempt to reconstruct an atmospheric history of this gas dating back to the early 1900s. The recent data show large seasonal variations at most sites in both hemispheres; summer mixing ratios at Arctic and continental US sites are 20-30% lower than observed in spring. In the northern hemisphere (NH), the timing of the seasonality lends support to strong summertime losses of COS owing to uptake by vegetation and/or soils. The only regular seasonality noted previously for COS in the NH was by total column absorption measurements at mid-latitudes that indicated slightly higher (~3%) mean tropospheric mixing ratios in summer. In the southern hemisphere (SH), smaller (~10% peak-to-peak) variations are observed at Tasmania and show a maximum during austral summer, perhaps owing to enhanced oceanic flux during that season. No seasonality is apparent at American Samoa (14 S), where larger sample-to-sample variations are observed. Our data suggest annual mean surface mixing ratios for COS that are slightly higher in the SH (by ~2%), but the NH/SH ratio varies by about ±6% depending upon the season.

Data from air trapped in the snow pack (firn) at South Pole suggest that COS mixing ratios in the early 1990s were ~20% lower than observed today. The mixing ratio increases appear to have occurred predominantly in the early part of that century.

A51F-0145 0830h POSTER

Collection and Analysis of Firn Air from the South Pole, 2001

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In January 2001, we collected an archive of 20th century air from the firn (snowpack) at the South Pole. Samples were collected into separate pairs of 3L glass flasks for measurements of O₂/N₂ (Bowdoin/Princeton) and carbon cycle gases (CMDL); individual 3L stainless steel and glass flasks for measurements of halocarbons, N₂O, SF₆, and COS; large (33L) stainless steel canisters for maintaining an archive of air for future analyses; and a few canisters each for measurement of 14CH₄ (NIWA/CSIRO) and very low-level analyses of SF₆ (SIO). Although it was hoped to obtain air dating back to the turn of the century, the analyses suggest that the earliest date was 1925 for CO₂ and the mid- to late teens for heavier gases such as methyl bromide or methyl chloride.

This talk will compare the analyses of halocarbons in these recently collected samples to those of air in flasks sampled at the South Pole in 1995. We also will present some results for compounds not measured in the 1995 South Pole samples owing to a paucity of air. Measurements made of the same gases in the firn air at both ends of this six-year interval, along with real-time atmospheric measurements of the same gases, are useful in evaluating assumptions about diffusion in the firn and may allow for the direct calculation of diffusion coefficients at low temperatures. This, in turn, would improve age estimates for firn air samples. New measurements will add to our existing histories established for the 20th century from analyses of firn air samples collected in both Greenland and Antarctica.

URL: <http://www.cmdl.noaa.gov>

A51G MC: 123 Friday 0830h

Diagnosing Systematic Errors in Numerical Models of the Climate System I

Presiding: G L Potter, Lawrence Livermore National Laboratory; J J Hack, National Center for Atmospheric Research

A51G-01 0830h INVITED

Addressing the Information Gap between Global Climate Models and Observations

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The output from a large number of model simulations is growing rapidly. This includes model data from Global Climate Models (GCMs), newer "World Models" (with more sophisticated treatment of terrestrial systems, the cryosphere, biogeochemistry, atmospheric chemistry, and/or oceanographic components), reanalysis model simulations, and numerical weather models. The data from these simulations if not now, will soon exceed the amount of archived observational data. Yet,