

A72B-0175 1330h POSTER

Sensitivity of Vegetation in the Western United States to Global Anthropogenic Changes in Atmospheric Carbon Dioxide Concentration: Forcing and Feedbacks in an RCM-EVM Coupling

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Anthropogenic increases in atmospheric carbon dioxide (CO₂) concentrations may affect vegetation distribution both directly through changes in photosynthesis and water-use efficiency, and indirectly through CO₂ induced climate change. Additionally, changes in vegetation distribution due to these direct and indirect effects may induce land surface-atmosphere feedbacks that create further change in both regional climate and regional vegetation distribution. Using a regional climate model (RegCM2.5) coupled to an equilibrium vegetation model (BIOME4), we quantitatively tested the sensitivity of climate and vegetation in the western United States to both the direct and indirect effects of doubled pre-Industrial atmospheric CO₂ concentrations and to land surface-atmospheric feedbacks induced by the initial vegetation sensitivities. In assessing regional vegetation responses to the initial effects of elevated CO₂ levels, vegetation in the western United States was sensitive to changes in photosynthesis and water use efficiency caused by increased CO₂ availability, with woody biome types replacing less woody types throughout the domain. Vegetation was also sensitive to the initial climatic effects of increased CO₂ concentrations, particularly at high elevations, both due to warming throughout the domain and to decreased precipitation in key mountain regions such as the Sierra Nevada and the Cascade and Blue Mountains of Oregon. Additionally, these patterns changed when the initial climatic and non-climatic effects of CO₂ on vegetation were tested in combination, creating sensitivities not seen in either of the individual cases and indicating that climatic and non-climatic effects must be considered in tandem when assessing the potential impacts of elevated CO₂ levels. Finally, asynchronous coupling of RegCM2.5 and BIOME4 tested the role of land surface-atmosphere feedbacks in shaping the regional response to elevated global atmospheric CO₂ concentrations. The initial regional vegetation responses to elevated atmospheric CO₂ levels resulted in regional land surface-atmosphere feedbacks that further altered regional climate and vegetation distribution, particularly along ecotones. Because the asynchronous coupling of RegCM2.5 and BIOME4 represents a new regional climate model application, further work is required to constrain the model sensitivity to choice in methodological variables such as length and number of iterations and domain size and placement.

A72B-0176 1330h POSTER

Using MISR/Terra Products to Support Regional Climate Modeling

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The MISR instrument on NASA's Terra platform routinely acquires spectro-directional measurements of the solar radiation reflected by the planet. These measurements, obtained at a spatial resolution of up to 275 m, provide a unique opportunity to improve regional climate models and forecasts, by delivering reliable and accurate descriptions of the observed geophysical environments. These can be used either to initialize surface, cloud and aerosol fields, or to evaluate RCM simulations. Examples of products delivered from MISR and currently available operationally will be exhibited.

A72B-0177 1330h POSTER

Comparison of Future Air Temperature Changes in six AOGCMs With Focus Over Scandinavia

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Predictions of near-surface air temperatures by six AOGCMs (CGCM2, ECHAM4, GFDL, HADCM3, MRI2, NCAR DOE PCM) included in the latest IPCC assessment are intercompared focussing over the land areas of northern Europe and its subdomain Scandinavia. Monthly data from transient runs under the A2- and B2- draft marker emission scenarios are analysed with respect to annual and monthly areal averaged temperature changes during the coming century and their geographical patterns.

Predicted temperature changes tend to increase when moving from the global to the regional scale of Scandinavia, although the GFDL B2-experiment projects lower sensitivities for northern Europe and Scandinavia than for global scales. The MRI-model simulates considerably lower sensitivities than the other models. Disregarding this model, results are in close agreement for global scales, while considerable intermodel variability arises for the regional scales. In contrast to global averages considerable month-to-month variation can be observed for Scandinavia, however the pattern varies between models. While some models lack a regular pattern in projected monthly temperature changes (e.g. GFDL, MRI), other models project a pronounced seasonal cycle with lowest sensitivities in summer and largest in winter (e.g. CGCM, HadCM). Most models predict an increase in warming towards the north over the Scandinavian area. Together with increased winter sensitivities this points to a coupling with Arctic sea ice processes. We find that there is a large model-to-model variability in Arctic sea ice change and the modelling of Arctic sea-ice appears to be crucial in determining high latitude response to global climate change.

A72B-0178 1330h POSTER

GCIP Water and Energy Budget Synthesis (WEBS)

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As part of the World Climate Research Program's (WCRP's) Global Energy and Water-Cycle Experiment (GEWEX) Continental-scale International Project (GCIP), a water and energy budget synthesis (WEBS) has been developed from the "best available" observations and models for the period 1996-1999. This WEBS includes a general description of the Mississippi River Basin climate, physiographic characteristics, available observations, representative types of models used for GCIP investigations, and a comparison of water and energy variables and budgets from models and observations. Besides this summary paper, a companion CD-ROM with more extensive discussion, figures, tables, and raw data is also available to the interested researcher.

Observations cannot adequately "close" budgets since too many fundamental processes are missing. Models that properly represent the many complicated atmospheric and near-surface interactions are required for overall descriptions of the budgets. Models will also be needed for eventual predictions of these water and energy processes. Therefore, different classes of models have also been compared with available observations. The comparison includes a representative global general circulation model, regional climate model, and a macroscale hydrologic model. There does appear to be a clear advantage to using a regional analysis over a global analysis or a regional simulation over a global simulation to describe the Mississippi River Basin budgets. There also appears to be some advantage to using a macroscale hydrologic model for at least the surface water budgets.

A72B-0179 1330h POSTER

The Impact of Historical Land-use Changes on the Short-term Mesoscale Climate: A Modeling Case Study

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In the second half of the 19th century land use and land cover in the three-lakes region on the Swiss Plateau was dramatically modified. Most of the formerly marshy and frequently inundated plains were drained and replaced by nowadays intensively used agricultural land with predominantly crops and vegetables.

This case study investigates the effects of these historical land-use and land-cover changes on the short-term climate of typical clear-sky summer days in July. In order to evaluate the influences, a mesoscale dynamical non-hydrostatic model was used with a very high horizontal resolution of 1x1km² nested in a coarser grid of 10x10km² with one-way interactions. The same atmospheric data were used for initial and boundary conditions for both simulations of historical and present conditions. Six sensitivity experiments were conducted in order to assess the importance of changes in the physiological, morphological, and soil properties for the changes in the short-term summer climate.

In the area of land-use changes, the daily average temperature was 0.25°C cooler for the present land-use conditions. During the day, heterogeneous changes in temperature were observed depending on the type of land-use conversion. In areas where afforestation took place over the last 150 years, an average warming of more than 1.0°C could be observed. In contrast, deforestation resulted in a cooling of up to 2.0°C. Furthermore, changes in the average water vapor mixing ratio are most pronounced during the day, with an average increase of 0.2 g/kg. During the night, the average temperature was up to 0.6°C cooler for the present land-use conditions. Due to topographical effects, the nighttime cooling is mainly restricted to low-lying areas on the formerly frequently inundated plains. The diurnal temperature range in the area of land-use changes increased by 0.1-0.3°C. Changes in the state of the atmosphere extended up to 40 km downstream of the area of land-use changes. Due to the ascending topography in the downstream area, the altered air masses were transported up to a height of ca. 2,500 m a.s.l.

With the sensitivity experiments, it could be shown that the daytime temperature decrease caused by morphological changes dominated the temperature increase due to changed physiological properties while changes in the mixing ratio during the day were mainly caused by changes in the physiological properties. In contrast, the altered physiological properties are the dominant factor for the nighttime cooling.

A72C MCC: Hall D Sunday 1330h

Atmospheric Chemistry: Trace Gases and Radical Chemistry Posters

Presiding: J H Butler, NOAA Climate Monitoring and Diagnostics Laboratory

A72C-0180 1330h POSTER

Methyl Halide Distributions and Fluxes in the Southern Ocean

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Methyl bromide and methyl chloride together constitute about one-quarter of the equivalent chlorine that participates in stratospheric ozone depletion. The primary sources for these compounds are natural, yet the atmospheric budgets are poorly constrained. The oceans are an important component of the methyl halide budgets, acting both as a source and a sink of these gases. As climate changes, the net oceanic fluxes of these gases are likely to change in response. Estimating the magnitude or direction of these changes will require an understanding of the cycling of methyl bromide and methyl chloride within specific regions, of which the Southern Ocean may be significant.

Air and water concentrations of methyl bromide, methyl chloride, and methyl iodide in and over the Southern Ocean were measured during the November-December 2001 CLIVAR SR3 transect between Australia and Antarctica, which was a reoccupation of the WOCE SR3 line. While methyl iodide was supersaturated throughout the cruise, methyl bromide and methyl chloride were significantly undersaturated over most of the cruise track, consistent with other studies suggesting that polar waters are a net sink for these

gases. Near the Antarctic coast, the degree of undersaturation of both gases more than doubled. These decreases, however, are likely the result of enhanced vertical mixing rather than an increase in the strength of chemical or biological sinks. The minimum degradation rate constants necessary to sustain these undersaturations in the presence of air-sea exchange are in the same range as the observed total degradation rate constants measured during this cruise by the University of California at Irvine. These results further suggest that there is no significant production of methyl bromide and methyl chloride in polar waters.

A72C-0181 1330h POSTER

Oceanic Uptake of Methyl Bromide: Implications for Oceanic Production

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Methyl bromide (CH₃Br) is a source of inorganic bromine (Br) in the stratosphere, where it contributes to the depletion of stratospheric ozone. Unlike the chlorofluorocarbons, which are entirely anthropogenic, methyl bromide has both natural and anthropogenic sources. At 10 parts per trillion in the troposphere, methyl bromide is believed to be the single largest contributor of stratospheric Br. Once in the stratosphere, Br is approximately 50 times more effective in depleting stratospheric ozone than Cl. However, the budget for CH₃Br remains largely unbalanced with known sinks outweighing sources by 50%.

With production and degradation occurring in the ocean, the ocean is both a source and a sink for CH₃Br. The balance between production and degradation results in the net undersaturation of CH₃Br that has been observed over much of the world's ocean with an estimated global net ocean sink ranging from -11 to -20 Gg/y [King et al., 2000 and references therein]. However, effects of climate change, such as changes in wind-speed distribution or sea-surface temperature could alter this balance. Modeling the potential effect of such forcing on the net flux of this important trace gas requires an understanding of the factors controlling the distributions of production and degradation in the surface ocean.

During three recent research cruises (North Atlantic, North Pacific, and Southern Ocean), CH₃Br degradation rate constants were measured along with saturation anomalies. Here we incorporate these data into a gridded global box model to examine the distribution of oceanic production rates necessary to support the observations.

King, D.B., J.H. Butler, S.A. Montzka, S.A. Yvon-Lewis, and J.W. Elkins, Implications of methyl bromide supersaturations in the temperate North Atlantic Ocean, *J. of Geophys. Res.*, 105 (D15), 19763-19769, 2000.

A72C-0182 1330h POSTER

Methyl Bromide and Methyl Chloride Degradation in the Southern Ocean

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The oceans are both a source and sink for atmospheric methyl bromide and methyl chloride and play a significant role in the atmospheric budgets of these ozone-active gases. We have carried out a series of shipboard studies designed to characterize the loss rate of

methyl halides in the surface ocean, using a 13C stable isotope incubation technique. Here we present the first degradation measurements of methyl bromide and methyl chloride in the Southern Ocean. The cruise was conducted from October to December, 2001, aboard the Australian icebreaker Aurora Australis. The cruise track extended from Hobart, Tasmania to Buchanan Bay (Mertz Glacier) at the coast of Antarctica (46-67°S, 138-145°E).

For methyl bromide, loss rate constants measured over the course of the cruise in unfiltered seawater samples ranged from 0.00 to 0.17 d⁻¹ with a mean of 0.040 d⁻¹ (n=102). Chemical loss rates in these waters were extremely low, because of the low seawater temperatures, and the observed loss rate constants are largely (98%) attributable to biological processes. For methyl chloride, loss rate constants measured over the course of the cruise in unfiltered seawater samples ranged from 0.00 to 0.22 d⁻¹, with a mean of 0.07±0.08 (n=43). Loss in filtered samples was undetectable, as expected from the known rate of hydrolysis. As in the case of methyl bromide, the loss mechanism for methyl chloride is presumed to be biological. These results demonstrate that biological degradation of methyl bromide and methyl chloride can occur at significant rates even in very cold, polar waters, and explain the tendency for high latitude waters to be undersaturated with respect to atmospheric methyl bromide. These are the first open ocean observations of atmospheric methyl chloride uptake. The high rates observed confirm earlier coastal measurements, and support the idea that the oceans can be a major sink for atmospheric methyl chloride.

A72C-0183 1330h POSTER

Marine Fluxes of Very Short-lived Gases and Their Potential Contribution to Stratospheric Ozone Depletion

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Current measurements suggest that the amount of ozone-depleting bromine in the lower stratosphere exceeds the amount of organic Br present in longer-lived compounds (halons, CH₃Br) in the troposphere. This, in turn, implies that very short-lived gases, such as CH₂Br₂ and CHBr₃, also contribute to the stratospheric burden of inorganic Br. Because of their low concentrations and short lifetimes in the troposphere (days to months), these gases have been largely ignored in models of stratospheric ozone depletion. However, models, and some earlier measurements, suggest that delivery mechanisms to the stratosphere may include rapid transport in deep convective zones and that Br and I could be brought to the stratosphere in inorganic or organic form. Many very short-lived, brominated and iodinated gases originate mainly in the ocean. They are produced in large amounts by marine organisms as well as by abiotic reactions. Most are highly supersaturated (100s to 1000s of percent) and have extremely high fluxes relative to their amounts in the troposphere. We present here measurements of CHBr₃, CH₂Br₂, CH₃I, and other very short-lived gases in the air and surface ocean from six cruises conducted during 1994-2001. The cruise tracks cover the Pacific, Atlantic, and Southern Oceans. Data show extreme supersaturations in the tropics, where deep convection is predominant, and high supersaturations throughout the rest of the ocean. Calculated sea-air fluxes of all of these compounds are very high everywhere.

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

A72C-0184 1330h POSTER

Recent Declines in Atmospheric Methyl Bromide From a Global Flask Sampling Network

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Results from the NOAA-CMDL flask sampling network over the past 8 years indicate that the global mean atmospheric mixing ratio of methyl bromide has decreased since 1998. Larger decreases have been observed in the Northern Hemisphere compared to the Southern Hemisphere. During 2002, the Northern Hemisphere mean mixing ratio was about 10% or 1 ppt lower than it was in 1995-1996 and 1999. This decline, however, has not been consistent over time; mixing ratios were elevated in 1997-1998, perhaps as a result of the large El Niño that occurred then. Despite this short-term perturbation, the longer-term decrease in mixing ratios and in the interhemispheric abundance ratio (North/South) of this gas are reasonably well explained by decreases in fumigation-related emissions given our present understanding of the methyl bromide budget and reported production declines. Global industrial production of methyl bromide reported to UNEP was down by 25% in 1999, in line with production restrictions outlined in the fully revised and amended Montreal Protocol on Substances that Deplete the Ozone Layer. Production was scheduled for a similar drop again in 2001. Methyl bromide is an important ozone-depleting substance that is emitted to the atmosphere as a result of both human and natural activities.

A72C-0185 1330h POSTER

Stable Carbon Isotopes of Background Atmospheric Methyl Bromide

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Methyl bromide (CH₃Br) constitutes the largest source of bromine atoms to the stratosphere and plays an important role in stratospheric ozone depletion. However the CH₃Br atmospheric budget remains unbalanced. We utilize an isotopic mass balance to constrain the CH₃Br atmospheric budget by analyzing the source signatures and the isotopic fractionations associated with sinks. Carbon isotope composition of background atmospheric CH₃Br is needed to test this approach. Thus far, the carbon isotope composition of background atmospheric CH₃Br was not analyzed due to its low atmospheric mixing ratio (10 pptv) and the relatively high amount of carbon needed to measure carbon isotope ratios. Therefore, preconcentration is necessary for isotopic analysis of atmospheric CH₃Br. Here we report the first measurements of stable carbon isotope ratios from background tropospheric CH₃Br. We developed a preconcentration technique for measuring the carbon isotope compositions of halogenated organic gases. We are able to sample 1100 Liters of air with a flow of 6.5L/min. We have solved the problem of separating CH₃Br from N₂ and O₂ in high pumping flow and the problem of saturation of the gas chromatograph column by CO₂. We show that it is possible to measure the delta13C values using a gas chromatograph isotope ratio mass spectrometer (GC-IRMS) for sample sizes down to 6 nanograms of carbon. This is the first time measurements of carbon isotope composition of atmospheric organic components have been achieved at a concentration of about 10 pptv.

A72C-0186 1330h POSTER

Quiescent Diffusive and Fumarolic Volcanic Bromocarbon Emissions

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Future scenarios of declining atmospheric burdens of Ozone Depleting Substances (ODS) such as halocarbons after phase-out following international regulation (Montreal Protocol) vary strongly depending on what contribution from natural sources is taken into account. In addition, current and pre-industrial global atmospheric budgets of ODS are poorly balanced by known natural and anthropogenic sources of halocarbons (Butler, 2000). Brominated halocarbons have a high Ozone Depletion Potential, Br is at least 40x as efficient as Cl in polar stratospheric ozone destruction (Solomon et al., 1992). CH₃Br is the dominant Br carrier to the stratosphere with sources being ca.: 32% anthropogenic, 39% natural, but ca. 29% unaccounted for (WMO, 1998). Natural sources have been reviewed recently (Gribble, 2000; Butler, 2000), including magmatic inorganic (Bureau, 2000) and volcanic organic sources (Rasmussen et al., 1980; Schwandner et al., 2002). CH₃Br and other bromocarbons have been reported in non-eruptive volcanic gases previously (Jordan et al., 2000; Schwandner et al., 2000). Due to its capability to extremely rapidly hydrolyse (Gan et al., 1995), CH₃Br should not be sampled by the caustic soda bottle technique as used by Jordan et al. (2000) whose samples also show signs of air contamination, but by cryogenic separation of steam with subsequent sorbent trapping, as used by Isidorov (1990), Wahrenberger (1996) and Schwandner et al. (2000, 2001). To contribute significantly to the natural Br budget, volcanic gases would have to at least contain 2 ppmv (dry gas) CH₃Br, scaled to a global CO₂ emission of 66 Tgy⁻¹ (Stoiber, 1995) based on CO₂ flux to halocarbon concentration correlations (e.g. CFC-11: R²=0.91, Schwandner et al., 2002). However, CH₃Br is not the only volcanogenic bromocarbon. Analysis of diffusive flank and crater degassing on Vulcano island (Italy) showed a strong diffusive component of CH₃Br and C₂H₅Br emissions in 60-100°C hot pristine unvegetated volcanic "soil" close to high-temperature fumaroles. Other ODS found significantly above air, field and analytical system blanks include CH₃Cl, CH₃I, chlorophenols and chlorobenzenes. Abundances range from upper pptv to ppmv (e.g. CFC-11: max. 1200 pptv diffusive, 3700 pptv fumarolic/dry gas, dry air: 268 pptv).

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A72C-0187 1330h POSTER

Understanding the Trends of Atmospheric Methane in the Past Decade

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Methane (CH₄) is the second most important anthropogenic greenhouse gas after carbon dioxide. In this study, the GEOS-CHEM global three-dimensional chemical transport model with assimilated meteorology is used to quantify the contributions of individual CH₄ sources and sinks to the trends of CH₄ concentration

in the past decade. The model is evaluated with observations from the NOAA CMDL network. The model accounts for interannual variations in meteorology and concentrations of OH radical. Emissions are scaled using yearly country-by-country socioeconomic and meteorological data. The model simulates well the horizontal and vertical distributions, seasonal cycles, trends, and interannual variations of CH₄, capturing over 80% of the variance between 1988 and 1997 at many sites. It appears that the observed decrease in growth rate of CH₄ over the past decade is a result of stabilization of global emissions from livestock, rice paddies, gas venting, and coal mining along with a slight decrease in CH₄ lifetime. The anomalous growth rates during 1991-1992 can be explained by changes in OH concentrations and wetland emissions due to the eruption of Mt. Pinatubo.

A72C-0188 1330h POSTER

Ground-based Measurements of Vertical Profiles and Columns of Atmospheric Trace Gases Over Toronto Using a New High-Resolution Fourier Transform Infrared Spectrometer

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The University of Toronto Atmospheric Observatory (TAO) has recently been established at Toronto, Canada. TAO includes several instruments, with a DA8 Fourier Transform Spectrometer (DA8 FTS, manufactured by ABB Bomem Inc., Québec, Canada) serving as the primary instrument at the facility. The geographic position of TAO (43.66°N, 79.40°W) makes it well suited for long-term measurements of mid-latitude stratospheric ozone and related species, while its urban setting enables measurements of tropospheric pollution.

The DA8 FTS is based on a Michelson interferometer with a maximum optical path difference of 250 cm, providing a maximum unapodized resolution of 0.0026 cm⁻¹. It is currently equipped with KBr and CaF₂ beamsplitters, and InSb and HgCdTe detectors, for coverage of the spectral range from 700 to 4100 cm⁻¹. A new heliostat (manufactured by Aim Controls Inc., California, USA) provides active solar tracking, collecting the incoming solar radiation and directing it into the FTS.

The TAO DA8 FTS incorporates a new optical design recently developed by ABB Bomem Inc., which results in a fixed optical axis through the beamsplitter (and a fixed focal point on the detector) as well as a more stable modulation efficiency. The new instrument optics will be discussed. Next, the performance of the instrument will be examined in the context of standard NDSC (Network for the Detection of Stratospheric Change) trace gas column and vertical profile retrieval techniques, which use least squares fitting algorithms (SFIT, SFIT2). TAO has been operational (weather permitting) since October 2001. We have been retrieving columns and vertical profiles of HCl, HF, CH₄, OCS, C₂H₆, CO, N₂O and NO₂ since May 2002. A detailed error analysis of retrieved columns and vertical profiles has been undertaken for the above species.

Future plans for the TAO FTS include comparing our measurements with satellite measurements made by MOPITT, OSIRIS, and the upcoming ACE and MAESTRO instruments. Finally, we are investigating the feasibility of making broadband infrared measurements of aerosols using the TAO DA8 FTS.

A72C-0189 1330h POSTER

The Hydrogen Isotopic Composition of Water Vapor Entering the Stratosphere Inferred From High Precision CH₄ and H₂ Measurements

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Precise knowledge of the hydrogen isotopic composition of water vapor entering the stratosphere can provide important constraints on mechanisms for mass transport of air across the tropical tropopause. Using an extensive set of high-precision measurements of the hydrogen isotopic compositions of stratospheric H₂ and CH₄ from whole air samples collected by the NASA ER-2 aircraft, the annual mean value of the hydrogen isotopic composition of water vapor entering the stratosphere can be inferred. The results will be presented and compared with previous estimates based on remote sensing measurements from balloon and space flights.

A72C-0190 1330h POSTER

Deuterium Enrichment in Stratospheric Molecular Hydrogen

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Molecular hydrogen (H₂) is the second most abundant reduced gas in the atmosphere (after methane) with a globally averaged mixing ratio of ~ 530 ppbv. Its largest source is believed to be photochemical oxidation of methane (C H₄) and non-methane hydrocarbons (NMHCs); other recognized sources include biomass burning, fossil fuel burning, nitrogen fixation, and ocean degassing. As with other atmospheric trace gases, the stable isotopic content of H₂ has the potential to help quantify various aspects of its production and destruction. The average deuterium content of H₂ (expressed as δD_{H2}) is enriched by ~110 ‰ relative to Vienna Standard Mean Ocean Water while CH₄ in the troposphere, the precursor for photochemical H₂ production, is depleted by ~ 90 ‰ relative to V-SMOW and similar values are expected for NMHCs. Both natural and anthropogenic combustion sources of H₂ have been shown to be depleted in deuterium by 200 to 300 ‰ (Gerst and Quay, 2001; Rahn et al., 2002), and the ocean and N₂ fixation sources are expected to be in near thermodynamic equilibrium with local H₂O and should have deuterium levels of ~ -700 ‰ (Rahn et al., 2002).

In order to offset these deuterium depleted sources and account for the observed tropospheric δD_{H2}, the balancing loss processes must discriminate against reaction with HD and/or the total fractionation associated with CH₄ oxidation and the subsequent reactions leading to H₂ must favor production of deuterated H₂. We have analyzed a suite of stratospheric air samples in order to investigate the photochemical processes influencing the deuterium content of H₂. While the mixing ratio of H₂ is nearly constant, the deuterium content increases such that δD=440 ‰ in samples with a stratospheric mean age of ~ 6 years. The constant mixing ratio results from the fact that production due to CH₄ oxidation and loss due to H₂ oxidation are approximately equal. The observed trend in δD of stratospheric H₂ can only be accounted for by an enrichment in the ratio of D to H of H₂ relative to that in precursor CH₄ in addition to the enrichment due to the slower oxidation of deuterated H₂. We calculate the fractionation associated with this enrichment to be α_{Total}=1.54. As with other trace gases, in situ photochemical processes and the return flux of air from the stratosphere must be accounted for to explain tropospheric observations.

Gerst, S., and P. Quay, *J. Geophys. Res.*, 106, 5021-5031, 2001. Rahn, T., N. Kitchen, and J. M. Eiler, *Geochim. Cosmochim. Acta*, 66, 2475-2481, 2002.

A72C-0191 1330h POSTER

Open-Path FTIR Spectroscopic Studies of trace gases over Mexico City

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Measurements of trace gas concentrations and other quantities are crucial for the investigation of the processes in the atmosphere of large urban areas. A Fourier Transform Infrared (FTIR) spectrometer was used in the open-path configuration to detect and monitor the concentrations of the main gaseous pollutants near downtown Mexico City. This technique relies on detecting the absorbance at specific wavelengths due to absorption of IR radiation by various pollutants. The modulated infrared beam with 0.5 cm⁻¹ spectral resolution is transmitted horizontally through the atmosphere and collected by a bistatic arrangement, which consists of a pair of 12" cassagrain telescopes. The signal is transferred back to the transmitter-end via a cable where data acquisition and quantitative analysis is performed. Approx. 180 spectra in the range 60074000 cm⁻¹ are measured and co-added giving rise to one concentration value every five minutes for every compound analyzed. Preliminary results are presented on measurements carried out in the spring of 2002 over the roofs of two buildings separated by 426 m. The site is next to one of the city's automatic monitoring stations, where point sampling data is available for comparison. While infrared absorption spectrometry has proven highly useful in atmospheric studies, it cannot measure all pollutants of interest with the desired sensitivity. Thus, absorption spectrometry in the UV/visible regions of the spectrum was performed with a Differential Optical Absorption Spectrometer (DOAS). Because its optical path was aligned parallel to that of the FTIR, direct comparisons could be done for the ozone and sulphur dioxide profiles.

A72C-0192 1330h POSTER

Environmental Impact of H₂ from Hydrogen Fuel Cell on the Stratosphere

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Hydrogen fuel cell technology seems poised to replace the internal combustion engine in the upcoming decade. Environmentalists tout the technology as environmentally friendly and stress its low tailpipe emissions resulting in cleaner urban air. At face value the technology should have a negligible impact because the major byproduct is water. What has not been considered is that it will take billions of liters of H₂ to power the future national (and international) fleet of fuel-cell vehicles and that the leading contenders to make that H₂ are the very fossil fuels that cause smog and greenhouse gases. If that does happen, there will be two important consequences. First, the current fossil fuel pollutants will not disappear, rather they will be shifted from tailpipe sources to where the fossil fuels are extracted and the hydrogen is made. In addition, the fuel to make the cells work, H₂, is an important trace constituent (0.5 ppmv) of the atmosphere [Novelli et al., 1999] and participates in reactions involving pollutants and greenhouse gases [Crutzen, 1977]. Thus, anthropogenic H₂ emissions could have significant indirect environmental consequences. The global annual H₂ production from current sources, anthropogenic plus natural, could be doubled in coming decades with the development of a hydrogen fuel economy [Zittel, 1996]. Such an increase could significantly impact the hydrogen cycle and other cycles with which it interacts in both the atmosphere and biosphere.

We have examined the potential environmental impact of additional H₂ release for several emission scenarios. We calculated the ODP of H₂. Given that the oxidation of H₂ is an important source of water vapor in the stratosphere, which is otherwise isolated from direct sources of H₂O by the cold trap at the tropopause. We calculated what kind of elevated concentrations of stratospheric water vapor could occur for the different emission scenarios. Not only will additional water vapor cool the stratosphere, but also it will allow heterogeneous chemical reactions to occur when it forms PSCs in polar regions. H₂ also reacts with atmospheric OH radicals, the premier oxidant in the earth's atmosphere. We will calculate how increasing fluxes of H₂ to the atmosphere will shift the balance of the earth's oxidation chemistry, potentially increasing the lifetimes of other more harmful gases.

A72C-0193 1330h POSTER

Atmospheric Ammonia Emissions from a Dairy

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Gaseous ammonia (NH₃) emissions at high concentrations can damage human and animal respiratory systems. NH₃ environmental impacts include aerosol formation, altering atmospheric chemistry, terrestrial and aquatic eutrophication, soil acidification and global warming. Preindustrial NH₃ emissions are estimated to be 21 Tg yr⁻¹ while current emissions are estimated to be 47 Tg yr⁻¹ with most of the increase coming from domestic animals [Galloway et al., 1995]. There is a lack of detailed emission data from the United States and there are many problems with applying emissions estimates from Europe due to the difference in farming practices between the two regions. Feed and manure management practices can have a large impact on emissions. We are studying NH₃ emissions at the WSU dairy located near Pullman, WA to provide a detailed emission inventory of the various sources at the dairy. The dairy has approximately 170 milking cows housed in open air barns and the waste from the milking cows is stored in liquid slurry lagoons until it is applied to grass fields in the late summer. NH₃ is measured using a short-path spectroscopic absorption near 200 nm with a sensitivity of a few ppbv and a time resolution of a few seconds. The open air short-path method is advantageous because it is self calibrating and avoids inlet wall adherence which is a major problem for most NH₃ measurement techniques. As part of the detailed emission inventory, NH₃ fluxes were determined from the milking stalls, main slurry lagoon and the application of slurry to the fields with a large sprinkler using a SF₆ tracer technique and a dense point Gaussian plume model. NH₃ emission fluxes from various parts of the dairy will be presented.

A72C-0194 1330h POSTER

Air Mass Characteristics Based on Aerosol Composition and Trace Gas Concentrations During the Phoenix Sunrise Experiment 2001

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Aerosol and trace gas samples were taken on top of the tallest building in downtown Phoenix during the Phoenix sunrise experiment. Collection times ranged from 1.5 hours for aerosols to 2 minutes for gaseous species. Four aerosol filter samples in total were collected each morning and analysis of the filter samples was carried out by total reflection X-ray fluorescence spectrometry for elements from Al to Pb.

A strong variation in aerosol elemental composition was found during the morning with very low particle concentrations during the first collection period and a maximum during the second collection period. A similar trend was also observed for reactive trace gas concentrations. Reference trace gas samples taken at a lower elevation of the same building did show this trend only at few occasions. The variation is attributed to a break-up of the nocturnal boundary layer shortly after sunrise. For the first collection period, the top of the building was often in relatively clean air above the polluted nocturnal boundary layer. During the second collection period the boundary layer started to lift and encompassed the higher elevation collection site.

Different air mass characteristics were found based on aerosol composition and concentration clean air, relative stable slightly polluted air, and highly polluted

air. The first few days of the campaign were characterized by a clean to slightly polluted situation with rather low elemental concentrations of soil dust (represented by Ca and Fe) and anthropogenic tracers (represented by Pb and Ni), and the last two days showed significantly higher anthropogenic pollution and soil dust. Interestingly the particulate sulfur concentration remained rather stable for almost all days except a very clean weekend day. The ozone precursor species NOy and NO were low during clean days as well, but increased for the last two days showing two distinct peaks. The highest temperatures and lowest relative humidity were found during the most polluted day suggesting a relationship between these parameters. The relationships among the gas phase and particle phase pollutants will be discussed, and the effect of mixing height and other meteorological variables on the chemical species will be explored.

A72C-0195 1330h POSTER

First Direct Measurement of the Rate Constant for the Reaction Cl + CH₃ and a Reexamination of its Role in Perturbing Laboratory Measurements of the Important Stratospheric Reaction Cl + CH₄

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Two recent papers, one experimental (Wang and Keyser, 1999) and one theoretical (Michelsen and Simpson, 2001) have called attention to possible contributions from the reaction Cl + CH₃ + M → CH₃Cl + M to the observed rate of loss of Cl in laboratory studies of the stratospheric reaction Cl + CH₄ → CH₃ + HCl, especially at low temperatures (T = 200-250 K) and low pressures (P = 1 Torr He). However, the only data available in the literature is from a very complex system, the photochlorination of methane (Timonen et al., 1986). The experiments were performed at P = 50-300 Torr CO₂ and T = 298-423 K and yield k = 3.7 × 10⁻¹⁰ exp(-185/T) with k(298 K) ~ 2 × 10⁻¹⁰, both in units cm³ molecule⁻¹ s⁻¹. The purpose of the present Cl + CH₃ experiments is to supply data under conditions appropriate for correction of laboratory experiments on Cl + CH₄. In our discharge flow-mass spectrometric study of Cl + CH₃, reaction of F with mixtures of HCl/CH₄ rapidly and simultaneously generates Cl and CH₃ in the ratio [Cl]/[CH₃] = 13:1 to 70:1. With Cl in excess, [Cl]₀ = (2 - 14) × 10¹² molecule cm⁻³ and [CH₃]₀ ~ 2 × 10¹¹ molecule cm⁻³, we monitor the decay of CH₃ via low energy (12eV) electron impact mass spectrometry. Under these conditions, the Cl + CH₃ reaction is well isolated and potential secondary reactions are negligible. The rate constant has been measured at P = 0.5, 1.0, 1.5 and 2.0 Torr He and at T = 298, 250 and 202 K. The rate constant is observed to increase with increasing pressure, i.e. the reaction is in the fall-off region. At each pressure k is observed to increase with decreasing temperature. At T = 202 K and P = 1 Torr He, k = 1.6 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The range of values for k now measured for T = 202-298 K and P = 1.0 Torr He are at least 10 times smaller than those used to correct previous Cl + CH₄ laboratory data at these temperatures and pressures. Since Wang and Keyser report that the value of k must be greater than about 5 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ to fit their observations at T = 298 K, P = 1 Torr He and we observe k = 6.6 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ under these same conditions, some other explanation besides contribution from Cl + CH₃ must be sought to account for the observations.

A72C-0196 1330h POSTER

A Chemical Ionisation Mass Spectrometer instrument for the Measurement of Tropospheric HO₂ and RO₂

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Laboratory characterisations and field deployments of a Peroxy Radical Chemical Ionisation Mass Spectrometer (PerCIMS) instrument have been performed. During peroxy radical measurements with this instrument, ambient air is sampled through a 20- μ m diameter orifice into an inlet held at low-pressure, typically 150 torr. Peroxy radicals are converted to other species in the instrument inlet through the addition of NO and SO₂ to the sampled ambient air. The PerCIMS uses this detection technique based on the amplified chemical conversion of ambient peroxy radicals (HO₂ and RO₂) into a unique ion (HSO₄⁻) following the gas phase reaction of NO and SO₂. HSO₄⁻ ions are then quantified by a quadrupole filter mass spectrometer. Speciated measurements of the total sum of peroxy radicals, HO₂+RO₂ (HO_x+RO_x mode) or the HO₂ component only (HO₂ mode) are achieved through controlling the concentration of the NO and SO₂ added to the inlet. This speciation of peroxy radicals measurement is important in the understanding of the natural oxidation of hydrocarbons that occurs in the troposphere. Both laboratory tests and in situ field measurements during recent aircraft missions and at a radical inter-comparison exercise indicate the PerCIMS to be a feasible field instrument for the fast and accurate evaluation of the concentration of peroxy radicals over a variety of atmospheric conditions.

A72C-0197 1330h POSTER

Laboratory Studies to Re-Evaluate the Atmospheric OH Production Rate

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The major atmospheric source of the hydroxyl radical is the photolysis of O₃ followed by the reaction of O(1D) with H₂O (1). The major competing loss process for O(1D) radicals is non-reactive quenching with other atmospheric molecules, particularly N₂ (2) and O₂ (3). The rate coefficients for the reactions of O(1D) with H₂O (k₁), N₂ (k₂) and O₂ (k₃), whose values are critical for calculating atmospheric OH production rates, were measured over a range of atmospherically relevant temperatures to be: k₁(H₂O) = (1.49 ± 0.49) 10⁻¹⁰ exp((80 ± 90)/T) cm³ molecule⁻¹ s⁻¹; k₂(N₂) = (0.195 ± 0.020) exp((125 ± 20)/T); k₃(O₂) = (0.365 ± 0.013) exp((20 ± 10)/T). The quoted uncertainties include estimated systematic errors and are at the 95% confidence level. In addition, k₁ was measured relative to k₂ and to k₃ by observing the relative OH concentration produced from reaction (1) with various concentrations of N₂ or O₂ present to be (2.37 ± 0.71) and (1.99 ± 0.91), respectively, at 295 K. Our results indicate that the uncertainties in the calculated atmospheric OH production rate due to the uncertainties in the rate coefficients are less than ± 20%. These results represent a significant improvement in the accuracy and precision of the ability to predict the atmospheric OH production rate.

A72C-0198 1330h POSTER

Infrared Spectroscopy and Kinetics of Alkyl Peroxy Radicals

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The IR spectra of gas phase alkyl peroxy radicals have been measured using an FTIR/long path length absorption apparatus. Radicals are generated by reaction of the parent alkane with atomic chlorine or fluorine followed by association with molecular oxygen. Spectra are confirmed using both experimental and computational techniques. The reaction with nitric oxide is used to titrate the peroxy radical bands attributed to their decrease in intensity strength while new bands stemming from the reaction products are observed. Ab initio methods are used to calculate the band frequencies and intensities. These also assist in assigning the bands to specific vibrational modes of the molecule.

Kinetics of the reactions of alkyl peroxy radicals with NO, NO₂, and other tropospheric pollutants are measured using a flash photolysis/thermal lensing apparatus in which a xenon flash lamp initiates the reaction mechanism by dissociating molecular chlorine. A pulsed CO₂ laser excites a vibrational band of the peroxy radical. A cw HeNe laser probes the resulting thermal gradient. The strength of the thermal gradient is proportional to the concentration of the absorbing species. The loss of peroxy radical is monitored as a function of time following initiation of the reaction by varying the time between firing of the flash lamp and CO₂ laser. Rate coefficients are measured under pseudo-first order conditions in which the concentration of NO or other reactants are in great excess of the peroxy radical. Spectroscopy results will be presented for ethyl peroxy and larger alkyl peroxy radicals. Kinetic measurements for ethyl peroxy radical will be presented.

A72C-0199 1330h POSTER

Measurement of peroxy radicals in the urban atmosphere by PERCA-LIF technique

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A new instrument has been developed for measuring peroxy radicals (RO₂) using the Chemical Amplifier-Laser Induced Fluorescence (PERCA-LIF) technique. RO₂ was converted to NO₂ via a chain reaction by the addition of NO and CO in a 1/4" Teflon tube. NO₂ was detected by LIF using Nd:YAG laser (532 nm, 5W at 10kHz). More selective detection of NO₂ is enabled by the LIF than by luminol chemiluminescence because of free from the interference by other oxidants when using luminol. LIF technique can be more sensitive detection of NO₂ than the luminol detector. Optimum conditions were investigated by varying reaction time (i.e. the length of reaction tube) and the concentrations of NO and CO. Maximum chain length of approximately 300 was obtained in dry conditions using a H₂O/O₂ simultaneous photolysis method. Experiments were performed to characterize the dependence of the chain length on humidity for this instrument. In August 2002, RO₂ measurements were performed in Osaka using this method. Maximum concentrations of RO₂ in the daytime were approximately 100 pptv. Nighttime observations were also conducted and significant concentrations of RO₂ were detected just after the sunset. Existence of formation processes in the dark condition was investigated.

A72C-0200 1330h POSTER

Kinetics of the Reaction of OH with Peroxynitric Acid (HO₂NO₂) between 218 and 358 K

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Peroxynitric acid (PNA), HO₂NO₂, is formed in the atmosphere by the HO₂ + NO₂ + M reaction. Removal of HO₂NO₂ in the upper troposphere and lower stratosphere occurs mainly via photo-dissociation and reaction with OH radicals. We present our results on the kinetics of OH radicals with PNA in the gas-phase as a function of temperature (T=218-358 K) obtained by using pulsed laser photolysis (at 193 and 248 nm) to generate OH and laser-induced fluorescence for monitoring its temporal profiles. The concentration of PNA in the reactor was measured by UV absorption. The unavoidable impurities present in the PNA samples (H₂O₂, HNO₃ and NO₂) were quantified by UV absorption or mass spectrometry to account for the contribution of the reactions of OH with these impurities to the measured rate coefficients. The bimolecular rate coefficients for the OH + PNA reaction was found to be independent of pressure between 10 and 125 Torr of Helium. The temperature dependence of the rate coefficients for the OH + PNA reaction showed non-Arrhenius behavior over the range studied. The discrepancy between our rate coefficients and those previously reported in the literature will be discussed. The implication of our measured rate coefficients to the upper troposphere and lower stratosphere will be also discussed.

A72D MCC: 125 Sunday 1330h

Advances in Physics and Chemistry of Clouds I (joint with H, GC)

Presiding: G Kramm, University of Alaska, Fairbanks; R M Rasmussen, National Center for Atmospheric Research

A72D-01 1335h INVITED

Turbulence-Particle Interactions in Clouds: Theory, Measurements, and Implications

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Droplets in a cloud often are not spatially distributed in a perfectly random manner: instead, they are clustered on various scales. However, most theories of cloud processes, such as collision-coalescence and radiative transfer, are based on the assumption that droplet positions are uncorrelated. Correlations in droplet positions can be caused by turbulent mixing of cloudy and clear air, by the inertial response of cloud droplets to fluid accelerations (preferential concentration), or even by gravitational sedimentation in still air. The degree of spatial correlation, quantified by the pair correlation function, is scale dependent and is a function of such variables as droplet size, energy dissipation rate, and turbulence Reynolds number. Spatial correlations measured in turbulent clouds with a Fast FSSP are observed to be strongest at centimeter scales and below and the pronounced clustering on these scales is consistent with the inertial clustering hypothesis.

Clustering on sub-centimeter scales is especially relevant to processes that occur on those scales, the collision-coalescence process being archetypal. For example, when droplets are not distributed with perfect randomness the coagulation equation (stochastic collection equation) used in cloud physics will give erroneous results. The coagulation equation can be modified, however, if the droplet pair correlation function is known. It follows that if the pair correlation function can be determined theoretically or measured directly the modified collision rate can be properly accounted for. As a specific example, an analytical form of the modified coagulation equation appropriate for a turbulent mixing zone, based on the Broadwell-Breidenthal mixing model, can be formulated and leads to enhanced droplet collision rates.