A51H-07 1150h

A Quantitative Method to Incorporate Atmospheric Transport Errors in Inverse Modeling Studies

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Previous inverse studies have pointed to the sensitivity of flux estimates to errors in atmospheric transport for tracers such as CO2. Current inverse approaches either neglect transport errors or only attempt to roughly assess their effects from the spread in results derived using different transport models or from "high-frequency variability" in observed tracer concentrations. We describe a method to quantitatively account for transport errors in inverse analyses by incorporating uncertainties in mean winds into the stochastic motions of air parcels. The magnitude of errors in wind fields, as well as their spatiotemporal covariances, are determined by direct comparison of assimilated winds to radiosonde observations. The transport error statistics established by the comparisons are propagated through the stochastic motions of air parcels as simulated by the Stochastic Time-Inverted Lagrangian Transport (STILT) model. We illustrate this method by using atmospheric CO2 observations over the continent and examine the effect of transport errors on estimates of regional terrestrial carbon fluxes.

A51H-08 1205h

Sensitivity of inverted carbon sources and sinks from seasonally and interannual varying fossil fuel emission estimates

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The possibility of a ?fossil fuel rectifier? is tested using two models (PCTM and MATCH:NCEP) that span the spectrum of vertical trapping and rectification as established in the TransCom 3 Atmospheric Carbon Inversion Intercomparison Experiment. Tests with a pseudo fossil fuel emissions field with varying seasonal amplitude suggests that a fossil fuel rectifier is likely to be a small factor in annual mean inversions. However, seasonality in the fossil signal and/or interannual variations in the spatial distribution has a significant impact on seasonal and interannual inversions. Though the level of seasonality in this emissions field is not well known, a 30% amplitude modification case in this exercise closely matches a recently suggested fossil amplitude derived from observational data. Inverse results including this level of fossil seasonality result in posterior flux estimates differing by up to 50% in the northern temperate land regions where the majority of the hypothesized northern land sink is located. This will vary with the extent to which simulated transport vertically traps surface fluxes as evidenced by the results from the two models chosen for this sensitivity study. The impact of interannual variations in the surface pattern of fossil fuel emissions have also be explored. In this experiment, inverse results which attempt to include regional shifts in fossil fuel over the last twenty years will be compared to a case in which the surface emission patterns are fixed. Exclusion of seasonal and interannual fossil fuel variations in inversion studies may lead to misinterpretation of results. This holds particular importance given that the proposed northern land sink and large fossil fuel emissions are coincident in space. Better representation of these variations is essential to maintain accuracy in inverse results as atmospheric inversion studies move to greater spatial and temporal resolution.

A52A MCC: Level 2 Friday 1330h

Isotopic Constraints on Global Budgets of Atmospheric Gases III Posters *(joint with B, H, OS, PP)*

Presiding: **K A Boering,** University of California, Berkeley**; N Jones,** University of Wollongong

A52A-0761 1330h POSTER

Regional Impact of Terrestrial Ecosystem on Global Carbon Cycle: Indicated by Isotopic Measurements of Atmospheric CO2 at Boreal Forest (Fraserdale, Canada)

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Eight intensive campaigns were conducted in different seasons over a 3-year period (1998 to 2000) at a boreal forest site, Fraserdale (50°N, 81°W) in northern Ontario, Canada. Flask air samples were taken both at the 20-m level of a 40-m tower and from aircraft profiles (six campaigns), and were analyzed for both CO2 concentration and their isotopic compositions ($\delta^{13}C$ and $\delta^{18}O$). The results from these intensive campaigns are compared with Marine Boundary Layer (MBL) data at the same latitude, derived from the observations obtained by the CMDL/NOAA cooperative air sampling network, in order to understand the impact of regional sources and sinks on global carbon cycle. The amplitude of variation in each ground campaign and the difference between the campaigns and MBL show typical seasonal patterns for both CO_2 concentration and isotopic compositions, with smaller values in the winter, and larger values in the summer and Fall, reflecting the strength and balance of regional sources/sinks driven by ecosystem processes. The most interesting discovery is that the minimum value of $\delta^{18}O$ from Fraserdale campaign data occurs in the September - October period, which does not match the minimum value of $\delta^{18}O$ in local precipitation (the latter occurs in December - January) but matches the pattern of MBL $\delta^{18}O$ in mid-high latitudes of the Northern Hemisphere. This indicates Sept. and Oct. are a very active time of year for CO_2 isotope exchange with soil water and that $\delta^{18}O$ of the respiration flux from the local ecosystem has a significant imprint on $\delta^{18}O$ in global background air (MBL). Similar comparisons are also applied to aircraft flask samples. Less variation (including daily and seasonal changes) and less difference between campaigns and MBL are found in aircraft data; and MBL and the aircraft data closely agree with each other. Comparison of ground and aircraft campaign data with MBL compositions reveals very valuable information for understanding the processes of propagation of terrestrial biosphere signals into global background values of the atmospheric compositions (CO_2, $\delta^{13}C$ and $\delta^{18}O$), and the impact of regional sources and sinks on global carbon cycle.

A52A-0762 1330h POSTER

Sensitivity of terrestrial ecosystem models of carbon isotope ratios to changes in vegetation properties and meteorology

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We look at the sensitivity of simulated carbon isotope ratios and CO2 fluxes from several terrestrial ecosystem models to variations in vegetation properties and meteorology. In particular, we compare results from the Community Land Model (CLM2.1); and two versions of the Simple Model of the Biosphere (SiB2.5 and SiB3), to changes in vegetative land cover data sets: Fourier-Adjustment, Solar zenith angle corrected, Interpolated Reconstructed Normalized Difference Vegetation Index (FASIR-NDVI); Global Inventory Monitoring and Modeling Studies NDVI (GIMMS-NDVI); and the CLM Plant Functional Type (PFT) classification scheme, and meteorology: European Center for Medium Range Forecast (ECMWF); National Center for Environmental Prediction (NCEP); and Community Climate Model (NCAR-CCM3). We compare spatial distributions of d13C of terrestrial plant carbon, the zonal gradient of d13C values, and time-series of mean annual d13C values. We also examine the response of the models to changes in meteorology (relative humidity and precipitation) and recycling of canopy CO2. Finally, we compare simulated seasonal cycles of d13C of atmospheric CO2 and the north-south d13C gradient to observed values at several NOAA Flask Stations using response functions (transport fields) developed in Transcom. Results highlight the importance of specified precipitation and precipitation anomalies to carbon isotope discrimination resulting from physiological stress.

A52A-0763 1330h POSTER

Disturbance-Induced Changes in the Oxygen Isotopic Composition of Atmospheric CO_2 at High Northern Latitudes

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At high northern latitudes, interannual variation in the seasonal cycle of atmospheric $C^{18}OO$ exceeds that observed for $^{13}CO_2$ or CO_2. Shifts in species composition or climate may contribute to this variability in $C^{18}OO$ by influencing the timing of photosynthesis and respiration and the cycling of meteoric water. We hypothesized that increased forest fire frequency contributes to variability in $C^{18}OO$ by changing surface energy partitioning, fluxes of water and CO_2, and vegetation structure and function. We measured the $\delta^{18}O$ of ecosystem water pools (leaf, stem, soil, water vapor, and precipitation) in an 80 year old Picea mariana stand and a 15 year old Populus tremuloides stand in the Alaskan interior. The two forests displayed similar $\delta^{18}O$ values for precipitation, soil, and stem water, however mid-day leaf water in P. mariana was consistently more enriched in ^{18}O than that of P. tremuloides on the order of 2 $^{o}/_{oo}$. We predicted differences in diurnal and seasonal $C^{18}OO$ fluxes between sites by incorporating net CO_2 eddy flux and micrometeorological measurements with oxygen isotopic signatures of ecosystem water pools, local background atmospheric CO_2, and nighttime ecosystem respiration. We then used a simple age-distribution model of boreal forests to predict changes in the shape of the seasonal cycle of $C^{18}OO$ that would accompany shifts in the disturbance regime.

A52A-0764 1330h POSTER

Absolute calibration of the intramolecular nitrogen isotope distribution in N_2O

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A mass spectrometric method to determine the absolute intramolecular (position-dependent) nitrogen isotope ratios of nitrous oxide (N_2O) has been developed. It is based on the addition of different amounts of doubly-labeled $^{15}N_2O$ to an N_2O sample of the isotope ratio mass spectrometer reference gas, and subsequent measurement of the relative ion current ratios of species with mass 30, 31, 44, 45 and 46. All relevant quantities are measured by isotope ratio mass spectrometers, which means that the latters inherent high precision of the order of 10^{-5} can be fully exploited. External determination of dilution factors with generally lower precision is avoided. The method itself can be implemented within a day, but a calibration of the oxygen and average nitrogen isotope ratios relative to a primary isotopic reference material of known absolute isotopic composition has to be performed separately. Considering all known statistical uncertainties of measured quantities and absolute isotope ratios of primary isotopic reference materials, we achieve an overall uncertainty of $0.9^o/_{oo}$ (1σ). Using tropospheric N_2O as common reference point for intercomparison purposes, we find a substantially higher relative enrichment of ^{15}N at the central nitrogen atom over ^{15}N at the terminal nitrogen atom than measured previously for tropospheric N_2O, based on a chemical conversion method: $(46.3\pm1.4)^o/_{oo}$ as opposed to $(18.7\pm2.2)^o/_{oo}$. However, our method depends critically on the absolute isotope ratios of the primary isotopic reference materials air-N_2 and VSMOW. If they are systematically wrong, our estimates will also necessarily be incorrect.

URL: http://www.princeton.edu/∼kaiser

A52A-0765 1330h POSTER

Changes in the Stable Carbon Isotope Composition of Methane at the end of the Younger Dryas

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The abrupt warming at the end of the Younger Dryas is associated with a significant rise in the atmospheric concentration of methane. A high-resolution record of $\delta\ ^{13}C$ of atmospheric methane covering this time interval was measured using samples from the ice margin at Pakitsoq, Western Greenland. Our CF-IRMS measurements show a prominent shift of almost $2\ ^o/_{oo}$ to heavier (^{13}C-enriched) values accompanying the concentration increase. The methane carbon isotope ratios then abruptly return to the initial values present prior to the concentration increase. This pattern suggests that the rising methane concentration was caused by a short perturbation to the system, rather than a gradual reorganization between two states. The most likely explanation for the observed carbon isotope shift is a temporary, enhanced input of methane from an isotopically heavier source. The source remains unclear, but possible candidates include increased emissions from wildfires, thermogenic reservoirs, wetlands or permafrost soils, etc. Secondary processes such as microbial methane oxidation may also contribute to the ^{13}C-enriched methane. Our initial results point away from marine, microbial methane sources.

URL: http://biogeochemistry.uvic.ca/

A52A-0766 1330h POSTER

Using Methane ^{14}C to Determine the Origins of the Rapid Methane Rise at the End of the Younger Dryas 11,600 Years Ago: Increased Wetland Production Only or a Contribution From Methane Hydrates? A Progress Report

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The global atmospheric methane concentration rose from about 500 parts per billion (ppb) to about 750 ppb over a period of just 150 years at the termination of the Younger Dryas cold interval 11,600 years ago, as indicated by Greenland ice core records. The start of this rapid methane increase was synchronous with an even more rapid climate warming – ice core nitrogen and argon isotope records indicate that temperatures in central Greenland rose about 10°C over just a few decades. Current hypotheses attribute this methane rise to increased bacterial methane production in wetlands, and/or to the dissociation of large quantities of methane hydrates. Here we describe the progress of a project whose aim is to quantify the role of methane hydrates in this observed methane rise by measuring the ^{14}C of methane derived from air bubbles in glacial ice. Methane hydrates are too old to contain measurable ^{14}C, whereas wetland-derived methane has a $\Delta^{14}C$ nearly identical to that of atmospheric CO_2 at the time of production. One ^{14}C measurement requires about 2 cubic meters of ice. We have located a site on the western margin of the Greenland ice sheet where sufficient amounts of uncontaminated ancient ice are available at the surface. We measured $\delta^{18}O$ of ice and $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2 and methane concentration in the trapped air along horizontal sample profiles collected in 2001 and 2002. Data from these profiles show a remarkable similarity to the GISP2 isotopic records, and uniquely identify the end-of-Younger-Dryas transition in the ice at our sampling site. Our measurements of methane concentration in samples collected in 2003 have allowed us to successfully re-establish the location of the end-of-Younger-Dryas transition, and measurements of $\delta^{18}O$ of ice, $\delta^{15}N$ of N_2 and $\delta^{18}O$ of O_2 on these samples are in progress. During the summer of 2003, we collected two 200-L air samples from approximately 5 tons of ice for methane ^{14}C analysis. Field methane measurements indicate that the age of one sample is confined to about 0-200 years immediately prior to the end-of-Younger-Dryas methane transition. The age of the second sample is confined to about 0-200 years immediately following the transition. Laboratory methane concentration measurements on these air samples (526 ppb for the pre-transition sample, and 735 ppb for the post-transition sample) are consistent with GISP2 methane values for these ages. CFC-12 measurements on these samples, as well as methane concentration measurements on our blanks show that our samples do not contain a significant amount of contamination and are suitable for methane ^{14}C analysis, which is currently in progress.

A52A-0767 1330h POSTER

An Update of the NOAA-University of Colorado Global Atmospheric Methane Isotope Record

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Starting in 1998, measurements of $\delta^{13}C$ of CH_4 began on samples collected weekly at six sites of the NOAA/CMDL Cooperative Air Sampling Network. Since then, six other sites have been added, expanding the global coverage of our measurements. Our measurements reveal no significant inter-annual trend since 1999, similar to the methane growth rate over the same time frame. However, annual mean $\delta^{13}C$ values in 1998 are more negative than the rest of the record, consistent with the hypothesis that the 1998 methane growth rate anomaly was caused, at least in part, by increased emissions from wetlands. The atmospheric inter-hemispheric gradient has also remained relatively constant through our record, which may be an indication of a steady distribution of sources. At higher time frequencies, seasonal cycle amplitudes of at least 0.5 per mil are observed at our high northern sites (Barrow and Alert), while we see small or no amplitude at our southern sites. The strong seasonal cycles in $\delta^{13}C$ observed at Barrow and Alert are out of phase with the seasonal cycle of methane, indicating a complex mixture of source and sink processes responsible for the observed variations in methane concentration at these sites. Finally, we will use our CH_4 and $\delta^{13}C$ measurements to derive multi-year average estimates (and uncertainty) for different methane sources using both a simple two-box model and a three-dimensional transport model.

A52A-0768 1330h POSTER

Measurements and Interpretation of Surface Mixing Ratios of CH_4 and CO and $\delta^{13}C$ and δD of CH_4 in Air from Pacific Ocean Transects Between Auckland, New Zealand and Los Angeles, California

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We report on measurements of atmospheric CH_4 and CO mixing ratios and $\delta^{13}C$ of CH_4 from air samples collected every 2.5 to 5° latitude along a transect over the Pacific Ocean using container ships of P&O Nedlloyd (formerly Blue Star) shipping line. Data presented here begins in June 1996 and extends to January 2002. Scientists from the National Institute of Water and Atmospheric Research in New Zealand and from University of California, Irvine alternate sampling trips so that a transect between Auckland, New Zealand (35°S) and Los Angeles, California (35°N) can be sampled over a period of ∼15 days approximately every four months. Data sets from the two laboratories are intercalibrated through a sample exchange program. The data provide detail on the spatial and seasonal variation of CH_4 and CO mixing ratios and stable isotope ratios of CH_4 over the Pacific equatorial region, including the Intertropical Convergence Zone (ITCZ) and both northern and southern temperate zones to about 30° latitude, including the South

Pacific Convergence Zone (SPCZ). Data from 18 transect samplings so far clearly show that $\delta^{13}C$ in the mid latitudes of both hemispheres are ∼6 months out of phase. In June, a minimum in $\delta^{13}C$ CH_4 in the southern hemisphere (SH) coincides approximately with the maximum in the northern hemisphere (NH) seasonal cycle. Because the NH is less enriched in ^{13}C than the SH this situation results in a remarkably flat gradient between 30°N and 30°S. In November the opposite situation occurs with the SH mid latitude maximum coinciding with the minimum in the NH cycle, leading to a relatively large gradient of $\sim 0.5^{o}/_{oo}$ between the hemispheres. We discuss how CH_4 and CO mixing ratios are related to the changing positions and strengths of the ITCZ and SPCZ and how this data can be used in multi-dimensional models of atmospheric chemistry and transport to better define CH_4 sources and sinks both temporally and spatially.

A52A-0769 1330h POSTER

The Temporal and Spatial Variations of the D/H Ratio of H_2 in the Free Troposphere: CARIBIC Results

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A new technique for the analysis of the D/H ratio in atmospheric H_2 using continuous-flow gas-chromatography isotope-ratio mass-spectrometry (GC/IRMS) that requires small amounts (∼ 300 mL, STP) of sample air and produces excellent results has been developed and applied to air samples from the CARIBIC passenger aircraft project. CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrumented Container) used a Boeing 767 on intercontinental flights to measure trace gases and aerosols between November 1997 and April 2002. From April 2004 onwards, a new Lufthansa Airbus A340-600 with a new inlet system and measurement container with 16 experiments will become operational for a projected period of 10 years. The isotopic ratios and atmospheric concentrations of H_2 were measured for 3 flights over Europe and Africa carried out in 2000. The flight tracks cover from 50°N to 30°S allowing us to investigate hemispheric variation along the route. As the air samples for 3 flights had been collected at different seasons of boreal spring (May), summer (July), and early winter (December), the seasonal variation of the isotopic ratios can be investigated. Although, during 3 seasons, biomass burning was always active in the tropics, the D/H isotopic ratios hardly give us clear evidence, except for the boreal summer when biomass burning peaks. A seasonal variation is clearly visible, but the trends are opposite in the two hemispheres: in the northern hemisphere deuterium is enriched in winter (December) and in the southern hemisphere in fall (May), suggesting the major process governing the seasonal variation might be different in the two hemisphere. In addition, the D/H ratios of H_2 in the southern hemisphere are higher than that in the northern hemisphere, in 3 seasons.

URL: http://www.caribic-atmospheric.com

A52A-0770 1330h POSTER

Modeling the Extreme Deuterium Enrichment in Stratospheric Hydrogen

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Observations of the isotopic composition of molecular hydrogen in whole air samples collected by the NASA ER-2 aircraft showed extreme enrichment in deuterium of up to 440 per mil on the V-SMOW isotope scale [Rahn et al., Nature, 2003]. In this study, we use the Lawrence Livermore National Laboratory 2D model to investigate the extreme deuterium enrichment in stratospheric H_2 and find that kinetic isotope effects (KIEs) in the oxidation of H_2 in the stratosphere account for over 60% of the enrichment while production of heavy H_2 from CH_4 oxidation accounts for the remainder. The sensitivity of the H_2 isotopic composition to uncertainties in the CH_4 oxidation pathway branching ratios, formaldehyde oxidation KIEs, formaldehyde photolysis isotope effects , and the H_2 oxidation KIEs is explored, and recommendations for needed laboratory and field measurements based on these model sensitivities are given. Finally, we investigate the global H_2 isotope budget using model estimates of δD-H_2 produced from CH_4 oxidation in both the stratosphere and troposphere.

A52A-0771 1330h POSTER

Isotopic Composition of Molecular Hydrogen Formed From the Photolysis of Formaldehyde in Sunlight

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The main source of atmospheric H2 is through the photochemical oxidation of methane, with the immediate precursor being formaldehyde. The isotopic composition of atmospheric H2 can be used to place contraints on the sources and sinks of H2 as each process has a specific fractionation. We present measurements of D/H from H2 generated from the photolysis of formaldehyde, showing that this process produces isotopically light H2(dD(H2)∼= -200 $^{o}/_{oo}$). This result is consistant with estimates by Rahn, et.al, 2003 of the fractionation required by this process to account for the observed D/H in stratospheric H2. Implications of this finding for the tropospheric H2 Budget will be discussed.

A52A-0772 1330h POSTER

Stable hydrogen isotope ratios in atmospheric formaldehyde: methods and preliminary measurements

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Formaldehyde (HCHO) is an integral component in the chemistry of urban, rural, and remote atmospheres. Photolysis and its reactions with the hydroxyl and nitrate radicals leads to the generation of hydroperoxyl radical and subsequently the hydroxyl radical and ozone. It is produced both as an intermediate in hydrocarbon oxidation and emitted by primary sources including biomass burning, fossil fuel combustion, and manufacturing processes. Products of its oxidation include carbon monoxide (CO), carbon dioxide, and molecular hydrogen (H_2). Studying the stable isotopic composition of gaseous HCHO can help clarify the origins of HCHO and provide budgetary constraints for photoxidation products H_2 and CO. Isotopic studies to date have been few and limited to the $^{13}C/^{12}C$ ratio in HCHO. Measurements of the D/H ratio in HCHO, in particular, will help constrain the photochemical source to the H_2 budget, which is currently thought to be roughly 30-50% of the total H_2 source. The development of an analytical method for the measurement of the D/H ratio in atmospheric HCHO is presented along with details of isotope calibration and sample collection. The technique utilizes a multistep preconcentration technique and online continuous flow gas chromatography isotope ratio mass spectrometry which provides the resolution and sensitivity necessary for analysis. Preliminary measurements are presented.

A52A-0773 1330h POSTER

Laboratory Studies of Stable Carbon Isotope Fractionation during The Formation of Secondary Particulate Organic Matter from Toluene-OH radical Initiated Reactions

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Stable carbon isotope measurements have become useful in the atmospheric chemistry for organic compounds in the gas phase as well as in airborne particulate matter. Although a reasonable understanding is developing for the gas phase isotope fractionation process, little is known about the isotope fractionation associated with the formation of secondary particulate organic matter (POM). The isotope fractionation study has potential: to understand more detail of the reaction mechanisms to form the secondary POM; and to estimate the contribution of secondary POM to the airborne particulate matter. These are important to trace the stable carbon isotope budget in the atmosphere. Here, we present the results of laboratory measurements of stable isotope ratio for toluene, a precursor gas, and secondary POM formed by its OH radical initiated gas phase oxidation. The reaction of toluene at ppm levels with OH radicals was studied in a flow reactor with a residence time of 3.3 minutes. The OH radicals were produced by the photochemical reaction of isopropyl nitrite in the presence of oxygen and nitric oxide. The concentration was in the range of 10^8 radicals cm^{-3}. Approximately 15 percent of the toluene reacted with the OH radicals. The secondary POM formed in the reactor was collected on quartz fibre filters and analyzed for the stable carbon isotope ratios. For these experiments, the toluene and the collected POM showed -26.7 and -31.8 permil in VPDB scale, respectively. Compared to 6.1 permil that is the kinetic isotope effect of toluene reacting with OH radicals, the isotope fractionation of 5.1 permil is in good agreement. Although these results may only be valid for very specific reaction condition, they nevertheless strongly suggest that the stable carbon isotope ratios of secondary POM in the atmosphere will be significantly influenced by the kinetic isotope effects of the oxidation reactions of the precursor compounds.

A52A-0774 1330h POSTER

The Stable Carbon Isotope Ratio Analysis of Atmospheric Non-Methane Hydrocarbons in Los Angeles, California

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Los Angeles type photochemical air pollution is caused by non-methane hydrocarbons (NMHCs) reacting with hydroxyl radicals and nitrous oxides in the presence of light. To create more effective control strategies in reducing such air pollution, it is essential to have both a better understanding of the complex photochemical processes of NMHCs and the sources of these compounds. From the past successful studies of other atmospheric trace gases such as methane and carbon monoxide, we expect that the stable carbon ratio ($^{13}C/^{12}C$, reported as a $\delta^{13}C$ value) of each of these hydrocarbons will also reflect the $\delta^{13}C$ value of the source material and/or provide formation on chemical loss processes that fractionate C isotopes. We have developed a NMHC preconcentrator system which enables us to measure $\delta^{13}C$ values using a continuous-flow gas chromatography combustion isotope ratio mass spectrometer (cf-GC/C/IRMS). Our system is similar to the successful design pioneered in Rudolph *et al.* (1997),

but is custom designed by our laboratory. Stable carbon isotope measurements of any of the C_2-C_5 NMHCs in field and/or lab studies are scarce to date. Our system allows us to report on $\delta^{13}C$ measurements of ethane, ethene, ethyne, propane, propene, n-butane, i-butane, 1-butene, n-pentane, i-pentane, and methyl chloride. To see if we can learn the specific sources contributing to the emissions of a given NMHC within a region by comparing isotopic signatures of its potential sources to $\delta^{13}C$ measurements of it within the local air mass, urban air samples were collected in 3 different cities of Los Angeles County, California, USA, during the summer of 2003 and analyzed for the concentrations and $\delta^{13}C$ values of NMHCs. To our knowledge, this is the first $\delta^{13}C$ analysis of ambient NMHCs conducted in the United States. We report the results of the $\delta^{13}C$ analyses and concentration measurements for selected NMHC species from the urban air samples, and their implications for the local atmospheric chemistry of Los Angeles Basin.

A52A-0775 1330h POSTER

Laboratory Studies of Stable Hydrogen Kinetic Isotope Effects for Reactions of Non-methane Hydrocarbons (NMHCs) With OH, Ozone, and Cl in the Gas Phase and Their Relevance for Studies of NMHCs in the Atmosphere

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During the last few years it has been shown that measurements of stable carbon isotope ratios of non-methane hydrocarbons (NMHCs) in the troposphere are useful for better understanding their sources, sinks, and distributions, and to quantify the extent of atmospheric processing of the studied NMHC. The ability to interpret atmospheric stable isotope ratio measurements of NMHCs depends on the knowledge of the stable isotope ratios of the emissions and the understanding of the isotope fractionation associated with the atmospheric NMHC removal processes. It seems reasonable that stable hydrogen isotope ratio measurements can serve a similar purpose; however, there is presently little information on isotope fractionations for reactions of NMHCs with close to natural stable hydrogen isotope abundance. Here we present the results of laboratory measurements of stable hydrogen kinetic isotope effects for some of the most important atmospheric removal reactions of NMHCs, namely the reaction with the OH radical, O_3, and the Cl atom. Based on these results, we predict that for many NMHCs, especially the alkanes, atmospheric reactions will cause substantial and significant changes in stable hydrogen isotope ratios. It is also demonstrated that combining measurements of stable hydrogen and stable carbon isotope ratios of atmospheric NMHCs has a very high potential to reduce uncertainties in estimates of the extent of photochemical NMHC processing and to reduce uncertainties resulting from variability of stable isotope ratios of emissions.

A52A-0776 1330h POSTER

Carbon Kinetic Isotope Effects in the Reactions of Atmospheric NMHC with OH, Cl and O_3

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It has recently been shown that stable carbon isotope measurements are extremely useful for better understanding of processes involving NMHC in the atmosphere. Knowledge of the isotopic fractionation associated with the chemical removal of NMHC is vital for the interpretation of these measurements. Oxidation by OH-radicals is by far the most important atmospheric removal process of NMHC. Contributions to isotopic fractionation due to removal by reactions with Cl and O_3 should also be understood to better interpret stable carbon isotope measurements. From our measurements, in normal urban and background air, reactions with O_3 account for 15-25% of the isotopic fractionation in light C2-C4 alkenes. In polar sunrise conditions, reactions with Cl atoms may have a significant impact on the isotopic fractionation in light alkanes. An overview of the measured KIEs for the reactions of C2-C9 NMHC with atmospheric oxidants OH, Cl and O_3 will be presented. Possibilities for using specific structural and thermal dependencies of measured KIEs for estimations of unmeasured KIEs of atmospheric interest will be discussed.

A52A-0777 1330h POSTER

Using Stable Carbon Isotope Ratios to Determine Mean Photochemical Ages of Ethane and Benzene in the Arctic Troposphere

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Between July 1999 and March 2001 fortnightly samples of ambient background air were collected at Alert (Canada 82.5°N, 62.3°W) and analysed for the concentrations and stable carbon isotope ratios of ethane and benzene. The results of these measurements are compared with the predictions of a 3D isotopic inclusive chemical tracer model using the EDGAR V.2 emission database. The model reproduces the shape of the seasonal variations of the concentrations of ethane and benzene, but the concentration levels calculated by the model are on average a factor of two too low, indicating a significant underestimation of the emission rates in the EDGAR V.2 database. Model predicted and observed seasonal variation of the stable carbon isotope ratio of ethane agree very well. However the observed benzene isotopic compositions in summer imply lower mean photochemical ages than predicted by the model. This finding can be explained by the existence of benzene sources at high northern latitudes which are not included in the emission database.

A52A-0778 1330h POSTER

Retrieval of Isotopomer-Specific Ozone Vertical Profiles from Solar Infrared Spectra Recorded at Lauder, New Zealand.

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The isotopic composition of atmospheric ozone column over Lauder has been studied by high resolution ground-based solar Fourier Transform Infrared Spectrometry, with retrievals being performed by the Optimal Estimation Method. Firstly, vertical profiles for the main isotopomer ($^{16}O^{16}O^{16}O$) were retrieved in the 1001.3-1004.3 cm^{-1} interval. Five vertically independent partial columns were obtained and validated against independent microwave radiometer measurements, balloon sonde data and Dobson spectrophotometer data. Profiles of the minor isotopomers ($^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{16}O^{17}O$, $^{16}O^{17}O^{16}O$) were then retrieved in separate spectral intervals with three vertically independent partial columns being achieved. For these retrievals, the profile of $^{16}O^{16}O^{16}O$ was constrained to the previously retrieved profile, which was also used as the a-priori profile for the target species. Results are compared to previous ground-based, balloon-based and satellite measurements of isotopic enrichments in atmospheric ozone and found to have smaller uncertainties. The results should therefore provide useful data for validating proposed mechanisms for the anomalous mass-independent isotopic enrichments in atmospheric ozone.

A52A-0779 1330h POSTER

Real-time in situ measurements of the H/D ratio in water vapour in a limestone cave

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The isotopic ratios recorded in speleothems in caves have been used as a measure of paleoclimate. The water on the surface of a growing speleothem contains dissolved C in the form of bicarbonate and O in water. The O incorporated into the speleothem is from surface water that is isotopically determined by the degree of surface evaporation, and has been seen to correlate to monsoonal activity. Cave temperature is likely to be relatively constant and unimportant for the isotopic signature. However, movement of air through the cave, driven by temperature differences between the cave and the external atmosphere could significantly change the isotopic signature and hence complicate the interpretation of any observed signal. We will report real-time measurements of the H/D ratio in water vapour measured in a cave system. The measurements have been made by continuously flowing air through a multi-pass gas cell and measuring the infrared spectrum with a low resolution Fourier Transform InfraRed spectrometer.

A52A-0780 1330h POSTER

Stable Water Isotopes as Evaluation Tools for Global Climate Model Simulations of the Amazon Basin Circulation

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The isotopic abundances of O-18 and Deuterium over the Amazon are used to constrain simulations of the water cycle in this, the largest river basin in the world. Based on data in the Global Network on Isotopes in Precipitation (GNIP) database, we analyze the simulation of the land surface hydrology and water cycling. Temporal changes between 1965 and 2000 in stable water isotopic signatures in the Amazon have been used to evaluate global climate model (GCM) predictions revealing notable anomalies. For example, the differences in the wet season deuterium excess between Belem and Manaus are consistent with recent GCM simulations only if there has been a relative increase in evaporation from non-fractionating water sources over this period. Despite earlier predictions that land-use change signals would be found, late twentieth century data reveal no significant change in dry season isotopic characteristics. On the other hand, more recent isotopic data do show trends at stations in the Andes, where as much as 88% of the rainfall is thought to be derived from recycled moisture. These data might be linked to land-use change impacts. Simultaneous tracking of the two primary isotopes in water (HDO and $H_2{}^{18}O$) makes it possible to trace the history of evaporative and condensation processes. Results of GCM simulations of Amazonian deforestation suggest that the recent stable isotope record is more consistent with the predicted effects of greenhouse warming, possibly combined with forest removal, than with the predicted effects of deforestation alone. At a minimum, large-scale simulations of South American climate ought to be tested against these isotopic data in any validation effort.