A42C-0782 1330h POSTER

Comparison of Limb Scattering Measurements Made by the Shuttle Ozone Limb Sounding Experiment (SOLSE), Limb Ozone Retrieval Experiment (LORE), and Stratospheric Aerosol and Gas Experiment (SAGE) III Instruments

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The reflight of the SOLSE (Shuttle Ozone Limb Sounding Experiment) and LORE (Limb Ozone Retrieval Experiment) instruments commenced with the launch of STS-107 on January 16, 2003. This 17-day mission yielded measurements of the radiance scattered by the limb of the atmosphere in the ultraviolet, visible, and near infrared portions of the spectrum. A subset of the measured radiance data was downlinked prior to the tragic destruction of STS-107 on February 1, 2003. A comparison of the limb scattered radiances measured by the SOLSE, LORE, and SAGE III instruments will be presented. Early results from the limb scattering ozone retrieval algorithm will also be analyzed. The ozone profiles derived from coincident measurements will be compared with each other, as well as with other correlative measurements.

A42C-0783 1330h POSTER

Analysis of SAGE III Spectral Survey Solar Occultation Events

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The Stratospheric Aerosol and Gas Experiment III (SAGE III) detector includes an 800-element CCD linear array that provides continuous spectral coverage between 290 and 1030 nm. During routine solar occultation measurements, SAGE III uses only 87 discrete spectral bands to retrieve gaseous species and aerosol parameters. SAGE III also has the capability to operate in a full spectral survey mode, sampling the entire spectral range of the detector, albeit at a decreased sampling rate. The spectral survey mode is primarily used to calibrate the instrument wavelength registration during exoatmospheric scans. On a few occasions, a full spectral survey of the atmosphere has been conducted. This spectral information serves as a useful SAGE III diagnostic tool: Does SAGE III use the optimal set of pixels for its gaseous species retrieval? Is the O_4 absorption signature a suitable method to improve altitude registration in the lower stratosphere and upper troposphere? Can SAGE III detect BrO? Is the etaloning behavior of the CCD at infrared wavelengths stable throughout an occultation event and is this information useful for the solar mode retrievals? Comparisons of coincident measurements taken by the Gas and Aerosol Monitoring Sensor (GAMS) during the SAGE III Ozone Loss Validation Experiment (SOLVE II) field campaign will also be presented. GAMS measures the same wavelength region as SAGE III but at a higher spectral resolution and a faster sampling rate. Two SAGE III spectral survey events were made coincident with GAMS measurements on SOLVE II DC-8 science flights, providing an opportunity for a comparison of spectral features and slant path transmittance through the same air mass.

A42D MCC: 3018 Thursday 1340h

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

Presiding: **J B Miller,** University of Colorado, Boulder**; M J Whiticar,** University of Victoria

A42D-01 1340h

Changes in Gross and Net CO2 Fluxes Over the Last two Decades Deduced from CO2, 13C, and 18O Atmospheric Measurements

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Year-to-year fluctuations in the growth rate of atmospheric CO2 are largely contributed by the effects of climate variability on terrestrial CO2 fluxes. High precision atmospheric 13C time series can be used in so called "double deconvolutions" to separate land from oceans fluxes. But 13C data alone provide almost no information on the interannual variability of the gross fluxes (Photosynthesis, Ecosystem Respiration, Combustion) controlling the carbon balance of terrestrial ecosystems. We used records of 18O in CO2 in addition to 13C and CO2 from the CMDL and CSIRO global air sampling networks, which span over the past two decades into a bayesian 'triple deconvolution". This method allows to infer year-to-year variations in photosynthesis and respiration at the hemispheric level, given additional a priori knowledge of the variability in isotopic fractionations and disequilibrium terms. The magnitude of the changes in gross CO2 fluxes that are required to explain the variability of the 18O signal will be compared to the magnitude of changes in the net fluxes.

A42D-02 1355h

Ten Years of Robust Sources and Sinks of Atmospheric CO2 inferred from 13CO2 and pCO2 Measurements in the NOAA/CMDL Network

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Prediction of future climate is dependent upon the trajectory of the rising concentration of carbon dioxide, which is, in turn, dependent upon the operation of both the terrestrial and oceanic components of the carbon cycle. Because the uptake of carbon in the oceans and land operates via different mechanisms, it is useful to calculate separately the uptake (or release) by each. Atmospheric measurements of CO2 concentrations and the relative carbon-13 content offer the possibility to resolve oceanic and terrestrial carbon fluxes at relatively high spatial and temporal resolution. Even though the global totals of oceanic and terrestrial uptake derived using d13C are somewhat uncertain, we will show that both the spatial and temporal patterns are robust. Since 1990, nearly 90,000 d13CO2 measurements have been made on air collected from more than 60 globally distributed sites in the NOAA/CMDL air sampling network. When combined with measurements of CO2 made on the same air, these data allow us to calculate the oceanic and terrestrial contributions to the total surface uptake of CO2 as a function of space and time. The most prominent result of our analysis is the large and sustained uptake of carbon in the temperate Northern Hemisphere (TNH), punctuated by periods of enhanced uptake centered around 1992 and 1997. The mean size of the uptake in the TNH is 3+/- 1 GTonC/yr, roughly half the size of the total fossil fuel flux to the atmosphere. The earlier period of enhanced uptake may be associated with the eruption of Mt. Pinatubo in 1991. The reasons for the enhanced terrestrial uptake in 1997 are less clear. The next result that stands out is the large release of carbon from the tropical biosphere that occurred during the 1997-1998 El Nino. The 1998 terrestrial flux in the tropics is about 2 to 3 GTon C more than the 1991-1997 mean. Coinciding with the SST transition typical of El Nino, we also estimate that tropical oceanic fluxes rose 2 by GtonC, sustained for two years. Perhaps the most interesting results derived from the atmospheric d13C data are the periods of enhanced terrestrial carbon uptake in the tropics in 1996 and the TNH in 1997. Whereas the other features of the record discussed so far have been previously addressed, these large signals have never been addressed and have no clear explanation.

A42D-03 1410h

Isotopic Signatures of net Carbon Fluxes and Pure Isotopic Exchange Fluxes as Determined From Atmospheric Data.

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For many years observed del-13C values of atmospheric CO2 have been used to partition net fluxes of carbon to the atmosphere into an oceanic and a terrestrial contribution. Additional information that is necessary is 1) an estimate of the isotopic "signature" (the difference from the atmosphere) of the fluxes, and 2) an estimate of the magnitude of pure isotopic exchange between all three reservoirs that is always taking place, also in the absence of net carbon fluxes. These estimates have traditionally been derived from other data or models. We are exploring a method to derive this information from the atmospheric CO2 and isotopic data themselves, which would be independent of earlier estimates and could help to uncover interannual variations of both the above quantities.

A42D-04 1425h

Towards A New Air-CO2 Isotopic Scale Based On Air Reference Material Generated From Carbonates

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Carbon and oxygen stable isotope ratios of atmospheric carbon dioxide provide important, independent information about carbon sources and sinks. Combined with CO2 mole fraction measurements, 13CO2 measurements can be used to quantitatively separate fluxes between atmosphere and terrestrial biosphere from fluxes between atmosphere and ocean. Highly precise and accurate isotopic data are needed for deriving accurate flux information using inverse modeling. For example, a change of just 0.02 $^{o}/_{oo}$ in 13C translates into an equivalent of 1.0 x 109 metric tons of carbon in models of surface fluxes. Such high degree of precision is possible, provided different laboratories agree on a common scale. Existing practice of using a carbonate reference material (NBS19) to unify scales has shown inadequate to this process in the past. Instead, CO2 admixture to CO2-free air where the CO2 is generated from a carbonate similar to NBS-19 in composition and texture has been proposed. We describe here an acid reaction and air mixing station (ARAMIX) setup at the Max Planck Institute for Biogeochemistry which is capable to introduce CO at ambient levels into an air mixture (without CO2) at the required precision level. This mixing station is used for generating CO2 by a conventional acid reaction (at 47 C the carbonate powder is reacted with pure ortho-phosphoric acid) and mixing the reaction gas with synthetic air. The mixture is distributed into several glass flasks (5l volume, 1.6 bar) attached to the system. Such flask air

samples were measured using two different extraction / mass spectrometer systems established previously in the Jena isotope facility. Using the same protocol we have generated CO2-in-air mixtures from NBS-19 and other internationally available carbonate standards for assigning isotopic values to our new carbonate reference material (MAR J1). The isotopic record in a number of batches prepared over months will be discussed. In addition, the relationship with existing CO2-in-air scales (e.g. CG-99, based on a pure CO2 gas) have been evaluated by direct CO2 admixture to synthetic air using the same setup.

A42D-05 1440h

Observations of the Isotopic Compositions of CH_4, H_2, N_2O, and CO_2 in the Stratosphere: Implications for Biogeochemical Tracer Studies and Global Isotope Budgets

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Because various sources and sinks of many trace gases in the atmosphere have distinct isotopic signatures, measurements of the isotopic compositions of these gases in the free troposphere provide a constraint beyond concentration measurements alone on their global budgets. For N_2O, for which the primary sink is photolysis and photooxidation in the stratosphere, Kim and Craig [Science, 1993] first suggested that a flux of isotopically heavy N_2O from the stratosphere could balance the known isotopically light surface sources to produce the observed nitrogen and oxygen isotopic compositions in the troposphere. For most other gases, however, the flux of an isotopic signature acquired through stratospheric photochemistry has been ignored in tropospheric studies, in part due to lack of knowledge of isotopic fractionation processes in the stratosphere and in part due to the idea that the mass of the stratosphere is small compared with that of the troposphere so that the influence of the stratosphere on tropospheric isotopic compositions must be negligible. We have recently quantified the fluxes of isotopically heavy isotopologues for CH_4, H_2, N_2O, and CO_2 from isotopic and trace gas measurements on whole air samples collected from the NASA ER-2 aircraft between 1996 and 2000. In each case, the magnitudes of the fluxes are found to be large enough to influence isotopic compositions in the troposphere. An overview of these fluxes and the implications of the stratospheric observations for the global isotope budgets and/or biogeochemical tracer studies in the troposphere will be given.

A42D-06 1455h

The Stable Isotopes of Atmospheric Methane: Long-Term Observations at Alert (Canada) and Neumayer (Antarctica)

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Ten years records of CH_4 concentration, $^{13}C/^{12}C$-CH_4 and ^2H/H-CH_4 from the background stations Alert, Arctic, (82.45°N) and Neumayer, Antarctica, (70.65°S) are presented. High volume integrated (Alert) and spot (Neumayer) samples are collected at the respective sites and are analysed in Heidelberg using GC-FID technique for mixing ratios, IRMS for $^{13}C/^{12}C$ and ^2H/H ratios, and, in the last two years, a TDLAS system for analysis of the ^2H/H ratio. At Neumayer we observe a seasonal CH_4 cycle with a peak-to-peak amplitude of about 28 ppb; minimum mixing ratios are ocurring in February/March, and maxima in August/September. The seasonalities of $^{13}C/^{12}C$ and ^2H/H are anticorrelated to the mixing ratio and average 0.12 $^o/_{oo}$ ($^{13}C/^{12}C$) and 2.4 $^o/_{oo}$ (^2H/H) peak-to-peak. Seasonal cycles at Neumayer can be explained by the seasonality of methane destruction in combination with a seasonally varying meridional circulation pattern in the atmosphere. The atmospheric OH sink (which contributes about 90% to the total sink of atmospheric methane) is stronger during summer. The long-term trends at Neumayer are 5.8 ppb/yr (mixing ratio), 0.04 $^o/_{oo}$/yr ($^{13}C/^{12}C$) and 0.8 $^o/_{oo}$/yr (^2H/H). At Alert we observe a seasonal amplitude of CH_4 about twice as large as at Neumayer, while the $^{13}C/^{12}C$ and ^2H/H seasonality is larger by a factor of three, with minimum mixing ratios in July, and maxima in January/February (isotopes almost anticorrelated, whereas minimum isotope ratios occur 2-3 month earlier than the maximum mixing ratios). Compared to Antarctica which is far away from any source region additional influences from methane sources lead to the larger seasonalities at Alert: The nearby wetland sources are emitting CH_4 during the summer season but they do not seem to affect much the mixing ratio. This is different for the isotope ratios. High methane concentrations during the winter months are caused by transport of stratified polluted air masses from mid latitudes to the Arctic station during this season. The long-term trends at Alert are 3.6 ppb/yr (mixing ratio), 0.03 $^o/_{oo}$/yr ($^{13}C/^{12}C$) and 1.4 $^o/_{oo}$/yr (^2H/H). At Alert and at Neumayer the mixing ratios are almost constant (except for seasonality) since about three years. From the difference between both stations a fractionation of -7.2 $^o/_{oo}$ ($^{13}C/^{12}C$) and -234 $^o/_{oo}$ (^2H/H) for the mean tropospheric methane sink can be derived. The same results are obtained from the analysis of the southern hemispheric seasonal cycle. With the two approaches one can estimate the isotopic signature of the mean source to -53.9 $^o/_{oo}$ ($^{13}C/^{12}C$) and -275 $^o/_{oo}$ (^2H/H). The continuing long term trend in both stable isotopes shows that in contrast to the mixing ratio the isotopes are still not in steady state with its sources and sinks.

A42D-07 1510h

Carbon-13 Evidence of the Causes of the Atmospheric Methane Concentration Increase Since 1700AD and of a Varying Methane Budget Beforehand

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The causes of the major increase in the concentration of atmospheric methane since 1700 AD are investigated. We measured d13CH4 in air extracted from Antarctic ice cores and firn and in air archived from Cape Grim, Tasmania. This was done using a newly developed GC-IRMS technique that analyses very small air samples with high precision. The results show that d13CH4 increased over the past century, consistent with the addition of isotopically enriched sources from anthropogenic activity. However a large increase (about 1.5 per mil) in d13CH4 from 1700AD back to about 1500AD was also observed. This was quite unexpected as it was previously assumed, based on the small observed changes in methane concentration, that the pre-anthropogenic methane budget was approximately in balance. Explanations for the cause of this d13CH4 increase invoke changes in enriched sources such as biomass burning with compensating changes in biogenic (mainly wetland) sources, or changes in a strongly fractionating sink.

A42D-08 1525h

Changes of Methane and Nitrous Oxide in the Atmosphere : new Constraints From Stable Isotope Analyses in Polar Firn and ice.

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Methane and nitrous oxide are two greenhouse gases playing a major role in atmospheric chemistry ; methane largely affects the oxidative capacity of the atmosphere whereas nitrous oxide participates in many atmospheric chemical reactions involving O_3 and NO_x in the stratosphere. A sharp increase in the mixing ratios of both gases has been observed since the beginning of the pre-industrial era, implying an increase of anthropogenic sources. Although these gases are important in global climate changes, their budget remains poorly known. The evolution of their isotopic composition in the atmosphere brings additional constraints as it represents the final signature of their budgets and reflects changes in the relative contribution of sources and sinks. We have measured preindustrial air from polar firn air and ice cores that will lead to the long term evolution of these gases. A continuous flow technique is used at the Laboratory of Glaciology and Geophysics of Environment (LGGE) in Grenoble, France to measure $\delta^{13}CH_4$, whereas a similar technique is used at the Max Planck Institute for Nuclear Physics, in Heidelberg, Germany to measure $\delta^{15}N_2O$ and $\delta N_2{}^{18}O$. Samples from both Antarctica (Vostok, Dome C, Berkner Island) and Greenland (North GRIP) were used. We will present these results and their tentative interpretation based on a diffusion model of gas isotopes in polar firn and on simple atmospheric box approaches.

URL: http://w3.agu.org

A42E MCC: 3016 Thursday 1340h

The Organic Aerosol Component: Impact on Reactivity, Optical Properties, Hygroscopicity, and Cloud-Condensation Properties III

(joint with AE)

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

A42E-01 1340h

Aerosol mass spectrometer measurements of organic aerosol

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Organic species are known to be ubiquitous and comprise a significant component of ambient aerosols. Identifying the sources, chemical compositions, and loadings of particulate organics remains a difficult, yet important problem as organic components may affect the formation, hygroscopicity, growth, reactivity, and radiative effects of ambient particles. Unraveling this complexity inherently must rely on chemical information (such as off-line filter analyses and collector/concentrator techniques), but also on real-time instruments that are capable of combining particle phys-