## A72C-0181 1330h POSTER

## Oceanic Uptake of Methyl Bromide: Implications for Oceanic Production

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Methyl bromide (CH<sub>3</sub>Br) 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 methyl bromide is believed to be the single largest con-tributor of stratospheric Br. Once in the stratosphere, Br is approximately 50 times more effective in depleting stratospheric ozone than Cl. However, the budget for CH<sub>3</sub>Br 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 CH<sub>3</sub>Br. The balance between production and degradation re-sults in the net undersaturation of CH<sub>3</sub>Br 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]. How-ever, effects of climate change, such as changes in wind-speed distribution or sea-surface temperature could al-ter this balance. Modeling the potential effect of such forcing on the net flux of this important trace gas re-quires an understanding of the factors controlling the distributions of production and degradation in the sur-face ocean.

distributions of production and degradation in the sur-face ocean. During three recent research cruises (North At-lantic, North Pacific, and Southern Ocean), CH<sub>3</sub>Br 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

bution 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 bro-mide 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 atmo-spheric 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 sta-ble 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- $67^\circ$ S, 138-145°E).

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 0.040.04 d-1 (n=102). Chemical loss rates in these waters were extremely low, because of the low seawa-ter 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 bronide, the loss mechanism for methyl chloride is presumed to be biological. These results demonstrate that biological degradation of methyl bro-mide and methyl chloride can occur at significant rates even in very cold, polar waters, and explain the ten-dency for high latitude waters to be undersaturated with respect to atmospheric methyl bromide. These are the first open ocean observations of biological methyl chloride uptake. The high rates observed confirm ear-lier 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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United States Current measurements suggest that the amount of ozone-depleting bromine in the lower stratosphere ex-ceeds the amount of organic Br present in longer-lived compounds (halons, CH<sub>3</sub>Br) in the troposphere. This, in turn, implies that very short-lived gases, such as CH<sub>2</sub>Br<sub>2</sub> and CHBr<sub>3</sub>, also contribute to the strato-spheric 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 in inorganic or organic form. Many very short-lived horminated and iodinated gases originate mainly in the ocean. They are produced in large amounts by marine organ-isms as well as by abiotic reactions. Most are highly supersaturated (100s to 1000s of percent) and have ex-tremely high fluxes relative to their amounts in the tro-posphere. We present here measurements of CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>, CH<sub>3</sub>I, and other very short-lived gases in the air and surface ocean. Fom six cruises conducted dur-ing 1994-2001. The cruise tracks cover the Pacific, At-lantic, and Southern Oceans. Data show extreme su-persaturations in the tropics, where deep convection is predominant, and high supersaturations in 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

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#### A72C-0184 1330h POSTER

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

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United States Results from the NOAA-CMDL flask sampling net-work over the past 8 years indicate that the global mean atmospheric mixing ratio of methyl bromide has decreased since 1998. Larger decreases have been ob-served 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 ra-tios were elevated in 1997-1998, perhaps as a result of the large El Nino 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 ex-plained by decreases in fumigation-related emissions given our present understanding of the methyl bro-mide budget and reported production declines. Global industrial production of methyl bromide reported to UNEP was down by 25% in 1999, in line with pro-duction restrictions outlined in the fully revised and amended Montreal Protocol on Substances that Deplete the Ozone Layer. Production was scheduled for a sim-ilar drop again in 2001. Methyl bromide is an impor-tant ozone-depleting substance that is emitted to the atmosphere as a result of both human and natural ac-tivities. Results from the NOAA-CMDL flask sampling nettivities

#### A72C-0185 1330h POSTER

## Stable Carbon Isotopes of Background Atmospheric Methyl Bromide

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CA 94720 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 un-balanced. We utilize an isotopic mass balance to con-strain the CH3Br atmospheric budget by analyzing the source signatures and the isotopic mass balance to con-strain the CH3Br atmospheric budget by analyzing the source signatures and the isotopic fractionations asso-ciated with sinks. Carbon isotope composition of back-ground atmospheric CH3Br is needed to test this ap-proach. 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 isotope ratios from background tropospheric CH3Br. Here we report the first measurements of stable carbon isotope ratios from background tropospheric CH3Br. We developed a preconcentration technique for measur-ing the carbon isotope compositions of halogenated or-ganic gases. We are able to sample 1100 Liters of air with a flow of 6.5L/min. We have solved the problem flow and the problem of saturation of the gas chromato-rranh column by CO2. We show that it is passible to of separating CH3Br from N2 and O2 in high pumping flow and the problem of saturation of the gas chromato-graph 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 at-mospheric organic components have been achieved at a concentration of about 10 pptv. concentration of about 10 pptv

#### A72C-0186 1330h POSTER

## **Quiescent Diffusive and Fumarolic** Volcanic Bromocarbon Emissions

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#### F120 2002 Fall Meeting

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dom Future scenarios of declining atmospheric burdens of Ozone Depleting Substances (ODS) such as halocar-bons after phase-out following international regulation (Montreal Protocol) vary strongly depending on what contribution from natural sources is taken into ac-(Montreal Protocol) vary strongly depending on what contribution from natural sources is taken into ac-count. In addition, current and pre-industrial global atmospheric budgets of ODS are poorly balanced by known natural and anthropogenic sources of halocar-bons (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 mag-matic inorganic (Bureau, 2000) and volcanic organic sources (Rassmussen 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), Wahren-berger (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<sup>-1</sup> (Stoiber, 1995) based on CO2 flux to halocarbon concentration correlations (e.g., CFC-11: of 66  $\text{Tgy}^{-1}$  (Stoiber, 1995) based on CO2 flux to of 66 Tgy<sup>-1</sup> (Stoiber, 1995) based on CO2 flux to halocarbon concentration correlations (e.g. CFC-11:  $R^2$ =0.91, Schwandner et al., 2002). However, CH3Br is not the only volcanogenic bromocarbon. Analysis of diffusive flank and cratter 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 (CH<sub>4</sub>) is the second most important an Methane (UH4) is the second most important an-thropogenic 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 ob-servations from the NOAA CMDL network. The model accounts for interannual variations in meteorology and concentrations of OH radical. Emissions are scaled us-ing yearly country-by-country socioeconomic and mete-orological data. The model simulates well the horizon-tal and vertical distributions, seasonal cycles, trends, and interannual variations of CH<sub>4</sub>, capturing over 80% of the variance between 1988 and 1997 at many sites. It appears that the observed decrease in growth rate of CH<sub>4</sub> over the past decade is a result of stabiliza-tion of global emissions from livestock, rice paddies, gas venting, and coal mining along with a slight decrease in CH<sub>4</sub> lifetime. The anomalous growth rates during 1991-1992 can be explained by changes in OH concen-trations and wetland emissions due to the eruption of Mt. Pinatubo. 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 Observa-The University of Toronto Atmospheric Observa-tory (TAO) has recently been established at Toronto, Canada. TAO includes several instruments, with a DA8 Fourier Transform Spectrometer (DA8 FTS, manufac-tured by ABB Bomem Inc., Québec, Canada) serving as the primary instrument at the facility. The geo-graphic position of TAO (43.66° N, 79.40° W) makes it well suited for long-term measurements of mid-latitude stratographic, gozone and related species while its urstratospheric ozone and related species, while its ur-ban setting enables measurements of tropospheric pollution.

The DA8 FTS is based on a Michelson interferome the DAG FIG IS based on a Michelson interferome-ter with a maximum optical path difference of 250 cm, providing a maximum unapodized resolution of 0.0026cm<sup>-1</sup>. It is currently equipped with KPs and C-Pproviding a maximum unaportized resolution of 0.0020 cm<sup>-1</sup>. It is currently equipped with KBr and CaF<sub>2</sub> beamsplitters, and InSb and HgCdTe detectors, for cov-erage of the spectral range from 700 to 4100 cm<sup>-1</sup>. A new heliostat (manufactured by Aim Controls Inc., Cal-ifornia, USA) provides active solar tracking, collecting the incoming solar radiation and directing it into the FTS.

FIS. The TAO DA8 FTS incorporates a new optical de-sign recently developed by ABB Bomem Inc., which results in a fixed optical axis through the beamsplit-ter (and a fixed focal point on the detector) as well as results in a fixed optical axis through the beamsplit-ter (and a fixed focal point on the detector) as well as a more stable modulation efficiency. The new instru-ment optics will be discussed. Next, the performance of the instrument will be examined in the context of stan-dard 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 retriev-ing columns and vertical profiles of HCl, HF, CH<sub>4</sub>, OCS, C2H<sub>6</sub>, CO, N<sub>2</sub>O and NO<sub>2</sub> since May 2002. A detailed error analysis of retrieved columns and verti-cal 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 MAE-STRO instruments. Finally, we are investigating the feasibility of making broadband infrared measurements of aerosols using the TAO DAS FTS.

#### A72C-0189 1330h POSTER

#### The Hydrogen Isotopic Composition of Water Vapor Entering the Stratosphere Inferred From High Precision CH<sub>4</sub> and H<sub>2</sub> Measurements

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for Atmospheric Research, Boulder, CO 80303 Precise knowledge of the hydrogen isotopic com-position 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 H<sub>2</sub> and CH<sub>4</sub> from whole air samples collected by the NASA ER-2 aircraft, the annual mean value of the hydrogen iso-topic composition of water vapor entering the strato-sphere 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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Issue Table Mesa Drive, Bolinder, CO 80305, United States Molecular hydrogen (H<sub>2</sub>) is the second most abun-dant reduced gas in the atmosphere (after methane) with a globally averaged mixing ratio of ~ 530 ppbv. Its largest source is believed to be photochemical ox-idation of methane (C H<sub>4</sub>) and non-methane hydro-carbons (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 H<sub>2</sub> has the po-tential to help quantify various aspects of its produc-tion and destruction. The average deuterium content of H<sub>2</sub> (expressed as  $\delta D_{H2}$ ) is enriched by ~110 °/ $_{OO}$ relative to Vienna Standard Mean Ocean Water while CH<sub>4</sub> in the troposphere, the precursor for photochemi-cal H<sub>2</sub> production, is depleted by ~ 90 °/ $_{OO}$  celative to V-SMOW and similar values are expected for NMHCS. Soth natural and anthropogenic combustion sources of H<sub>2</sub> have been shown to be depleted in deuterium by 200 to 300 ° $_{OO}$  (Gerst and Quay, 2001; Rahn et al., 2002), and the ocean and N<sub>2</sub> fixation sources are expected to be in near thermodynamic equilibrium with local H<sub>2</sub>O and should have deuterium levels of ~-700 °/ $_{OO}$  (Rahn et al., 2002). In order to offset these deuterium depleted sources

and should have deuterium levels of ~-700  $^{O}/_{OO}$  (Rahn et al., 2002). In order to offset these deuterium depleted sources and account for the observed tropospheric  $\delta D_H 2$ , the balancing loss processes must discriminate against reaction with HD and/or the total fractionation associated of the source action with HD and/or the total fractionation associ-ated with CH<sub>4</sub> oxidation and the subsequent reactions leading to H<sub>2</sub> must favor production of deuterated H<sub>2</sub>. We have analyzed a suite of stratospheric air samples in order to investigate the photochemical processes in-fluencing the deuterium content of H<sub>2</sub>. While the mix-ing ratio of H<sub>2</sub> is nearly constant, the deuterium con-tent increases such that  $\delta D=440^{-O}/_{oo}$  in samples with a stratospheric mean age of ~6 years. The constant mixing ratio results from the fact that production due to CH. oxidation and loss due to H<sub>0</sub> oxidation are an a stratespheric mean age of ~60 years. The constant mixing ratio results from the fact that production due to CH<sub>4</sub> oxidation and loss due to H<sub>2</sub> oxidation are ap-proximately equal. The observed trend in  $\delta D$  of strato-spheric H<sub>2</sub> can only be accounted for by an enrich-ment in the ratio of D to H of H<sub>2</sub> relative to that in precursor CH<sub>4</sub> in addition to the enrichment due to the slower oxidation of deuterated H<sub>2</sub>. We calculate the fractionation associated with this enrichment to be  $\alpha_{Total}$ =1.54. As with other trace gases, in situ photo-chemical processes and the return flux of air from the stratosphere must be accounted for to explain tropo-spheric 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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