

B11A-11 1120h

**Observations of Concentration and  $\delta D$  of Atmospheric  $H_2$  in an Alaskan Boreal Forest**

Thom Rahn<sup>1</sup> (626-395-2383; trahn@gps.caltech.edu)

Nami Kitchen<sup>1</sup> (nkitchen@gps.caltech.edu)

Julianna Fessenden<sup>1</sup> (fessenden@gps.caltech.edu)

James T Randerson<sup>1</sup> (jimr@gps.caltech.edu)

John M Eiler<sup>1</sup> (eiler@gps.caltech.edu)

<sup>1</sup>California Institute of Technology, Geological and Planetary Sciences mail code 150-21, Pasadena, CA 91125, United States

Molecular hydrogen is the second most abundant reduced gas in the atmosphere with a seasonally dependent mixing ratio averaging  $\sim 0.5$  ppmv; the budget is thought to be controlled by sources from photo-oxidation of hydrocarbons, biomass burning and anthropogenic emissions and sinks dominated by soil uptake and oxidation by OH radicals. We are examining the isotopic signatures of these processes using a new method of  $H_2$  recovery and mass spectrometry on sub-liter-sized air samples (i.e.,  $< 20$  nmoles  $H_2$ ). Our work is motivated by the need to characterize and monitor the global  $H_2$  cycle before and during the anticipated rise in anthropogenic emissions associated with a developing hydrogen fuel cell economy. In addition, since soil uptake is the principal sink of  $H_2$  and since soil conditions are dependent on climatic influences, particularly in mid to high latitudes, observations of  $H_2$  and  $\delta D$  of  $H_2$  hold the potential to serve as proxies for observing global climate change. We report here the results of a study of the stable isotope systematics of  $H_2$  in east central Alaskan boreal forests during July and August of 2001.

Flask samples were collected during nighttime inversions in both mature spruce forest and in young mixed forest; concurrent sampling of  $CO_2$  concentration was performed in the field with a LiCor 6200 IR analyzer. An additional series of samples was collected over a period of 24 hours at a tower site in a 14 year old mixed forest; samples were collected at 4 hour intervals at ground level (0.8 m) and above canopy (10 m).

Samples collected during nighttime inversions exhibited vigorous  $H_2$  uptake and were negatively correlated with respiring  $CO_2$  ( $-0.8$  to  $-1.2$  ppb  $H_2$ /ppm  $CO_2$ ). Decreases in  $H_2$  concentration are correlated with increases in  $\delta D$ , indicating that one or more steps in the process of hydrogen consumption (presumably either diffusion into the soil or microbial utilization) is isotopically fractionating. Based on these data, we derive a fractionation factor,  $\alpha = D/H_{residual}/D/H_{consumed} = 0.960,01$ . This value is within the range of previous flux-chamber experiments [Gerst and Quay, 2001]. Data from the 24 hour time series yielded a similar nighttime draw down of  $H_2$  and elevated  $CO_2$  (observable even above canopy) and comparable fractionation factors for D/H. Unexpectedly, samples collected during daylight hours when the canopy was well flushed (evidenced by background  $CO_2$  levels) exhibited a modest positive correlation between hydrogen concentration and its deuterium content. We speculate that these enrichments may be the first observational verification of photochemically induced enrichment during oxidation of methane and non-methane hydrocarbons such as that proposed by Gerst and Quay [2001].

Gerst, S. and P. Quay, *J. Geophys. Res.*, 106, 5021-5031, 2001.

B11A-12 1135h

**The Triple Isotopic Composition of Atmospheric  $O_2$  as a Tracer of the Rate of Global Photorespiration**

Alon Angert<sup>1</sup> (972-2-6586874; alto@vms.huji.ac.il)

Boaz Luz<sup>1</sup> (boazluz@cc.huji.ac.il)

Eugeni Barkan<sup>1</sup> (eugenib@cc.huji.ac.il)

Shimon Rachmilevitch<sup>2</sup> (shimoni@vms.huji.ac.il)

<sup>1</sup>The Institute of Earth Sciences, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel

<sup>2</sup>Department of Plant Sciences, Institute of Life Sciences, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel

The triple isotopic composition of atmospheric  $O_2$  is controlled by different signatures of biological and stratospheric processes. Ultraviolet induced interactions in the stratosphere cause an equal depletion of  $^{17}O$  and  $^{18}O$  of atmospheric  $O_2$  (mass-independent fractionation). This equal lowering is in contrast to biological processes, and most terrestrial processes, in which the discrimination against  $^{17}O$  is about half of the discrimination against  $^{18}O$  relative to  $^{16}O$  (mass-dependent fractionation). Thus,  $O_2$  that was produced

by photosynthesis and was affected only by biological consumption will have excess  $^{17}O$  relatively to atmospheric  $O_2$  with the same delta  $^{18}O$ . In previous interpretations of changes in the triple isotopic composition, it was assumed that the ratio of discrimination against  $^{17}O$  to the discrimination against  $^{18}O$  is identical for all biological processes. In the present study, we evaluated this ratio, for the first time, for some of the most important oxygen consumption processes: The cytochrome and alternative pathways of dark respiration, and photorespiration. The value for the dark respiration processes was evaluated in dark incubation experiments, and inhibitors were used to separate the two pathways. The value for photorespiration was evaluated from experiments in airtight terrarium containing soil, plant and water. We have found similar discrimination ratio for the cytochrome and alternative pathways, but considerably lower ratio for photorespiration. One important conclusion derived from this finding is that much of the change in the atmospheric  $^{17}O$  depletion during the LGM can be related to an increase in the global rate of photorespiration. The increased rate of photorespiration during the LGM was the result of lower atmospheric  $CO_2$  concentrations. Previous interpretations of the  $^{17}O$  depletion change in the LGM attributed it only to changes in global productivity, and in stratospheric processes. Another important conclusion is that the current global rate of photorespiration can be evaluated from the parameters we provide, and from published data about the rate of mass-independent processes in the stratosphere.

**B12A MC: Hall D Monday 1330h**

**Biological Processes and the Isotopic Composition of the Atmosphere II**

(joint with A)

**Presiding: D E Pataki, University of Utah; J Ehleringer, University of Utah**

**B12A-0096 1330h POSTER**

**The Carbon Isotope Composition of Ecosystem Respiration in North and South America**

Diane E Pataki<sup>1</sup> (801-581-3545;

pataki@biology.utah.edu); James R Ehleringer<sup>1</sup> (ehleringer@biology.utah.edu); Lawrence B Flanagan<sup>2</sup> (larry.flanagan@uleth.ca); Dan Yakir<sup>3</sup> (ciyakir@wis.weizmann.ac.il); David R Bowling<sup>1</sup> (bowling@biology.utah.edu); Christopher Still<sup>4</sup> (still@sequoia.atmos.berkeley.edu); Nina Buchmann<sup>5</sup> (buchmann@bgc-jena.mpg.de); Joseph A Berry<sup>6</sup> (joeberry@catalase.Stanford.EDU)

<sup>1</sup>University of Utah, Dept. of Biology 257 S 1400 E, Salt Lake City, UT 84112, United States

<sup>2</sup>University of Lethbridge, Dept. of Biological Sciences 4401 University Drive, Lethbridge, AB T1K3M4, Canada

<sup>3</sup>Weizmann Institute of Science, Dept. of Environmental Science, Rehovot 76100, Israel

<sup>4</sup>University of California, Berkeley, Center for Atmospheric Sciences, Berkeley, CA 94720, United States

<sup>5</sup>Max Planck Institute for Biogeochemistry, P.O. Box 10 01 64, Jena 07701, Germany

<sup>6</sup>Carnegie Institution of Washington, Dept. of Plant Biology 290 Panama St., Stanford, CA 94305, United States

Measurements of the isotopic composition of atmospheric carbon dioxide have become a critical tool for understanding the role of terrestrial ecosystem processes in the carbon cycle. Photosynthesis and respiration impart distinct isotopic signatures to the atmosphere that may be used to constrain carbon source/sink estimates and partition ecosystem fluxes. These applications require an understanding of the processes that influence isotopic discrimination of whole canopies and ecosystems. The "Keeling plot" method is a common approach used in determining the isotopic composition of ecosystem fluxes and estimating ecosystem discrimination. An increasing amount of information is becoming available from numerous ecosystems around the world on the isotopic composition of ecosystem respiration ( $d^{13}CR$ ) over short and long time scales. In this presentation we synthesize emergent patterns in  $d^{13}CR$  by analyzing 146 Keeling plots constructed at numerous sites across North and South America as part of the Biosphere-Atmosphere Stable Isotope Network (BASIN). We calculated  $d^{13}CR$  uniformly for all sites in order to analyze the environmental controls on  $d^{13}CR$  temporally and across the landscape. We did not find differences in mean  $d^{13}CR$  between tropical, temperate broadleaf, temperate coniferous, and boreal forest biomes, indicating that fac-

tors other than species/functional type and temperature were driving canopy discrimination. Rather, we found that precipitation was a major driver of both temporal and spatial variability of  $d^{13}CR$ , illustrating the importance of water availability as a key control of ecosystem function. These results highlight the potential of  $d^{13}CR$  as a useful tool for integrating environmental effects on dynamic canopy processes.

**B12A-0097 1330h POSTER**

**Integrating and Testing a Mechanistic Model of  $H_2^{18}O$  and  $CO^{18}O$  Ecosystem Fluxes in a Coupled Land Surface and Global Climate Model**

William J Riley<sup>1</sup> (510-486-5036; wjriley@lbl.gov)

Noone C David<sup>2</sup> (dcn@caltech.edu)

Margaret S Torn<sup>1</sup> (mstorn@lbl.gov)

Joe A Berry<sup>3</sup> (joeberry@biosphere.stanford.edu)

Chris J Still<sup>4</sup> (still@atmos.berkeley.edu)

<sup>1</sup>Lawrence Berkeley National Lab, Earth Sciences Div, Bldg 90/1116, 1 Cyclotron Rd, Berkeley, CA 94720, United States

<sup>2</sup>California Institute of Technology, Division of Geological and Planetary Sciences, 1200 E. California Blvd., Pasadena, CA 91125, United States

<sup>3</sup>Carnegie Institution of Washington, Department of Plant Biology, 260 Panama St., Stanford, CA 94305-1297, United States

<sup>4</sup>University of California, Berkeley Atmospheric Sciences Center, 307 McCone Hall, Berkeley, CA 94720-4767, United States

We describe a mechanistic model that simulates  $H_2^{18}O$  and  $CO^{18}O$  fluxes between ecosystems and the atmosphere. The model is integrated into the land surface model LSM, which in turn is coupled to a version of the CCM3 GCM that simulates  $H_2^{18}O$  in precipitation and water vapor to allow transient simulations of vegetation, soil, and atmospheric mechanisms important in ecosystem isotope fluxes. The land surface isotope model comprises modules to compute canopy vapor, leaf water, and vertically resolved soil water  $H_2^{18}O$  content; leaf photosynthetic and retro-diffusive fluxes of  $CO^{18}O$ ; root and microbial production of  $CO_2$ ; soil diffusive fluxes of  $CO_2$  and  $CO^{18}O$  and equilibration of  $CO_2$  with  $^{18}O$  in soil water; and abiotic soil exchanges of  $CO^{18}O$ . Off-line model testing in a  $C_4$  dominated tallgrass prairie in Oklahoma will be presented. We then apply the model to better understand the impact on ecosystem  $CO^{18}O$  fluxes of the (a) soil abiotic flux; (b) carbonic anhydrase distribution within the soil; (c)  $C_3$  versus  $C_4$  mixtures and variations in carbonic anhydrase activity within each photosynthetic type; and (d) method used to compute surface  $H_2^{18}O$  fluxes. Sensitivity analyses of ecosystem  $H_2^{18}O$  and  $CO^{18}O$  fluxes to model parameters will also be presented. Preliminary results indicate that the near-surface soil moisture isotopic composition is strongly dependent on the  $H_2^{18}O$  surface flux method used; the opposite is true for deeper soil layers. The resulting ecosystem  $CO^{18}O$  flux is less dependent on the method of computing the  $H_2^{18}O$  surface flux. The carbonic anhydrase concentration in the soil also impacts the isotopic composition of the evolved  $CO_2$  flux. Finally, we present simulation results for selected ecosystem types from the coupled GCM and isotope model and a method to simplify the  $CO^{18}O$  surface flux calculation.

**B12A-0098 1330h POSTER**

**Measuring and Modeling the Component Influences of Soil, Vegetation and the Atmospheric Source on the Isotopic Composition of Canopy Air**

Theresa A Krebs<sup>1</sup> (tess@atmos.colostate.edu)

Joseph Berry<sup>2</sup> (joeberry@catalase.stanford.edu)

A. Scott Denning<sup>1</sup> (denning@atmos.colostate.edu)

Neil Suets<sup>1</sup> (nsuets@atmos.colostate.edu)

James R. Ehleringer<sup>3</sup> (ehleringer@biology.utah.edu)

<sup>1</sup>Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, United States

<sup>2</sup>Department of Plant Biology, Carnegie Institution of Washington 260 Panama St., Stanford, CA 94305, United States

<sup>3</sup>Department of Biology, University of Utah 257 South 1400 East, Salt Lake City, UT 84112, United States

Models of canopy transport and the fractionation of isotopes have both matured to a stage in which they demand to be used in concert. Measured profiles of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of  $\text{CO}_2$  at a mixed deciduous site near Willow Creek, Wisconsin, USA are represented by a three-component mixing model in which soil, vegetation, and planetary boundary layer (PBL) signals are each apparent. Profiles are simulated using a second-order Eulerian closure model with a superposition of isotopic sources and tracers. The transport model is informed by micro-meteorological measurements at the Willow Creek flux tower. This paper presents challenges to the three-component mixing model and the Eulerian closure model due to the changing influences of soil, vegetation, and the PBL. In particular, we find that the influence of the leaf source on daytime plots of  $1/[\text{CO}_2]$  vs.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  is evident in the measurements even under conditions of weak stratification. The ability of the transport model to represent the influence of the leaf source on a well-mixed daytime profile is discussed. The strongest measured signals are those above the canopy, suggesting that models of ecosystem-level exchange with the PBL should yield rich information. The strength of the above-canopy signal, together with PBL signals measured in the region, point to a need for future modeling of coupled canopy and PBL mass budgets.

#### B12A-0099 1330h POSTER

##### Use of stable isotopes in the study of $\text{CO}_2$ fluxes between terrestrial vegetation and the atmosphere in shortgrass steppe

Jee H. Shim<sup>1</sup> (1-970-491-8150; jhshim@nrel.colostate.edu)

Elise Pendall<sup>2</sup> (1-303-492-5792; elise.pendall@colorado.edu)

Dennis S. Ojima<sup>1</sup> (1-970-491-1976; dennis@nrel.colostate.edu)

<sup>1</sup>Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO 80523-1499, United States

<sup>2</sup>Institute for Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, United States

The shortgrass steppe ecosystem is ecologically sensitive to climate change due to the mixture of C3 and C4 plant species and the semi-arid environment. In order to make reliable predictions about effects of climate change on plant communities, it is prerequisite to understand how individual C3 and C4 plant functional groups contribute gross photosynthetic activity and respiration in the semi-arid grassland. We observed diurnal and seasonal changes of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{N}_2\text{O}$  fluxes, and associated isotopic signatures of  $^{13}\text{C}$  and  $^{18}\text{O}$  from air flasks above canopy at 1 and 2m heights, to estimate changes in activity of C3 and C4 plants and gross photosynthesis and respiration fluxes during the growing seasons of 2000 and 2001 in the shortgrass steppe region of north-eastern Colorado. Flasks were collected from a tower instrumented with Bowen ratio equipment, allowing us to evaluate latent heat fluxes simultaneously with flask measurements. We partitioned gross fluxes using the  $^{13}\text{C}$  and  $^{18}\text{O}$  isotopic mass balance method outlined by Yakir and Wang (1996). The results indicated that the grass canopy was a sink for  $\text{CO}_2$  during the daytime, as we expected, but peak times for  $\text{CO}_2$  uptake varied seasonally. Peak patterns of daily photosynthesis were attributed microclimatic variables such as leaf to air vapor pressure deficit related to stomatal conductance. The diurnal patterns of gradients for  $\text{d}^{13}\text{C}$  were similar to those for  $\text{d}^{18}\text{O}$ . Discrimination against  $^{13}\text{C}$  associated with  $\text{CO}_2$  fixation and isotopic exchange with  $^{18}\text{O}$ -enriched leaf water during daytime may be correlated process in this ecosystem. Seasonally, gross photosynthesis was positively correlated to magnitude of depleted  $\text{d}^{13}\text{C}$  of  $\text{CO}_2$  from all sources, latent heat flux at night, and total greenness of plants. Seasonal changes in atmospheric  $\text{d}^{13}\text{C}$  and  $\text{d}^{18}\text{O}$  values,  $\text{CO}_2$  fluxes and gross photosynthesis reflected changes in plant biomass and its composition by functional groups (C3, C4 and CAM) and environmental variables especially related to hydrological cycling such as evapotranspiration. We compared local-scale (10 to 100 m) flask results with observations from chambers to assess fine-scale (0.1 to 1 m) differences in respiration and  $^{13}\text{C}$  and  $^{18}\text{O}$  values from selected species and bare ground.

#### B12A-0100 1330h POSTER

##### Understanding the variation of carbon isotopic composition among contrasting ecosystems preliminary results and its implications

Chun-Ta Lai<sup>1</sup> (801-581-8917; lai@biology.utah.edu)

Andrew Schauer<sup>1</sup> (801-581-8917; schauer@biology.utah.edu)

Jim Ehleringer<sup>1</sup> (801-581-7623; ehleringer@biology.utah.edu)

<sup>1</sup>Department of Biology, University of Utah, 257S 1400E, Salt Lake City, UT 84112-0840, United States

Measurements of stable isotopic ratio of atmospheric  $\text{CO}_2$  are key elements to constrain interpretations of terrestrial carbon fluxes between the biosphere and the atmosphere. The present study focuses on identifying the photosynthetic and respiratory isotopic composition of  $\text{CO}_2$  at four Ameriflux sites: Harvard Forest, Wind River Research Crane, Howland Forest and Konza Prairie. These sites represent four contrasting ecosystems in terms of both vegetation composition and seasonal dynamics. An automated sampling system for atmospheric  $\text{CO}_2$  was developed to collect and store air samples at multiple heights within plant canopies in order to monitor the impact of environmental conditions on the variation of atmospheric isotopic ratios. Field measurements collected in this study are used to address both flux partitioning within ecosystems and to provide useful information for regional and global scale modeling studies. The long-term objective of this project is to investigate the mechanistic control of carbon gain and loss within an ecosystem, including the impact of land use history. Preliminary results showed that the carbon isotope ratio of ecosystem respiration ( $^{13}\text{C}_R$ ) can vary by 2 per mil on time spans as short as a month. Across different forest ecosystems, we observed that  $^{13}\text{C}_R$  values varied as much as 2 per mil during the summer of 2001.

#### B12A-0101 1330h POSTER

##### Carbon Isotope Discrimination in Forest and Pasture Ecosystems of the Amazon Basin, Brazil

James R Ehleringer<sup>1</sup> (ehleringer@biology.utah.edu);

Jean Ometto<sup>1,3</sup> (ometto@biology.utah.edu);

Lawrence B Flanagan<sup>2</sup> (larry.flanagan@uleth.ca);

Luiz A Martinelli<sup>3</sup> (zebu@cena.usp.br); Marcelo Z Moreira<sup>3</sup>; Niro Higuchi<sup>4</sup>

<sup>1</sup>Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112-0840, United States

<sup>2</sup>Department of Biological Sciences, University of Lethbridge, 4401 University Drive, Lethbridge, AB T1K 3M4, Canada

<sup>3</sup>CENA, University of Sao Paulo, Av. Centraio, 303, Piracicaba, SP 1340-970, Brazil

<sup>4</sup>Departamento de Silvicultura Tropical, Instituto Nacional de Pesquisas da Amazonia, C.P. 478, Manaus, AM 69011-970, Brazil

Our objective was to measure the stable carbon isotope composition of leaf tissue and  $\text{CO}_2$  released by respiration ( $\delta_R$ ), and to use this information as an estimate of changes in ecosystem isotopic discrimination that occur in response to seasonal and interannual changes in environmental conditions, and land-use change (forest-pasture conversion). We made measurements in primary forest and pastures in the Amazon Basin of Brazil. At the Santarem forest site  $\delta_R$  values showed a seasonal cycle varying from less than  $-29\text{‰}$  to approximately  $26\text{‰}$ . The observed seasonal change in  $\delta_R$  was correlated with variation in the average monthly precipitation. In contrast there was no significant seasonal variation in  $\delta_R$  at the Manaus forest site (average  $\delta_R$  approximately  $-28\text{‰}$ ), consistent with a narrower range of variation in monthly precipitation that occurred in Santarem. Despite substantial ( $9\text{‰}$ ) vertical variation in leaf  $\delta^{13}\text{C}$ , the average  $\delta_R$  values observed for both forest sites were similar to the  $\delta^{13}\text{C}$  values of the most exposed, sun foliage of the dominant tree species. This suggested that the major portion of recently respired carbon dioxide in these forests was metabolized carbohydrate fixed by the sun leaves at the top of the forest canopy. There was no significant seasonal variation observed in the  $\delta^{13}\text{C}$  values of leaf organic matter for the forest sites. We sampled in pastures dominated by the C4 grass, *Brachiaria spp.*, which is planted after forest vegetation has been cleared. The carbon isotope ratio of respired  $\text{CO}_2$  in pastures was enriched in  $^{13}\text{C}$  by approximately  $10\text{‰}$  compared to forest ecosystems. A significant temporal change occurred in  $\delta_R$  after the Manaus pasture was burned. Burning removed much of the encroaching C3 shrub vegetation and so allowed an increased dominance of the C4 pasture grass, which resulted in higher  $\delta_R$  values.

#### B12A-0102 1330h POSTER

##### Succession after fire: variation in $\delta^{13}\text{C}$ of organic tissues and respired $\text{CO}_2$ in boreal forests

Julianna E Fessenden<sup>1</sup> (626-395-4290;

fessenden@gps.caltech.edu); Huiyu Li<sup>1</sup>

(lihy@gps.caltech.edu); Michelle Mack<sup>2</sup>

(mmack@lter.uaf.edu); Ted Schuur<sup>3</sup>

(tschuur@uci.edu); Sarah Warren<sup>1</sup>

(sarahw@its.caltech.edu); James T Randerson<sup>1</sup>

(jimr@gps.caltech.edu)

<sup>1</sup>California Institute of Technology, Department of Geological and Planetary Sciences, Pasadena, CA 91125, United States

<sup>2</sup>University of Alaska, Fairbanks, Arctic Institute of Biology, Fairbanks, AK 99775, United States

<sup>3</sup>University of California, Irvine, Earth System Science Department, Irvine, CA 92717, United States

Isotope ratios of carbon dioxide and leaf organic matter were measured in 5 neighboring forests of varying ages: 7, 14, 45, 140, and 160 years. These forests are composed primarily of black spruce (*Picea Mariana*) and quaking aspen (*Populus tremuloides*) with a shift in species dominance from aspen to spruce 50 years after fire disturbance. Research on the carbon isotope ratios of leaf material and  $\text{CO}_2$  was conducted to look for influences from species composition, forest age, and time after most recent burn. Samples of organic  $\delta^{13}\text{C}$  in whole leaf tissue were collected from the dominant species of each forest. Concurrent aboveground NPP measurements allowed us to estimate total ecosystem  $\delta^{13}\text{C}$  by providing a method for weighting  $\delta^{13}\text{C}$  of individual species and plant tissues.  $\delta^{13}\text{C}$  and  $[\text{CO}_2]$  were measured on canopy  $\text{CO}_2$  to determine the isotopic ratio of ecosystem respiration. The atmospheric results indicated that the  $\delta^{13}\text{C}$  of ecosystem respiration changes with successional stage. Specifically, the aspen dominating forests showed  $^{13}\text{C}$  depleted values relative to the spruce dominated forests. Organic results showed more  $^{13}\text{C}$ -enriched values with increased forest age and vegetation functional type. Specifically, oldest trees within the coniferous species had the most  $^{13}\text{C}$ -enriched values in leaf tissues. These results suggest that increases in the disturbance regime of northern boreal forests will lead to a decrease in the  $\delta^{13}\text{C}$  of ecosystem carbon with consequences for the atmospheric  $\delta^{13}\text{C}$  budget.

#### B12A-0103 1330h POSTER

##### Isotopic Partitioning of $\text{CO}_2$ and Evapotranspiration Fluxes in a Semi-Arid Savanna: Effects of Sampling Height and Monsoon Rains

Enrico A. Ypez<sup>1</sup> (1-520-626-7131; yepezglz@ag.arizona.edu)

Guanghui Lin<sup>2</sup> (1-520-896-6478; glin@bio2.edu)

David G. Williams<sup>1</sup> (1-520-621-7257; dgw@ag.arizona.edu)

Joost van Haren<sup>2</sup> (1-520-896-5018; jvanhare@bio2.edu)

Danielle Pierce<sup>2</sup> (1-520-896-5091; dpierce@bio2.edu)

<sup>1</sup>School of Renewable Natural Resources, Biosciences East University of Arizona., Tucson, AZ 85721, United States

<sup>2</sup>Biosphere 2 Center, Columbia University., 32540 S. Biosphere Road, Oracle, AZ 85623, United States

Changes in climate and land use have the potential to dramatically alter ecosystem physiology and biosphere-atmosphere interaction through changes in the partitioning of energy, water, and carbon fluxes among ecosystem components. Here we present preliminary results from a field study in a mesquite forest with a C4 grass understorey in southeastern Arizona. One of our primary goals was to use sampling height and Keeling-plot relationships to distinguish component contributions within this two-layered canopy. We collected air and vapor from ten heights (0.1-14m) in the vegetation profile, twice during daylight and once at night during pre-, mid- and post-monsoon field campaigns. We also collected samples for stable isotope analysis of plant and soil water and plant and soil carbon. We used the Keeling plot approach to partition the net ecosystem  $\text{CO}_2$  exchange (NEE) and evapotranspiration flux (ET) into the relative contributions from ecosystem components over the summer growing season of 2001.

## B12A-0104 1330h POSTER

## Partitioning the Components of Net Ecosystem Exchange in a Northern Hardwood Forest

Brian D Bovard<sup>1</sup> (614-292-6454; bovard.1@osu.edu)Eric Singaas<sup>2</sup> (Eric.Singaas@uwsp.edu)Peter Curtis<sup>1</sup> (curtis.7@osu.edu)<sup>1</sup>The Ohio State University, Dept. of Evolution, Ecology and Organismal Biology 1745 Neil Ave., Columbus, OH 43210, United States<sup>2</sup>Univ. of Wisconsin-Stevens Point, Biology Dept., Stevens Point, WI 54481, United States

At the University of Michigan Biological Station Forest Carbon Cycle Research Program, part of the AmeriFlux network, we are using eddy covariance techniques to measure the net ecosystem exchange (NEE) of CO<sub>2</sub> in a mixed hardwood ecosystem in northern lower Michigan. NEE is the difference between carbon assimilated by the forest through gross photosynthesis and carbon lost through ecosystem respiration. Ecosystem respiration is composed of autotrophic respiration (R<sub>A</sub>) from leaves, boles, and roots, and heterotrophic respiration (R<sub>H</sub>) from microbial decomposition of soil organic matter, leaf litter, and coarse woody debris. We expect that climate change will affect R<sub>A</sub> and R<sub>H</sub> differently, with important consequences for carbon sequestration by forest ecosystems. Because eddy covariance techniques measure only the net carbon exchange, we are using a combination of stable isotope techniques and chamber flux measurements in coordination with the eddy covariance measurements to develop a mechanistic understanding of the underlying environmental controls on forest carbon assimilation and respiration. An initial survey of carbon isotope signatures of the forest components yielded δ<sup>13</sup>C values of -29.3‰, -28.9‰, -28.4‰, -27.5‰, and -24.8‰ for the leaf, leaf litter, root, bole, and soil organic carbon, respectively. Our research indicates that soil moisture and temperature play critical roles in controlling root and microbial components of soil respiration. However, they do not show the same temperature response curves. This suggests that shifts in temperature likely will have different effects on the underlying components of NEE.

## B12A-0105 1330h POSTER

Isotopic Study of the Sources and Emissions of CO<sub>2</sub> From an Hydroelectric Reservoir of the Boreal Forest of Eastern CanadaJean-François Hélie<sup>1</sup> (514-987-4630; d150200@er.uqam.ca)Claude Hillaire-Marcel<sup>1</sup> (514-987-4630)Louis Varfalvy<sup>2</sup> (514-289-2211)<sup>1</sup>GEOTOP Université du Québec à Montréal, C.P.8888 succ. Centre ville, Montréal, Qc H3C3P8, Canada<sup>2</sup>Hydro-Québec, 75 boul. René-Lévesque ouest, Montréal, Qc H2Z 1A4, Canada

The issue of greenhouse gas budget, in the boreal forest domain, is still largely open. In Eastern Canada, where possibilities of additional production of hydroelectricity exist, the impact of hydroelectric impoundment on carbon fluxes, at the scale of large drainage basins, is not totally elucidated. From this view point, deeper insights into carbon metabolism and fluxes in the aquatic environments are needed, notably for the large hydroelectric reservoirs of the eastern James Bay area, such as the reservoir Robert-Bourassa (2835 km<sup>2</sup>) examined here. Despite many recent studies, uncertainties still exist about carbon fluxes. Carbon isotope measurements in DOC, POC and DIC, as well as dissolved oxygen isotope measurements are used here to obtain information on carbon metabolism and to put constraints on the relative rates of production or consumption of carbon compounds. At the study site, in situ measurements included: water and air temperatures, pH, alkalinity and wind speed. Samples were collected for the measurement of concentrations and isotopic compositions of DOC, DIC, dissolved oxygen (DOX) and air CO<sub>2</sub>. Sampling was performed in summer during three consecutive years (1999-2001). Survey stations were selected according to their bathymetry (from a shallow 5m-deep site to a ~150 m-deep site). At these stations, surface waters were sampled during two periods of 24 hours, at 1-hour intervals, respectively under low and high wind conditions. At each station, samples were also collected at several depths, once during maximum photosynthetic activity (1 PM) and once in the middle of the night (1 AM). In addition, a network of stations (from 11 to 18 sites), provided surface water samples for both calm and agitated conditions. The <sup>13</sup>C content of the air CO<sub>2</sub>, sampled from 5 cm above the water level, up to 5m varies between -12.1 and -8.7‰ (δ units vs V-PDB).

This layer seems to be turbulent and shows isotopic properties that seem dependent upon wind speed and CO<sub>2</sub>-emission rates. δ<sup>13</sup>C values of dissolved CO<sub>2</sub> vary between -20.0 and -11.2‰; δ<sup>13</sup>C values of DOC vary between -29.9 and -26.8‰; and δ<sup>18</sup>O values of DOX vary between 20.1 and 22.4‰ (vs. V-SMOW). A strong direct relationship is observed between the water depth at the sampling station and the isotopic composition of dissolved CO<sub>2</sub> in the corresponding surface water layer (R<sup>2</sup>=0.84). Reverse relationships are observed respectively between the isotopic composition of dissolved CO<sub>2</sub> and the concentration of DOC, and the isotopic composition of dissolved CO<sub>2</sub> or air-CO<sub>2</sub> vs. wind speed. Oxygen isotope values in DOX (as low as 20‰ vs. V-SMOW) respond to the photosynthetic activity in the photic zone (with diffusive isotopic gradients from the overlying air and the underlying water layer, both showing δ<sup>18</sup>O - DOX values of approximately +22.5‰). Chemical (i.e., based on pCO<sub>2</sub>) and isotopic calculations of CO<sub>2</sub> emissions from the reservoir suggest a mean rate of ~1gC/m<sup>2</sup>.day during the survey period. However, discrepancies as high as 40% are observed between the two methods, suggesting that emissions calculated from dissolved pCO<sub>2</sub> values are over-estimated during periods of high photosynthetic activity. The study also suggests that oxydation of DOC, photochemical as well as microbial, represents a major source of CO<sub>2</sub> in the reservoir.

## B12A-0106 1330h POSTER

## Assessing the Impact of Land-use on Soil C Sequestration by Means of Soil Organic Matter Fractionation and Stable C Isotopes

M. Francesca Cotrufo<sup>1</sup> ("39-0823-274647"; fcotrufo@unina2.it)Alessandro Peressotti<sup>2</sup> ("39-0432-558616"; Peressotti@palantir.dpvta.uniud.it)Ilaria Del Galdo<sup>1</sup> (lilidg@hotmail.com)Johan Six<sup>3</sup> ("970-491-5599"; johan@nrel.colostate.edu)<sup>1</sup>Dip. Scienze Ambientali, Seconda Università di Napoli, Via Vivaldi, 43, Caserta 81100, Italy<sup>2</sup>DPVTA, Università di Udine, Viale delle Scienze, 208, Udine 33100, Italy<sup>3</sup>Natural Resource Ecology Lab., Colorado State University, Natural Environmental Sciences Bldg, Fort Collins, CO 80523, United States

The potential to sequester soil carbon will be a major driving factor for land-use policies in the future. Storage of carbon as soil organic matter (SOM) is, in fact, one of the better long-term options for C storage in terrestrial ecosystem, in particular if C is sequestered in SOM fractions with a high residence time. However, the quantification of C sequestration in soils is often limited by methodological constraints. We present the results of an experiment in North Eastern Italy where three mixed deciduous forests plots were planted 20 years ago on a continuous corn field with a strong isotopic C signature. This particular land use history offered the opportunity to compare the impacts on soil C storage and SOM dynamics with the conventional agricultural management of the site and with natural grasslands. Soil samples from the forest, grassland and maize systems were separated in three aggregate size classes, and inter- versus intra-aggregate particulate organic matter was isolated. All fractions were analyzed for their C content and isotopic signature. The distinct <sup>13</sup>C signature of the maize residue allowed calculating proportions of crop residues incorporated in the physically defined fractions. In 20 years, afforestation significantly increased the total amount of soil C with respect to agricultural fields but without reaching the SOM levels of the permanent grasslands. Aggregate size classes distribution was comparable between afforested and agricultural soils, with a lower concentration of macro-aggregates as compared to permanent grassland. Our data suggest afforestation may result in significant soil carbon sequestration but the sequestration seems to occur, at least during the first 20 years, in carbon pools with low residence time.

## B12A-0107 1330h POSTER

Evaporative Water Loss from Soil Reduced by Elevated Atmospheric CO<sub>2</sub>Dominic Ferretti<sup>1</sup> (dominic.ferretti@colorado.edu);Elise Pendall<sup>1</sup> (303-492-5792; elise.pendall@colorado.edu); Pieter P Tans<sup>2</sup> (ptans@cmdl.noaa.gov); Arvin R Mosier<sup>3</sup> (amosier@lamar.colostate.edu); Jack Morgan<sup>4</sup> (morgan@lamar.colostate.edu); James WC White<sup>1</sup> (jwhite@spot.colorado.edu); James A Nelson<sup>4</sup> (janelson@lamar.colostate.edu)<sup>1</sup>University of Colorado, INSTAAR 450 UCB, Boulder, CO 80309, United States<sup>2</sup>NOAA-CMML, 325 Broadway R/CMDL1, Boulder, CO 80305, United States<sup>3</sup>USDA-ARS, PO Box E 301 S. Howes, Fort Collins, CO 80522, United States<sup>4</sup>USDA-ARS, Crops Research Lab 1701 Center Ave, Fort Collins, CO 80526, United States

In the shortgrass steppe, a mixed C3/C4 grassland on the western border of the Great Plains, doubled atmospheric CO<sub>2</sub> has led to increased soil water content despite greater biomass growth. We evaluated whether elevated CO<sub>2</sub> led to differences in the two main pathways of water loss, evaporation and transpiration, using stable isotopes for partitioning. In our Open-Top Chamber (OTC) experiment, elevated and ambient chambers (EC and AC) were compared with non-chambered control plots (NC) for the period May, 1999-October, 2000. All plots received similar rainfall inputs, but AC plots had significantly lower volumetric water content than EC plots during the entire study period, and than NC plots during 1999. Changes in the soil water balance were apparent in the δ<sup>18</sup>O values of soil CO<sub>2</sub>. AC plots had significantly higher δ<sup>18</sup>O values than EC plots during the dry summer of 2000, but not during the moister summer of 1999. We established a strong relationship between δ<sup>18</sup>O of soil CO<sub>2</sub> and soil water at the same depths in soils adjacent to the OTC plots. We used this relationship, together with soil water content and known values of precipitation inputs, in a simple mass-balance model that allowed us to partition evapotranspiration into its components. During the period October, 1999, to October, 2000, the relative loss by evaporation averaged 20 percent lower in EC than AC plots. This reduction of evaporation may have resulted from increased biomass transpiring more, drainage of water below the rooting zone, and/or from reduced vapor diffusion across the more densely vegetated soil surface.

## B12A-0108 1330h POSTER

## Seasonal and Interannual Variation in Oxygen Isotope Discrimination in a Temperate Grassland Ecosystem

Linda Wever<sup>1</sup> (wevela@uleth.ca)Lawrence B Flanagan<sup>1</sup> (larry.flanagan@uleth.ca)David R Bowling<sup>2</sup> (bowling@biology.utah.edu)<sup>1</sup>Department of Biological Sciences, University of Lethbridge, 4401 University Drive, Lethbridge, AB T1K 3M4, Canada<sup>2</sup>Department of Biology, University of Utah, 257 South 1400 East, Salt Lake City, UT 84112-0840, United States

Our objective was to analyze the effects of seasonal and interannual climate variation on the oxygen isotope composition of carbon dioxide exchanging with the atmosphere in a temperate grassland ecosystem. On-line photosynthetic discrimination measurements were combined with analyses of the oxygen isotope composition of leaf water and respired carbon dioxide. In addition, we made continuous measurements of net ecosystem carbon dioxide exchange using the eddy covariance technique. Our study period included a year with near average precipitation (1999), and a year with below average precipitation (2000). The dry conditions in the summer of 2000 resulted in higher leaf water isotopic enrichment than was observed in 1999. Reduced stomatal conductance caused chloroplast carbon dioxide concentrations to be 30 ppm lower on average, so oxygen isotope discrimination during photosynthesis was only moderately higher in 2000 than in 1999. On-line discrimination during photosynthesis was approximately 35‰ in 2000. The oxygen isotope composition of ecosystem respired carbon dioxide did not differ between the study years. The effect of higher oxygen isotope discrimination during photosynthesis in 2000 was also partly reduced by the lower rates of gross photosynthesis caused by the drought.

## B12A-0109 1330h POSTER

### Anomalous Oxygen Isotopic Composition of Tropospheric CO<sub>2</sub> as a Potential Tracer of Biosphere Productivity

Katherine J. Hoag<sup>1</sup> (1-510-642-4499; kхоаg@uclink4.berkeley.edu)

Christopher J. Still<sup>2</sup> (1-510-643-9371; still@sequoia.atmos.berkeley.edu)

Inez Y. Fung<sup>2</sup> (1-510-643-9367; ifung@uclink4.berkeley.edu)

James T. Randerson<sup>3</sup> (1-626-395-2683; jimr@gps.caltech.edu)

Kristie A. Boering<sup>1,4</sup> (1-510-642-3472; boering@cchem.berkeley.edu)

<sup>1</sup>Department of Earth and Planetary Science, University of California, Berkeley, CA 94720-4767

<sup>2</sup>Berkeley Atmospheric Sciences Center, University of California, Berkeley, CA 94720-4767

<sup>3</sup>Divisions of Engineering and Applied Science and Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

<sup>4</sup>Department of Chemistry, University of California, Berkeley, CA 94720-1460

Stratospheric photochemistry leads to anomalously enriched CO<sub>2</sub> which is defined as  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 * \delta^{18}\text{O} \neq 0$ . Since there is no stratospheric sink for this enrichment, the anomalous stratospheric signature is not lost until air returns to the troposphere and the CO<sub>2</sub> exchanges oxygen isotopes with liquid water in soils and chloroplasts of leaves. Therefore, this anomaly may potentially be used to constrain the amount of carbon passing through the open stomata of plants and gross primary productivity. Currently,  $\delta^{18}\text{O}$  of tropospheric CO<sub>2</sub> is used to constrain models of GPP. Such models require knowledge of a wide variety of parameters that are difficult to model, such as the  $\delta^{18}\text{O}$  of leaf and soil water. In contrast, when modeling the  $\Delta^{17}\text{O}$  anomaly,  $\delta^{18}\text{O}$  does not need to be known explicitly because equilibration of the oxygen isotopes with liquid water resets the anomaly to  $\Delta^{17}\text{O} = 0$ . The GISS-UCB tracer-transport model coupled to a terrestrial biosphere model was used to investigate the interaction between the rate of transport of the anomaly from the stratosphere and the rate of destruction by the terrestrial biosphere. The results will be presented with a view towards estimating the strength of the signal and the potential use as a tracer.

## B12A-0110 1330h POSTER

### Model of N<sub>2</sub>O production, consumption and diffusion in tropical rain forest soil depth profiles, Paragominas, Para State, Brazil.

Tibisay J Perez<sup>1</sup> (949 824-3878; tjperrez@uci.edu);

Susan E Trumbore<sup>1</sup> (949 824-6142; setrumb@uci.edu); Stanley C Tyler<sup>1</sup> (949 824-2685; styler@uci.edu); Eric A Davidson<sup>2</sup> (508 540-9900; edavidson@whrc.org); Plinio de

Camargo<sup>3</sup> (55 19 4294788; pcmargo@mail.cena.usp.br); Louis Verchot<sup>4</sup> (+1 650 833 6645; l.verchot@cgiar.org)

<sup>1</sup>University of California Irvine, Dept of Earth System Science University of California at Irvine, Irvine, CA 92697-3100, United States

<sup>2</sup>The Woods Hole Research Center, P.O. Box 296, Woods Hole, MA 02543, United States

<sup>3</sup>Centro de Energia Nuclear na Agricultura, Av Centenario, 303, Cep 13416-000, Piracicaba, SP, Brazil

<sup>4</sup>Ecosystem Processes and Management, ICRAF, P. O. Box 30677, Nairobi, Kenya

N<sub>2</sub>O is an important greenhouse gas which concentration is increasing in the atmosphere since pre-industrial times. Mechanisms of production in tropical soils, which is the largest single source of atmospheric N<sub>2</sub>O, are poorly understood. We combine measurements of N<sub>2</sub>O mixing ratios, and stable isotopes with depth to study the seasonal changes in production and emission of N<sub>2</sub>O from soils in an evergreen tropical forest near Paragominas, Para State, Brazil. N<sub>2</sub>O concentrations in soil pore space are always higher than the atmospheric mixing ratio (314 ppb). In the wet season, maximum N<sub>2</sub>O values of 4 to 8 ppm occur at 1m depth, with concentration decreasing above and below. In the dry season, this feature is absent, and overall concentrations of N<sub>2</sub>O in soil pore space are lower (1ppm). Stable isotope signatures show increases in <sup>15</sup>N and <sup>18</sup>O of N<sub>2</sub>O from the surface to 1m depth in the wet season. Below 1m, isotope values decrease.

A model of N<sub>2</sub>O production, consumption and diffusion was used to simulate seasonal and depth changes of soil N<sub>2</sub>O and stable isotopes signatures. Model results are compared with measurements of mixing ratio and isotopic signature with depth. The model suggests that during the rainy season the N<sub>2</sub>O production is enhanced at approximately 75 to 100 cm depth and that N<sub>2</sub>O production occurs only in the upper meter of soil. High N<sub>2</sub>O mixing ratios deep in soil profiles are derived from downward diffusion of N<sub>2</sub>O produced near the surface, rather than in situ production.

## B12A-0111 1330h POSTER

### Effects of Copper Availability on Methanotroph Growth and Activity in Rice Paddy Soil

Jennifer Macalady<sup>1</sup> (macalady@geology.wisc.edu)

Kate M. Scow<sup>2</sup> (kmscow@ucdavis.edu)

<sup>1</sup>University of Wisconsin Department of Geology and Geophysics, 1215 W. Dayton St. Weeks Hall, Madison, WI 95616, United States

<sup>2</sup>University of California Department of Land, Air and Water Resources, One Shields Ave. Hoagland Hall, Davis, CA 95616, United States

Methanotrophs (aerobic, obligate methane-oxidizing bacteria) represent the largest sink for methane in the terrestrial environment, oxidizing a significant fraction of methane produced in anoxic regions of flooded soils and sediments before it reaches the atmosphere. Two unrelated methane monooxygenase (MMO) enzymes observed in methanotrophs have different kinetics, and have isotope fractionation effects for methane C which vary by about 12 per mil. Expression of the two enzymes in methanotroph cell cultures is controlled by copper, leading to the hypothesis that copper availability in soils could influence methane isotope fractionation in wetlands and rice paddies. Soil incubations using added copper chelate indicate that methanotroph growth and methane oxidation rates in a California rice soil are not limited by copper. Copper to methanotroph biomass ratios were in the range predicted for the expression of the particulate form of MMO (pMMO), the enzyme associated with the larger isotope fractionation factor (approx. -25 per mil).

## B12A-0112 1330h POSTER

### Inverse Modeling of Tropospheric Methane Constrained by <sup>13</sup>C Isotope in Methane

Sara E. Mikaloff Fletcher<sup>1</sup> (1-303-497-6535; sfletcher@cmdl.noaa.gov)

Pieter P. Tans<sup>2</sup> (1-303-497-6678; ptans@cmdl.noaa.gov)

Lori M. Bruhwiler<sup>2</sup> (1-303-497-6921; lbruhwiler@cmdl.noaa.gov)

<sup>1</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Boulder, CO 80309-0216, United States

<sup>2</sup>Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway R/E/CG1, Boulder, CO 80303, United States

Understanding the budget of methane is crucial to predicting climate change and managing earth's carbon reservoirs. Methane is responsible for approximately 15% of the anthropogenic greenhouse forcing and has a large impact on the oxidative capacity of Earth's atmosphere due to its reaction with hydroxyl radical. At present, many of the sources and sinks of methane are poorly understood, due in part to the large spatial and temporal variability of the methane flux.

Model calculations of methane mixing ratios using most process-based source estimates typically over-predict the inter-hemispheric gradient of atmospheric methane. Inverse models, which estimate trace gas budgets by using observations of atmospheric mixing ratios and transport models to estimate sources and sinks, have been used to incorporate features of the atmospheric observations into methane budgets. While inverse models of methane generally tend to find a decrease in northern hemisphere sources and an increase in southern hemisphere sources relative to process-based estimates, no inverse study has definitively associated the inter-hemispheric gradient difference with a specific source process or group of processes.

In this presentation, observations of isotopic ratios of <sup>13</sup>C in methane and isotopic signatures of methane source processes are used in conjunction with an inverse model of methane to further constrain the source estimates of methane. In order to investigate the advantages of incorporating <sup>13</sup>C, the TM3 three-dimensional transport model was used. The methane and carbon

dioxide measurements used are from a cooperative international effort, the Cooperative Air Sampling Network, lead by the Climate Monitoring Diagnostics Laboratory (CMDL) at the National Oceanic and Atmospheric Administration (NOAA).

Experiments using model calculations based on process-based source estimates show that the inter-hemispheric gradient of  $\delta^{13}\text{C}_{\text{CH}_4}$  is not reproduced by these source estimates, showing that the addition of observations of  $\delta^{13}\text{C}_{\text{CH}_4}$  should provide unique insight into the methane problem.

## B12A-0113 1330h POSTER

### Budget of Methyl Bromide in the Atmosphere: Isotopic Constraints

Markus Bill<sup>1</sup> (510-643-6449; mbill@nature.berkeley.edu)

Laurence G Miller<sup>2</sup> (650-329-4475; lgmiller@usgs.gov)

Robert C Rhew<sup>3</sup> (949-824-1726; rob@gaslub.ucsd.edu)

Allen H Goldstein<sup>1</sup> (510-643-2451; ahg@nature.berkeley.edu)

<sup>1</sup>University of California, Department of Environmental Science, Policy and Management Division of Ecosystem Sciences 151 Hilgard Hall, Berkeley, CA 94563-3110, United States

<sup>2</sup>United States Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, United States

<sup>3</sup>University of California Irvine, Earth System Science 284 Rowland Hall, Irvine, CA 92697-3100, United States

Bromine radicals contribute significantly to stratospheric ozone loss through coupled reactions with ClO, HO<sub>2</sub>, and NO<sub>2</sub> radicals. Bromine is approximately 40-100 times more effective, atom for atom, at destroying ozone than chlorine. For instance, Br coupled reactions are responsible for 30 to 50% of the total ozone loss in the polar vortex. The largest source of bromine to the stratosphere is methyl bromide (CH<sub>3</sub>Br). CH<sub>3</sub>Br has a concentration in the troposphere of about 10 pptv, a total estimated lifetime of 0.6 to 0.9 years, and has the highest concentration of any long lived organobromine. Unlike chlorofluorocarbons, which are produced entirely by humans, methyl bromide is produced by both anthropogenic and natural processes.

We are developing the use of stable isotopes to constrain the budget of CH<sub>3</sub>Br through quantification of the source signatures and the isotopic fractionations associated with sinks. The largest natural sources appear to be biological production in oceans (~35%), biomass burning (~13%), and salt marshes (~10%). Thus far, the only natural emissions to be isotopically characterized is from salt marsh plants. Carbon isotopic ratios of CH<sub>3</sub>Br emitted from the salt marsh have a strong diurnal variation from -65‰ during daytime when emission rates are highest to -12‰ at night when emissions are ~13% of the daytime rates. The  $\delta^{13}\text{C}$  weighted mean of salt marsh emission is -43‰ CH<sub>3</sub>Br.

Anthropogenically produced CH<sub>3</sub>Br is used for fumigation of soils, harvested crops and structures, and represents approximately 30% of the total source flux. The fumigation of harvested crops and structures constitutes approximately one third of the anthropogenic source to the atmosphere and, because the release rate of applied CH<sub>3</sub>Br approaches 100%, it should have a mean isotopic composition equal to industrially manufactured CH<sub>3</sub>Br, -54.4‰. However during soil fumigation, some of the CH<sub>3</sub>Br is consumed in situ causing isotopic fractionation. Thus the CH<sub>3</sub>Br that escapes to the atmosphere during soil fumigation is isotopically heavier (-48.7‰) than the CH<sub>3</sub>Br applied. The weighted mean  $\delta^{13}\text{C}$  of industrially manufactured CH<sub>3</sub>Br emitted to the atmosphere is approximately -50‰.

In order to utilize the stable carbon isotope approach for constraining the global budget, we still need to quantify the signatures of biomass burning emissions and oceanic emissions, investigate the kinetic isotope effect associated with oxidation by hydroxyl radicals in the atmosphere, measure the kinetic isotope effects associated with soil consumption at atmospheric concentrations, and begin measurements of the isotopic composition of methyl bromide in the atmosphere.

## B12A-0114 1330h POSTER

### Carbon Isotope Fractionation Effects During Degradation of Methyl Halides in Agricultural Soils

Laurence G. Miller<sup>1</sup> (650-329-4475; lgmiller@usgs.gov)

Shaun M. Baesman<sup>1</sup> (650-329-4459; sbaesman@usgs.gov)

Ronald S. Oremland<sup>1</sup> (650-329-4482; rorem@usgs.gov)

Markus Bill<sup>2</sup> (510-643-6449; mbill@nature.berkeley.edu)

Allen H. Goldstein<sup>2</sup> (510-643-2451; agoldstein@nature.berkeley.edu)

<sup>1</sup>U.S. Geological Survey, Mail Stop 465 345 Middlefield Road, Menlo Park, CA 94025, United States

<sup>2</sup>Environmental Science Policy Management, University of California, Berkeley, CA 94720, United States

Fumigation of agricultural soils prior to planting row crops constitutes the largest anthropogenic source of methyl bromide (MeBr) to the atmosphere. Typically, more than 60% of the MeBr added is lost to the atmosphere during the 5-6 day fumigation period. The remainder is oxidized by bacteria or otherwise degraded in the soil. In experiments using washed cells of methylophilic bacteria isolated from agricultural soil (strain IMB-1), oxidation of MeBr, methyl chloride (MeCl) and methyl iodide to CO<sub>2</sub> resulted in large (up to 70‰) fractionation of stable carbon isotopes (Miller, et al. 2001). By contrast, fractionation measured in field soils using both in situ techniques and bottle incubations with MeBr was less than 35‰. This discrepancy was initially attributed to the large transportation losses that occur without isotopic fractionation during field fumigation. However, this rationale cannot explain why bottle incubations with soil resulted in lower fractionation factors than incubations with bacterial cultures.

We conducted additional laboratory bottle experiments to examine the biological and chemical controls of carbon isotope fractionation during degradation of MeBr and MeCl by soils and bacteria. Soils were collected from a strawberry field in Santa Cruz County, California within two weeks of the start of each experiment. The rate of removal of methyl halides from the headspace was greatest during incubations at soil moisture contents around 8%. Increasing the amount of soil and hence native bacteria in each bottle minimized the lag in uptake by up to several days. No lag was observed during incubations of soils with added IMB-1. Stable isotope fractionation factors were similar for degradation by live soil and live soil with added IMB-1. Heat-killed controls of cell cultures showed little uptake (<10% over 5 days) and no isotope fractionation. Heat-killed soil controls, by contrast, demonstrated significant loss of MeBr (20-30%) with isotope fractionation factors comparable to live soil. Loss of MeCl during the same time was lower (<10%) however isotope fractionation was comparable to live soil.

Our results indicate that bacterial oxidation in soil rapidly consumes methyl halides but only partly controls the fractionation of carbon isotopes. Two chemical processes also act to remove MeBr in soil, hydrolysis and nucleophilic exchange with Cl<sup>-</sup>, both of which result in fractionation of carbon isotopes. Hydrolysis does not remove MeCl. It seems likely that fractionation in soil could result from a combination of biological and chemical processes, but since they all have sizeable fractionation factors associated with the removal of methyl halides, the relative rate of each process may not be as important as the total amount of methyl halide degraded. Attempts to constrain our understanding of atmospheric methyl halide budgets using stable isotope signatures of sources and sinks will have to rely on this type of information regarding the net isotopic impact of methyl halide uptake by soils.

Miller, L.G., Kalin, R.M., McCauley, S.E., Hamilton, J.T.G., Harper, D.B., Millet, D.B., Oremland, R.S., and Goldstein, A.H. (2001) Large carbon isotope fractionation associated with oxidation of methyl halides by methylophilic bacteria, PNAS, vol. 98, 5833-5837.

#### B12A-0115 1330h POSTER

### Simulating the interannual variability of the <sup>13</sup>C isotope signature of the atmospheric CO<sub>2</sub> concentration with an integrated soil-vegetation-atmosphere-transfer and carbon cycle model

Jörg D. Kaduk<sup>1</sup> (+44 (0) 116 252 3848; j.kaduk@leicester.ac.uk)

Christopher J. Still<sup>2</sup> (still@sequoia.atmos.berkeley.edu)

Neil Suits<sup>3</sup> (nsuits@atmos.colostate.edu)

Christopher B. Field<sup>4</sup> (chris@jasper.stanford.edu)

Joseph A. Berry<sup>4</sup> (joeberry@biosphere.stanford.edu)

<sup>1</sup>Department of Geography, University of Leicester University Road, Leicester LE1 7RH, United Kingdom

<sup>2</sup>Center for Atmospheric Sciences, University of California Berkeley, Berkeley, CA, United States

<sup>3</sup>Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, United States

<sup>4</sup>Carnegie Institution Department for Plant Biology, 260 Panama Street, Stanford, CA 94305, United States

Interannual variations of the global mean atmospheric concentrations of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> largely reflect climate induced year-to-year imbalances of the carbon fluxes from the different global carbon reservoirs and, thus, their climate sensitivity. We employ the apparent interannual variation of the global terrestrial carbon fluxes as inferred from inversion studies of the atmospheric CO<sub>2</sub> concentration to evaluate simulations with the integrated soil-vegetation-atmosphere-transfer and carbon cycle model SCS. The model, driven by satellite observations and meteorology, is designed to be employed as a land surface parameterization within an atmospheric general circulation model. In addition it simulates complete cycling of <sup>12</sup>C and <sup>13</sup>C through the terrestrial biosphere using ecophysiological approaches. For the simulations on a global 1x1 degree grid reported here, the model was forced with NDVI data from satellite observations and ECMWF reanalysis data for the time period 1983-1993. We discuss the climate sensitivities of the various modeled carbon transfers and identify the most important fluxes on the interannual time scale. Furthermore we examine the isotope fluxes, the climate induced changes in <sup>13</sup>C discrimination of C<sub>3</sub> photosynthesis and the variability of the isotopic signature from resulting from carbon cycling in ecosystems dominated by C<sub>3</sub> or C<sub>4</sub> plants. Inversion approaches to the determination of terrestrial and oceanic carbon sinks depend partially on assumptions about the isotope signature of the fluxes. We use our results to evaluate the sensitivity of those inversion based estimates of the terrestrial and oceanic carbon sinks on the isotopic signatures of the fluxes.

#### B12B MC: Hall D Monday 1330h

### Geomicrobiology and Biogeochemistry of Gas Hydrate Systems I (joint with A, OS)

Presiding: C Zhang, University of Missouri; B D Lanoil, Univ of California

#### B12B-0116 1330h POSTER

### Sulfate Profiles and Barium Fronts in Sediment on the Blake Ridge: Present and Past Depths of Anaerobic Methane Oxidation Above a Large Gas Hydrate Reservoir

Gerald R Dickens<sup>1,2</sup> (713 348-4880; Jerry@rice.edu)

<sup>1</sup>Department of Earth Sciences, Rice University, Houston, TX 77005, United States

<sup>2</sup>School of Earth Sciences, James Cook University, Townsville, QLD 4811, Australia

Ocean Drilling Program (ODP) Sites 994, 995, and 997 were drilled into a large gas hydrate deposit on the crest of the Blake Ridge (southeast U.S. margin) where upward CH<sub>4</sub> fluxes (F<sub>Out</sub>) quantitatively consume pore water SO<sub>4</sub><sup>2-</sup> over a narrow interval of sediment through anaerobic methane oxidation. High-resolution pore water SO<sub>4</sub><sup>2-</sup> and sediment Ba profiles have been constructed at these sites to assess present and past depths of the SMI and (F<sub>Out</sub>). Pore water SO<sub>4</sub><sup>2-</sup> profiles are linear with zero SO<sub>4</sub><sup>2-</sup> concentration occurring at 21.4, 21.6, and 22.8 mbsf at holes 994A, 995A and 997A, respectively. Using steady state solutions to diffusion equations with appropriate parameters, the steep SO<sub>4</sub><sup>2-</sup> gradients support upward CH<sub>4</sub> fluxes between 7.2 and 8.6 mol/m<sup>2</sup>ky at present-day, with the range primarily reflecting different approaches for incorporating porosity. Taking into account the generally decreasing porosity with depth and the high clay content of the sediment, the best estimates for F<sub>Out</sub> are 7.9, 7.6 and 7.2 mol CH<sub>4</sub>/m<sup>2</sup>ky at sites 994, 995 and 997, respectively. However, non-steady state solutions to diffusion equations show that the SO<sub>4</sub><sup>2-</sup> gradients do not imply steady state conditions. Elevated Ba concentrations (530-1410 ppm) exist in sediment between 18.23 and 20.65, between 17.31 and 20.31, and between 19.40 and 21.80, and between 19.58 and 21.91 mbsf at holes 994A, 994C, 995A, and 997A, respectively. These Ba fronts coincide with highs in bulk sediment Ba/Al (to 0.025) and are caused by Ba cycling just above time averaged depths of the SMI. Because the Ba fronts lie immediately above the present-day depths of pore water SO<sub>4</sub><sup>2-</sup> depletion, because the Ba fronts contain substantial Ba, and because no other Ba fronts are found in the upper 25 m at the three sites, the depth of the SMI beneath the seafloor has been nearly constant for considerable time (>18,000 years). Thus, CH<sub>4</sub> fluxes can be determined through SO<sub>4</sub><sup>2-</sup> gradients and steady state solutions to diffusion equations. More importantly, F<sub>Out</sub> through the crest of the Blake Ridge has not varied significantly across major changes in sea level and hydrostatic pressure.

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#### B12B-0117 1330h POSTER

### Biogeologic Control of Methane—Implications for Global Climate Change

Keith A. Kvenvolden (650-329-4196; kkvolden@usgs.gov)

U.S. Geological Survey, 345 Middlefield Road, MS 999, Menlo Park, CA 94025, United States

Methane, the most simple of organic molecules, is perhaps the most complex in terms of its role in the exogenic global organic carbon cycle. Sources of methane at the earth's surface are both biologic and geologic, with activities of humankind adding to the mix of sources. Of particular interest currently is methane from geological sources in the surface and shallow lithosphere. The amount of geological methane is enormous (likely exceeding 10 million metric tons of carbon as methane) with much of it stored in the form of methane hydrate. Methane hydrate, being both a sink and source of methane, is a major reservoir that acts to control the amount of methane that leaks from the lithosphere into the hydrosphere/atmosphere system. A second major controlling factor is methane oxidation, both anaerobic and aerobic, which converts leaking methane to carbon dioxide. Anaerobic methane oxidation is carried out by a consortia of archaea and bacteria, whereas, aerobic oxidation results from methanotrophy. Thus methane-hydrate storage and methane oxidation in sediment and water operate in concert to limit the amount of methane that escapes from the lithosphere/hydrosphere into the atmosphere. These controls have implications for global climate change because the storage and conversion of geological methane strongly limit the amount of methane that ever reaches the atmosphere where its greenhouse-gas properties could be effective. Only when the rates of methane oxidation cannot keep up with the rates of methane release from storage, can methane reach the atmosphere and become a factor in global climate change.

#### B12B-0118 1330h POSTER

### Dissolution Rates of Synthetic Methane Hydrate and Carbon Dioxide Hydrate in Undersaturated Seawater at 1000m depth

Gregor Rehder<sup>1</sup> (1-831-775-1982;

grehder@mbari.org); Stephen H Kirby<sup>2</sup> (skirby@usgs.gov); William B Durham<sup>3</sup> (durham1@lml.gov); Peter G Brewer<sup>1</sup> (brpe@mbari.org); Laura Stern<sup>2</sup> (lstern@usgs.gov); Edward T Peltzer<sup>1</sup> (etp3@mbari.org); John Pinkston<sup>2</sup> (jpinkston@isdml.wr.usgs.gov)

<sup>1</sup>Monterey Bay Aquarium Research Institute, 7700 Sandholdt Rd, Moss Landing, CA 95039-0628, United States

<sup>2</sup>U. S. Geological Survey, 345 Middlefield Rd, Menlo Park, CA 94025, United States

<sup>3</sup>UCLLNL, PO Box 808, Livermore, CA 94550, United States

Dissolution of synthetic methane and carbon dioxide hydrates was monitored after their transport to the ocean floor at 1000m depth. Cylindrical test specimens were initially grown in the laboratory by combining either cold, pressurized methane gas or pressurized liquid CO<sub>2</sub> with sieved granular water ice, then heating the reactants through the H<sub>2</sub>O melting point. Samples were then hydrostatically compacted to near-zero porosity, with resulting geometry of approximately 2.5 cm in diameter by 3-4 cm in length. Two samples each of methane and carbon dioxide hydrate were placed in a custom-made sample display rack having individual compartments for each sample with a transparent polycarbonate front window, and side and back walls of a flexible fine-mesh screen that permitted seawater flow around the hydrates. The sample rack was then transferred to the ocean in a stainless steel transport vessel pressurized with 10 MPa methane using the (ROV) Ventana.

On the seafloor, the sample display rack was removed from the pressure vessel and secured in a stand attached to an autonomous underwater video recorder system using a time-programmable Hi8 video recorder. The samples were continuously monitored for 2.30 h using Ventanas HDTV camera system, then followed by 20.75 h observation with the autonomous Hi8 time-lapse camera system (15 s every 0.25 h), and additional 3.33 h HDTV observation at the end of the experiment. Loss of volume and dissolution rates of the hydrates were derived from the measurement of the change of the projected diameter of the individual samples over time.