GEOPHYSICAL RESEARCH LETTERS, VOL. 16, NO. 8, PAGES 799-802, AUGUST 1989

AMAZON CAPIMS (FLOATING GRASSMATS): A SOURCE OF ^{13}C ENRICHED METHANE TO THE TROPOSPHERE

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Abstract. The ^{13}C isotopic composition of methane emitted to the troposphere from Amazon capims (floating grassmats) ranged from -36.9 to -48.0 o/oo, averaging -44.4 ± 4.2 o/oo. All pools of methane associated with the grassmats were ^{13}C enriched; methane withdrawn from plant stems ranged from -39 to -49 o/oo while bubbles stirred from the root mat averaged -41.4 o/oo. As the CH_4 flux from these habitats makes up some 40% of the total flux from the Amazon floodplain, CH_4 emissions from the region as a whole must be enriched in the heavy carbon isotope. Methane withdrawn from the stems of five genera of rooted macrophytes ranging in latitude from the Florida Everglades to the Alaskan Arctic exhibited ^{13}C enrichment relative to the sedimentary methane bubble reservoir. Several hypotheses based upon isotopic fractionation by methane transport, oxidation and production processes are proposed to explain this phenomenon.

Introduction

The steady increase in the tropospheric concentration of methane is well documented [Rasmussen and Khalil, 1981; Fraser et al., 1984; Ehhalt et al., 1983; Pearman et al., 1986; Rinsland et al., 1985; Dickinson and Cicerone, 1986]. Attention has recently been directed toward quantifying tropospheric methane sources and their isotopic composition [e.g. Chanton et al., 1988] and preparing mass flux and isotopic budgets [Stevens and Rust, 1982; Stevens and Engelkemeir, 1988; Tyler, 1986; and Quay et al., 1989]. Recently Craig et al. [1988] presented evidence for a temporal shift in the isotopic composition of atmospheric methane. Knowledge of the isotopic composition of methane sources is useful in identifying contributors to the steadily increasing tropospheric concentration and constraining estimates of source strength. Cicerone and Oremland [1988] have recently reviewed biogeochemical aspects of atmospheric methane.

Wetlands are large contributors of microbially produced methane to the atmosphere [Matthews and Fung, 1987; Khalil and Rasmussen, 1983; Ehhalt and Schmidt, 1978]. Generally, biogenic methane is ^{13}C depleted, having an isotopic composition of approximately -60 ± 10 o/oo [Bernard et al.,1976]. Here we report that methane fluxes from Amazonian floating grassmats or meadows (*capims*), dominated by the plants *Echinochloa* and *Paspalum* [Junk, 1970], are a source of atypical ^{13}C enriched methane to the troposphere. Fluxes from these habitats make up a significant contribution of the total methane emitted from the Amazon floodplain.

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Paper number 89GL01282.
0094-8276/89/89GL-01282$03.00

Methods

Methane was collected from Amazonian capims (floating grassmat islands) and one rooted fringing grassmat in the central Amazon floodplain east of Tefe' to Obidos during late April and May, 1987, as part of the GTE ABLE-2B/AGE (NASA's Global Tropospheric Experiment--Amazon Boundary Layer Experiment - Amazon Ground Emission). Water levels were high and rising on the floodplain during this period. Methane emitted from the grassmats was captured over 2 hour periods (8 hours for two samples, Table 1) in solar reflecting floating aluminum chambers which were used to measure methane fluxes. Fluxes were quantified using the gas filter correlation (GFC) technique [Sebacher and Harriss, 1982], which permits separation of emissions due to ebullition (bubble flux) from those due to diffusive or plant mediated transport [Dacey and Klug, 1979]. In one experiment a gas chromatograph was used for the flux determination so this discrimination was not achieved. Samples of chamber atmospheres were stored in stainless steel flasks pressurized to 35 psi. Methane concentrations were in the range of 20 to 35 ppm for samples from the 2 hour collection periods, and 1000-2000 ppm for the overnight collections. Carbon monoxide concentrations were 0.4 ppm or less (Crill, unpublished data). Methane was also sampled from the stems of capim plants several cm below the water line by withdrawing it via syringe. Methane rich bubbles were stirred from the capim root mat and captured in inverted funnels fitted with stopcocks at their tops. Both plant stem gas and bubble samples were transferred to vials by water displacement and sealed with butyl rubber stoppers. Samples from other environments in Florida, N. Carolina, Virginia, and Alaska were collected in a similar manner, except that bubbles were stirred out of waterlogged anaerobic soils in these cases.

Methane was prepared for isotopic analysis by combustion to CO_2 in a helium gas stream passed over 800° copper oxide [Chanton and Martens, 1988]. Resultant CO_2 was purified cryogenically, sealed into glass tubes, and analyzed on a Finnigan Mat 251 Isotope Ratio Mass Spectrometer at the Center for Applied Isotopic Studies, University of Georgia. Methane concentrations were determined by flame ionization gas chromatography and by manometric measurement of CO_2 resulting from methane combustions.

Results and Discussion

Isotopic Composition of Methane Emitted from Emergent Aquatic Plants

Methane emissions from grassmats ranged in isotopic composition from -36 o/oo to -48 o/oo (Table 1). Results are reported in the familiar ∂ ^{13}C notation relative to Peedee belemnite (PDB) [Hoefs, 1987]. Replicate flasks (2) of chamber headspace samples were within 0.1 and 0.3 o/oo while replicate chambers at a site yielded results within 1.4 o/oo. At three sites, the methane flux was dominated by ebullition (Table 1), while at two sites molecular diffusion or plant transport was the dominant gas transport mechanism. The average carbon isotopic composition released from the 6 capim sites was -44.4 ± 4.2 o/oo. The average of the sites dominated by ebullition was -44.6 ± 0.6 o/oo, while the non-bubbling sites averaged -43.3 ± 6.2 o/oo.

Table 1. Amazon grassmat flux methane, collected from April 23 to May 16, 1987--rising water season.

SITE	% BUBBLE FLUX	$\partial^{13}CH_4$ o/oo
LAGO ARANUPU*	ND	-47.3
LAGO COARI-1A	0	-44.2
LAGO COARI-1B	0	-43.9
PARANA NHAMUNDA**	0	-45.2
LAGO CANACARI	82	-48.0
PARANA LIMON-1	92	-46.3
PARANA LIMON-2A	97	-45.0
PARANA LIMON-2B	97	-44.9
LAGO ZEACU	93	-36.3
avg. of 6 sites ± σ		-44.4 ± 4.2
avg. of bubbling sites		-44.6 ± 0.6
avg. of non-bubbling sites		-43.3 ± 6.2

* 8 hour collection from floating grassmat
** 8 hour flux collection from rooted grassmat. All other collections were for periods of 2 hours from floating mats.

The carbon isotopic composition of methane supporting the fluxes quantified above varied from -49 to -39 o/oo (Table 2). Methane concentration in plant stems was between 60 ppm and 1.3 % by volume. Bubbles stirred from the capim root mat were 55-59 % methane with an isotopic composition of -41.4 ± 0.4 o/oo. All methane associated with the capim grassmats was enriched in ^{13}C relative to a sample collected from the submerged soils of the flooded forest, which had a more typical biogenic methane signature of -57.5 o/oo.

The departure of what is presumably biogenic methane from typical $\partial^{13}C$ values of -60 ± 10 o/oo, is interpreted to be due to the effects of methane oxidation by aerobic microbes, a process which preferentially utilizes methane containing the lighter isotope [Coleman et al., 1981; Barker and Fritz, 1981; Oremland and DesMarais, 1983], leaving heavy or ^{13}C enriched methane behind to be transported to the troposphere. The floating grassmats (capims) should be excellent environments for methane oxidizing bacteria. Methane is obviously abundant, and oxygen is present in plant stems and is at concentrations ranging from 0.5 to 1.0 $mg \cdot l^{-1}$ within the capim root mat [Bartlett et al., 1988a]. The floating grassmats therefore provide an environment in which methane is either generated in situ or else trapped as bubbles rising from the sediment below, and in which oxygen is supplied by plant metabolism and diffusive transport. This oxidation effect is added to the ^{13}C enrichment already caused by the C-4 photosynthetic pathway which is employed by both *Paspalum* and *Echinochloa* [Araujo-Lima et al., 1986].

Table 2. Methane Sources, $\partial^{13}C \pm \sigma$, number of replicates, and concentration.

Source	$\partial^{13}C$ o/oo	N	CH_4 ppm
Plant Stems			
Echinochloa polystachya	-40.0 ± 4.0	4	180 - 13000
Paspalum repens	-39.0 ± 3.1	4	60 - 1990
Victoria regia	-49.0	1	190
Leersia hexandra	-46.0	1	362
Gas Bubbles			% CH_4
Capim	-41.4 ± 0.4*	2	55 to 59%
Flooded Forest	-57.5	1	57%

* range of two

Table 3. Isotopic fractionation by emergent macrophytes at sites in the U.S.A. Plant stem and sedimentary bubble methane isotopic composition are listed with the difference between them and the number of replicates.

Genus	Site	Stem CH_4 o/oo	Sediment Bubble CH_4 o/oo	Δ o/oo	N
Pontederia	N. Carolina	-47	-63	16	3
Peltandra	Virginia	-48	-56	8	4
Peltandra	Florida	-51	-63	12	2
Sagittaria	Florida	-60	-64	4	2
Nymphaea	Florida	-74	-64	-10	1
Arctophila	Alaska	-46	-55	9	4
Carex	Alaska	-48	-61	13	2
Typha	Virginia	-55	-56	1	3
Typha	N. Carolina	-62	-63	1	3

Other data (Table 3) suggest that as a rule macrophyte plants may be sources of ^{13}C enriched methane to the atmosphere, and that fractionation during transport through aquatic plants may be a common phenomenon [Chanton et al., 1988]. We have observed isotopic fractionation between methane bubbles in sediments and plant stems in five other species (Table 3) ranging in latitude from the subtropical Everglades to the Arctic. The data in Table 3 were collected from plants rooted in soils as opposed to the floating Amazon grassmats. Sedimentary bubble methane isotopic composition has been shown to be indicative of dissolved methane in the sedimentary methane production zone [Martens, et al.,1986; Chanton, unpublished data]. *Typha* (cattails) appear not to exhibit isotopic fractionation between stem and soil methane (Table 3). Methane may be isotopically fractionated in the rhizosphere, as it is transported from the sedimentary/soil environment into the plant root/rhizome and passes through the gauntlet of a community of methane oxidizing microbes. Such communities may exist at the chemical interface where methane produced in the sediments meets oxygen brought down to the rhizosphere in the process of root ventilation.

Alternative hypotheses for the fractionation observed in plant stems relative to the sedimentary methane reservoir include the possibility that isotopic fractionation occurs as the methane exits the leaf, where the lighter isotope may be released preferentially, leaving the heavier isotope behind inside the plant stem. The diffusion of methane in air should promote the more rapid transport of the lighter isotope by a factor on the order of 19 o/oo, as calculated by the inverse square root reduced mass law for diffusivities [Mason and Marrero, 1970]. This same relationship was used by Farquhar et al. [1982] for calculating isotopic fractionation in the diffusion of CO_2 into leaves, an effect on the order of 4 o/oo. The effect is larger for methane because of its lower molecular weight. A third hypothesis is the possibility that plants take up soil methane from a zone other than the main methane bubble zone.

Global Significance

Based upon the recent redetermination of the fractionation factor for the oxidation of atmospheric methane [Davidson et al., 1987], it has been postulated that the global methane emission to the troposphere should have an isotopic

Table 4. Importance of grassmats in Amazon CH_4 flux. Flux units are in mg CH_4 m^{-2} d^{-1}.

Environment	Area %	Bartlett et al. 1988a July / Aug. 1985	Bartlett et al. 1988b April / May 1987
Open Water	21%	27 (5)*	74 (14)
Grassmats	27%	230 (72)	201 (35)
Flooded Forest	52%	192 (27)	126 (20)

CAPIM FLUX 1.3 to 8.7 x 10^{12} g CH_4 y^{-1}

TOTAL FLUX 3.0 to 21.0 x 10^{12} g CH_4 y^{-1}

capim flux about 40 % of total Amazon floodplain methane flux.

* standard error

composition of -55.4 o/oo [Craig et al., 1988]. The methane flux from the Amazon capims is significantly heavier than that value, and is among the first wetland sources recognized to fall on the enriched side of the balance described by Stevens and Engelkemeir [1988]. Tyler et al. [1988] have recently measured ^{13}C enriched methane emitted from Kenyan *papyrus*.

The capims have the highest methane flux per unit area of the three main types of environments recognized on the Amazon floodplain [Table 4, Bartlett et al., 1988a, Bartlett et al., 1988b; Devol et al., 1988]. Bartlett et al. [1988a] have estimated that the capims make up 27% of the areal extent of the floodplains. Based upon these factors, the capim methane flux is on the order of 40% of the total methane flux from the Amazon floodplain, which comprises 1 to 12% of the total flux of methane from all natural sources [Bartlett et al., 1988a]. Although the isotopic signature for emissions from other habitats was not examined in our work, the average $\partial^{13}C$ CH_4 value of -44.4 o/oo from mat environments suggest that emissions from the region as a whole may be significantly enriched in the heavy isotope. Quay et al. [1988] have recently estimated a value of -53 ± 8 o/oo for the whole wetland, which suggests that Amazon habitats other than the capims contribute isotopically light methane.

The values reported here are similar to the more ^{13}C enriched values reported by other workers for Amazonian methane. Devol et al. [1988] reported methane isotopic compositions ranging from -42 to -73 o/oo. Quay et al. [1988] reported methane bubble isotopic compositions ranging from -44 to -73 o/oo, and chamber flux samples ranging in isotopic composition from -41 to -72 o/oo. In both of these studies, the specific environments within which these samples were collected was not reported. Tyler et al. [1987] stirred isotopically light methane (-64 o/oo) from a mass of floating dead vegetation within the Amazon, not a living capim (S. Tyler, personal communication, 1989).

Our data emphasize that methane flux and isotopic data from specific ecosystems within larger wetlands should be considered when preparing estimates of tropospheric input. Our results also suggest that gas transport modes effect the isotopic composition of transported methane, and that the composition of methane from the sedimentary reservoir may not always be indicative of methane emanating to the troposphere.

Conclusions

The methane emission from Amazon capims (floating grassmats) sampled in this study was enriched in the heavy isotope of carbon and was -44.4 ± 4.2 o/oo. Flux from capim environments makes up about 40% of the total methane emission from the Amazon floodplain. Isotopic fractionation of methane in association with emergent macrophytes is a widespread phenomenon, and probably results from methane oxidation, or differential transport of isotopes across the leaves of plants.

Acknowledgements. We thank Jeffrey Richey, Bruce Forsberg, the crew of the Amanai, and the INPA (Instituto Nacional de Pesquisas da Amazonica) for their cooperation and support. We also thank Randy Culp of the University of Georgia Center for Applied Isotopic Studies for isotopic analyses. Cheryl Kelley and Kelley Cox collected and prepared Arctic samples. Thanks are due to Mary Campbell, Shirley Kilpatrick, and Faye Harris. This work was supported by grants from the NASA Biospheric Research Program (NAGW 1455), and the NASA Interdisciplinary Program (NAGW 834).

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(Received April 3, 1989.
Accepted June 20, 1989.)