

TEMPORAL VARIATIONS IN THE STABLE
CARBON ISOTOPIC COMPOSITION OF
METHANE EMITTED FROM MINNESOTA
PEATLANDS

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Abstract. The stable carbon isotopic composition of methane ($\delta^{13}\text{C}$) emitted from two peatland sites in the Marcell Experimental Forest in northern Minnesota was investigated during the snow-free season of 1989-1990. A seasonal range in $\delta^{13}\text{C}$ values of 13 ‰ was seen for a forested bog with heavier (^{13}C enriched) methane emitted during the warmer summer months. This shift was correlated with water table level suggesting control by microbial oxidation. Methane from a nearby poor fen transitional to bog dominated by *Carex oligosperma* showed a similar temporal trend but with a much smaller range of 5 ‰ during the same time period and with no water table level correlation. The methane emitted from the fen was consistently heavier than that emitted by the bog.

INTRODUCTION

The atmospheric budget of methane, a radiatively active trace gas, has been markedly improved by the use of isotopic analyses. Both stable and radioactive carbon isotopes can be used to put constraints on source estimates in the methane budget. Wahlen et al. [1989], Lowe et al. [1988], and Manning et al. [1990] have reported that 21 to 32 % of atmospheric methane is derived from fossil carbon sources,

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such as coal mining and natural seepage from gas reservoirs. Of the biogenic sources, wetlands appear to emit ^{13}C depleted methane relative to the average $\delta^{13}\text{C}$ composition of total methane emissions to the troposphere [Stevens and Engelkemeir, 1988; Cicerone and Oremland, 1988; Tyler, 1989].

Isotopic studies of methane emissions from wetlands have generally not taken into account possible seasonality in isotopic composition of the emitted methane. However, recent reports [Martens et al. 1986; Burke et al., 1988; Chanton and Martens, 1988] have shown that such seasonal changes occur in organic-rich marine and tidal freshwater sediments in temperate environments, apparently in response to variations in methane production rates and pathways. The objective of the present research was to seek evidence for similar seasonal shifts in the isotopic composition of methane emitted from two northern peatlands.

STUDY SITE

Minnesota peatlands have been the focus of several methane emission studies [Williams and Crawford, 1984; Harris et al., 1985; Crill et al., 1988] since northern peatlands and wetlands are believed to be a major source of tropospheric methane [Matthews and Fung, 1987]. The isotopic composition of methane emitted from Minnesota peatlands during spring and summer months has also been measured in previous investigations [Quay et al., 1988; Stevens and Engelkemeir, 1988]. Two sites, S2 Bog and Junction Fen, located in the U.S. Department of Agriculture's Marcell Experimental Forest, Itasca County, in northern Minnesota (Figure

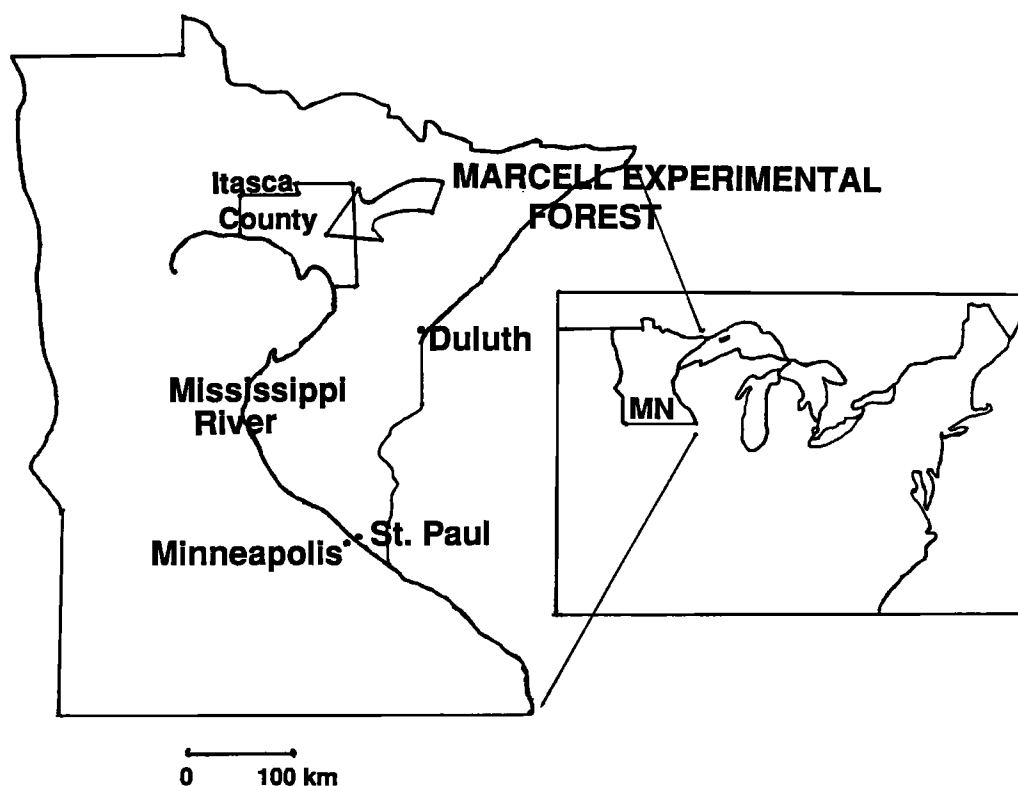


Fig. 1. Location of Marcell Experimental Forest, northern Minnesota.

1) were chosen for this isotopic study because concurrent methane flux measurements were also being made on a seasonal basis [Dise, 1992].

Both watersheds are small (less than 10 ha) with ground cover consisting of *Sphagnum* mosses with sedges (*Carex* spp.) and scattered ericaceous shrubs. S2 Bog is entirely forested with black spruce (*Picea mariana*), while Junction Fen is treeless and dominated by *Carex oligosperma*. Hydrologically, S2 is a perched ombrotrophic bog receiving its water and nutrient supply from atmospheric deposition. Junction Fen is a poor fen transitional to a bog indicating some groundwater interaction. A more detailed description of these sites can be found in the work by Dise [1992].

METHODS

Beginning in June 1989 and continuing until April 1990, the isotopic composition of the methane emanating via diffusion was monitored using static chamber techniques. Using a gas filter correlation technique [Sebacher, 1985] which distinguishes between diffusive and bubble methane flux, Crill et al. [1988] found bubble frequency to be very low at the Marcell sites. Samples were taken at monthly to bimonthly intervals, for a total of six measurements in each watershed. A frozen peat layer, approximate-

ly 15 cm thick, was found during the April 1990 sampling at both sites at depths of about 5 to 20 cm at S2 Bog and 10 to 25 cm at Junction Fen. Peat was unfrozen during the June, July, August, September, and November 1989 sampling dates. Permanent methane collection sites, one in each of the two watersheds, were set up using aluminum collars to which static aluminum flux chambers could be attached. The collar site at S2 Bog was dominated by *Sphagnum*, while *Carex* dominated the collar site at Junction Fen. Each chamber fit into a V-shaped notch at the top of the collar which was then sealed with water to prevent leakage. Methane concentrations increased linearly [Dise, 1991] within the chamber until approximately 100 ppm was reached (2 to 24 hours). This linear increase in methane concentration indicated both that bubble ebullition did not occur at these particular sites and that flux was not inhibited by the increase in methane concentration within the chambers. Once 100 ppm was obtained, chamber air was then pumped into an evacuated stainless steel can and pressurized to 35 psi (241 Pa). Approximately 4 to 6 % of the chamber air was removed for isotopic analyses. To avoid depressurization effects (i.e., creation of a partial vacuum) within the chamber while sampling, a stopper located away from the sample intake line was cracked open.

When possible, duplicate samples were collected from the chambers.

The methane from aliquots of the can samples was prepared for isotopic analysis by combustion to CO₂ in a helium gas stream flowing over 800° C cupric oxide at 50 mL/min [Mathews and Hayes, 1978; Chanton et al., 1992]. An in-line column of Schutze reagent (I₂O₅) followed by a liquid nitrogen trap was used to remove any carbon monoxide in the gas sample [Stevens and Rust, 1982]. The CO₂ produced from methane combustion was purified cryogenically and sealed in 6-mm OD glass tubes. The CO₂ was analyzed for ¹³C/¹²C abundances on a Finnigan Mat Delta D isotope ratio mass spectrometer in the laboratory of Neal Blair at North Carolina State University. Low concentration (approximately 100 ppm) methane standards utilized throughout the study period were prepared to mimic chamber head-space by injecting small volumes of North Carolina State University methane standard gas into an evacuated can and pressurizing to 35 psi (241 Pa) with outside air. The mean value (± 1 standard deviation) of 7 such standards was $-39.24 \pm 0.24 \text{ ‰}$,

which agrees with the ¹³C/¹²C ratio previously determined for the tank standard, $-38.9 \pm 0.2 \text{ ‰}$. All results are reported in terms of $\delta^{13}\text{C}$ (‰) defined as $[(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$, where R is the ¹³C/¹²C ratio and the standard is referenced to PeeDee belemnite (PDB). The results have also been corrected using a mass balance approach for dilution by atmospheric methane (1.8 ppm, -47 ‰) and blank carbon (-24 ‰) from the vacuum preparation line. The size of the blanks ranged from 6.67×10^{-5} to 2.83×10^{-4} $\mu\text{moles CO}_2$ per minute of run time on the vacuum line. Samples and standards ran between 20 to 80 min accumulating 1.1 to 3.6 $\mu\text{moles CO}_2$. The blanks translated to 0.1 to 0.6 % of the samples which shifted the measured isotopic signal to lighter values by, at most, 0.3 ‰.

RESULTS

In general, the $\delta^{13}\text{C}$ signature of methane from both wetland sites shifted toward heavier, less negative values (¹³C enriched) during the warm

TABLE 1. Monthly Mean Methane Fluxes and Isotopic Signatures for Both Sites

Month	Methane Flux ^a , mg m ⁻² d ⁻¹	Percent of Total Flux ^b , %	$\delta^{13}\text{C}$ -Methane, ‰
<u>S2 Bog</u>			
June 1989	51.4 (5, 17.3)	14.8	-70.06 (2, 0.40, June 15)
July 1989	150.1 (7, 49.7)	43.2	-64.22 (2, 0.54, July 20)
August 1989	71.1 (4, 30.9)	20.5	-63.01 (1, August 16)
September 1989	46.9 (4, 10.1)	13.5	-70.55 (2, 0.01, Sept. 29)
November 1989	18.8 (2, 0.3)	5.4	-69.06 (2, 0.44, Nov. 8)
April 1990	9.2 (1)	2.6	-76.15 (2, 0.09, April 20)
			$\bar{x} = -66.26 \pm 0.55^c$
<u>Junction Fen</u>			
June 1989	278.9 (6, 93.3)	16.2	-64.05 (1, June 14)
July 1989	541.3 (5, 181.5)	31.4	-59.84 (2, 0.18, July 20)
August 1989	350.0 (4, 32.3)	20.3	-61.76 (1, August 16)
September 1989	328.5 (4, 33.3)	19.1	-63.04 (3, 0.56, Sept. 29)
November 1989	112.4 (2, 8.6)	6.5	-65.03 (2, 0.27, Nov. 8)
April 1990	112.5 (1)	6.5	-59.19 (1, April 21)
			$\bar{x} = -61.83 \pm 0.32^c$

^aData are from Dise [1991].

^bOnly for months in which isotope samples were obtained.

^cFor the determination of weighted averages, data were used only from months in which isotope measurements were made. In the case of single monthly samples, the greatest percent uncertainty for flux (43 % for S2 Bog; 34 % for Junction Fen) and greatest uncertainty for isotopic composition (0.54 ‰ for S2 Bog; 0.56 ‰ for Junction Fen) were used.

The Number of samples, standard deviation or 1/2 the range or 1/2 the range if n=2, and date of isotope sampling are also given (n, standard deviation, date).

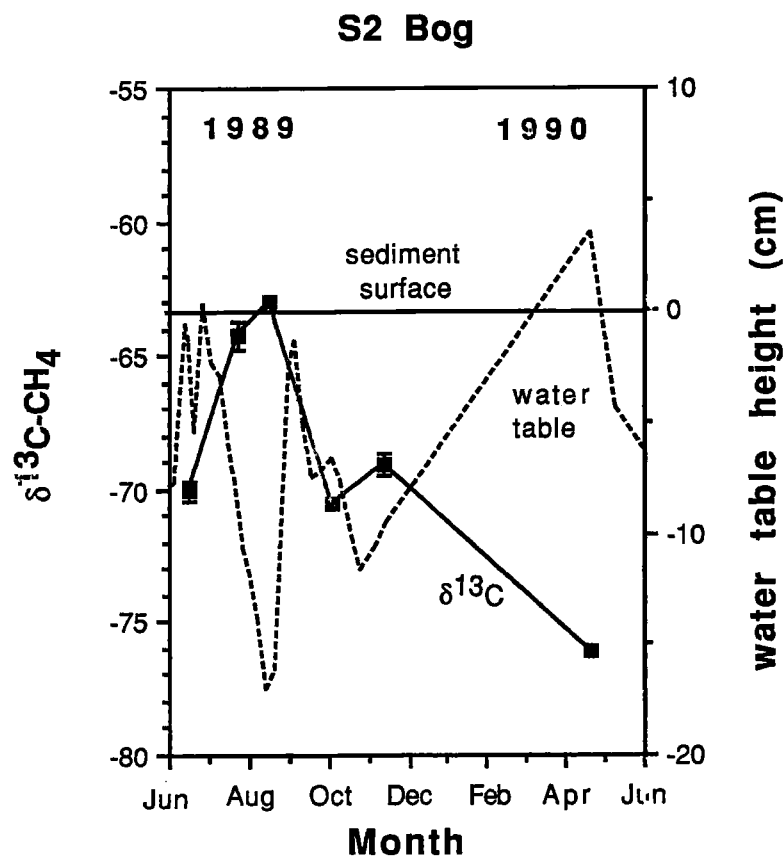


Fig. 2. Temporal isotopic composition of emitted methane (closed symbols) and water table level (dashed line) relative to the sediment surface (solid line) from S2 Bog. Water table data is from Dise [1991]. Every other month is denoted beginning with June 1989.

summer months (Table 1). The $\delta^{13}\text{C}$ value of methane emitted from S2 Bog (Figure 2) showed a greater seasonal shift from warm summer months to cold winter/spring months than did that of methane from Junction Fen (Figure 3) during the course of this study. This shift at S2 Bog is approximately 13 ‰, whereas that for Junction Fen was approximately 5 ‰ between July and November. The methane emitted from S2 Bog was systematically lighter (more negative values; ^{12}C enriched) than that from Junction Fen.

DISCUSSION

The stable isotopic composition of methane emitted from a site reflects the balance of productive and oxidative processes occurring there. Variations in isotopic composition can occur when this balance shifts. The predominant pathways of biogenic methanogenesis are acetate dissimilation and bicarbonate reduction, which together can account for more than 95 % of the methane produced in freshwater and marine sediments [Lovley and Klug, 1983; Crill and Martens, 1986]. Other substrates utilized include

methylamines, methanol and methylated sulfur compounds [Oremland and Polcin, 1982; Kiene et al., 1986; Oremland et al., 1989]. It has been hypothesized that acetate dissimilation produces methane with a heavier $\delta^{13}\text{C}$ (^{13}C enriched) and lighter δD (^1H enriched) isotopic signature than does bicarbonate reduction based on observations from marine and freshwater sediments [Whiticar et al., 1986; Woltemate et al., 1984]. The oxidation of methane results in a shift towards heavier $\delta^{13}\text{C}$ and δD values since methane containing the lighter isotopes, ^{12}C and ^1H , is oxidized preferentially [Coleman et al., 1981; Barker and Fritz, 1981; Alperin et al., 1988].

Summer increases in ^{13}C abundances have been observed in methane-rich bubbles escaping from the sediments of an organic-rich marine site [Martens et al., 1986], a southeastern tidal freshwater estuary [Chanton and Martens, 1988] and Alaska tundra lakes [Martens et al., 1992]. At these sites, variations in methane production processes, rather than oxidation, are apparently the dominant source of the seasonality. Burke et al. [1988] found that the δD signature of methane bubbling from marine sedi-

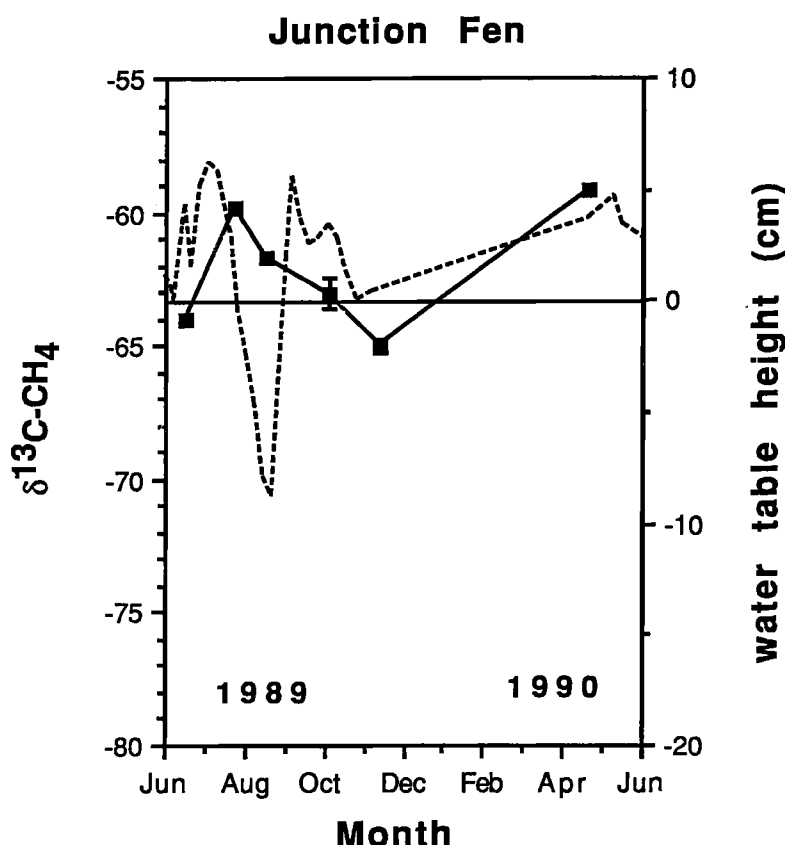


Fig. 3. Same as Figure 2 except for Junction Fen.

ments in Cape Lookout Bight, NC varied inversely with $\delta^{13}\text{C}$, that is δD became lighter in the summer when $\delta^{13}\text{C}$ became heavier. This same result was seen for the Alaska lake sites [Martens et al., 1992]. If oxidation had been a significant process at either site, then both isotopic signatures ($\delta^{13}\text{C}$ and δD) of methane should have become heavier. Both studies concluded that for these wetland environments, methanogenesis via acetate dissimilation is apparently a more important pathway during the warmer summer months, causing the observed seasonal shifts in methane isotopic composition.

We observed similar temporal variations ($\delta^{13}\text{C}$ heaviest during the summer) at the Minnesota peatland sites. Our hypotheses for these variations follow. In the dryer S2 Bog, it appears that water table level is a major control of the $\delta^{13}\text{C}$ of the emitted methane (Figure 2). A strong correlation ($r^2 = 0.75$) exists between water table level measured on the date closest to that of isotope sampling and the methane $\delta^{13}\text{C}$ signature. As the water table in this bog dropped, the isotopic composition of the emitted methane became ^{13}C enriched. The lowest water table was in August 1989 which corresponded to the heaviest $\delta^{13}\text{C}$ value. This relationship suggests that atmospheric oxygen penetration into the *Sphagnum*

peat occurs which results in methane oxidation. Fechner and Hemond [1992] have shown that approximately 90 % of the methane flux from deep methanogenic sediments of a northern *Sphagnum* bog were consumed in the unsaturated zone, the upper 12 - 15 cm of the peatland. If similar consumption occurred in the S2 Bog, oxidation could easily account for the shifts in emitted $\delta^{13}\text{C}$ values. Junction Fen, with a water table generally above the sediment surface, showed no such correlation between water level and $\delta^{13}\text{C}$ (Figure 3).

A distinct difference in $\delta^{13}\text{C}$ values occurs between the two peatlands (Table 1; Figures 2 and 3), with S2 Bog emitting substantially lighter methane than Junction Fen on every sampling date. This suggests that there may be differences in pathways of methane production between the two sites.

Plant species differ between the two sites with Junction Fen dominated by *Carex* sedges. Vascular plants, such as sedges, can act as conduits for methane escaping from anaerobic sediments to the atmosphere [Sebacher et al., 1985; Chanton et al., 1992]. These same vascular plants can also provide methanogenic substrate through root exudates. Root exudates, in general, are mainly composed of sugars and low molecular weight organic acids [Marschner,

1986] which can be precursors to acetate and, ultimately, methane. The temporal variations in methane isotopic composition in Junction Fen may be connected to the cycle of growth and senescence of the vascular plant community. During the summer when plants are most active, labile organic matter is apparently exuded from the roots to the methanogenic zone. The process of acetate dissimilation generally dominates over bicarbonate reduction in the degradation of fresh organic matter [Schoell, 1988]. At other times of the year, the process of acetate dissimilation for methane production appears to decrease in relative importance. This active balance between pathways connected to the growth cycles of the rooted macrophytes could create the seasonality in methane isotopic composition that is observed.

At the S2 Bog site, ground cover consists primarily of *Sphagnum* mosses which have neither vascular tissue nor root systems and so cannot facilitate methanogenesis by exuding acetate or acetate precursors to the sediment. S2 Bog peat is also denser and more recalcitrant than Junction Fen based on the von Post humification scale [Dise, 1992]. The bicarbonate reduction pathway for methanogenesis generally dominates during the degradation of older organic matter [Schoell, 1988]. This pathway was found to account for greater than 80 % of the methane produced in a northern bog in the Cascades [Lansdown et al., 1991] and H₂/CO₂ were the primary substrates for methanogens in another *Sphagnum* dominated Minnesota peatland [Williams and Crawford, 1984]. The lighter methane δ¹³C signature at S2 Bog suggests that bicarbonate reduction is a more important methanogenic pathway than in Junction Fen sediments.

Isotope samples were collected during the months in which almost 80 % of the yearly methane flux occurred (79 % at Junction Fen; 77 % at S2 Bog) [Dise, 1991, 1992]. In order to compare our results for these two sites in the Marcell Experimental Forest with previously reported isotope data from a number of Minnesota peatlands, we have calculated flux weighted isotopic averages and standard deviations. The standard deviation of the flux weighted average (SD_{wa}) was determined from the square root of the variance [Martens et al., 1986],

$$SD_{wa}^2 = \sum_i SD_{f_i}^2 (x_i - \delta^{13}C_{wa})^2 + \sum_i SD_{x_i}^2 f_i^2 \quad (1)$$

where f_i = flux percentage or flux fraction, and x_i = δ¹³C for each month. These flux weighted averages for Junction Fen and S2 Bog are -61.83 ± 0.32 ‰ and -66.26 ± 0.55 ‰, respectively (Table 1). These values are within the range of literature values previously reported. Quay et al. [1988] reported a mean value of -66 ± 4 ‰ for samples collected during April to June, while Stevens and Engelkemeir [1988] obtained a value of -67 ± 5 ‰ for June samples.

In this study, the methane isotopic composition varied temporally by up to 13 ‰. Seasonal studies

of stable isotopes of methane may be necessary to place better constraints on source isotopic inputs to the troposphere and to sort out the complex interplay of processes occurring in wetlands.

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