METHANE FLUX FROM MINNESOTA PEATLANDS

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Abstract. Northern ($>40^{\circ}\text{N}$) wetlands have been suggested as the largest natural source of methane (CH_4) to the troposphere. To refine our estimates of source strengths from this region and to investigate climatic controls on the process, fluxes were measured from a variety of Minnesota peatlands during May, June, and August 1986. Sites included forested and unforest ed ombrotrophic bogs and minerotrophic fens in and near the U. S. Department of Agriculture Marcell Experimental Forest and the Red Lake peatlands. Late spring and summer fluxes ranged from 11 to 866 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, averaging 207 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ overall. At Marcell Forest, forested bogs and fen sites had lower fluxes (averages of $77 \pm 21 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and $142 \pm 19 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) than open bogs (average of $294 \pm 30 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$). In the Red Lake peatland, circumneutral fens, with standing water above the peat surface, produced more methane than acid bog sites in which the water table was beneath the moss surface (325 ± 31 and $102 \pm 13 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, re-

spectively). Peat temperature was an important control. Methane flux increased in response to increasing soil temperature. For example, the open bog in the Marcell Forest with the highest CH_4 flux exhibited a 74-fold increase in flux over a three-fold increase in temperature. We estimate that the methane flux from all peatlands north of 40° may be on the order of 70 to 90 Tg/yr though estimates of this sort are plagued by uncertainties in the areal extent of peatlands, length of the CH_4 producing season, and the spatial and temporal variability of the flux.

1. INTRODUCTION

Northern ($>40^{\circ}\text{N}$) peatlands are believed to be an important source for global tropospheric methane (CH_4) [Harriss et al., 1985; Matthews and Fung, 1987]. A recent estimate, based on an improved global data base for the spatial extent of wetlands and CH_4 flux data from published literature, suggests that about 66% of the total global CH_4 emissions from natural wetlands come from northern ($>40^{\circ}\text{N}$) regions [Matthews and Fung, 1987]. It has been suggested that the expansion of northern peatlands, an interglacial phenomenon that may continue today, could contribute to a long-term increase in atmospheric CH_4 concentrations [Harriss et al., 1985]. This source could be particularly important to understanding variations of CH_4 observed in pre-1860 ice core air [e.g., Craig and Chou, 1982; Stauffer et al., 1985, 1988] and seasonal variations in atmospheric CH_4 observed in northern high latitudes [e.g., Steele et al., 1987]. However, the relatively recent rapid ($\sim 1\% \text{ yr}^{-1}$) increase in global atmospheric CH_4 [e.g., Rasmussen and Khalil, 1981; Blake et al., 1982; Rinsland et al., 1985] undoubtedly reflects a more complex interaction of source/sink dynamics perturbed by human activities [e.g., Khalil and Rasmussen,

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1983; Seiler, 1984; Ehrlert, 1974, 1985; Thompson and Cicerone, 1986].

Previous field studies on factors controlling CH_4 emissions from northern peatlands and lakes have documented potential effects of changing soil temperature, water table level, organic matter input and character, and gas transport mechanisms on flux rates, with time scales that range from hourly to annually [e.g., Svensson, 1976; Baker-Blocker et al., 1977; Dacey and Klug, 1979; Kelly and Chynoweth, 1981; Svensson and Rosswall, 1984; Sebachner et al., 1986]. The quantitative response of CH_4 flux from natural wetland ecosystems to any single variable (for example, soil temperature) defies global extrapolation based on studies at a few sites because numerous factors interact to influence methanogenesis and gas transport. Adequate assessment of global CH_4 emissions from natural wetlands requires field measurements, with at least seasonal temporal resolution. Consistent with this strategy we report here results of an intensive investigation, during the summer of 1986, of CH_4 sources and emissions from Minnesota peatlands. We studied both ombrotrophic bogs whose surfaces receive only atmospheric deposition and minerotrophic fens whose surfaces also receive water that has percolated through mineral soils [cf. Gorham, 1987; Gorham et al., 1987]. Our sampling strategy in the Marcell Experimental Forest was designed to characterize variations in CH_4 flux during the late spring to mid summer period. Because limited resources forced us to choose, we selected the period of maximum rates of change in soil temperature and moisture for our field work. This process-oriented approach was used in conjunction with a wider survey of north central Minnesota mires in order to place our intensive work at Marcell into the broader framework of boreal peatlands.

2. STUDY AREA AND METHODS

2.1. Study Area

This study follows a preliminary survey of CH_4 fluxes from boreal bogs and fens in north central Minnesota [Harriss et al., 1985]. The U.S. Department of Agriculture's Marcell Experimental Forest (47°32'N, 93°28'W), Itasca County, Minnesota, United States, was chosen for study because existing long-term data bases on the hydrology and water chemistry of many of the watersheds within the forest [cf. Boelter and Verry, 1977; Verry, 1975; Verry and Timmons, 1982] provide a broader context within which our measurements could be placed. Also, our surveys of CH_4 flux through this region [Harriss et al., 1985] and other northern wetlands [Sebachner et al., 1986] revealed that boreal peatlands are a potentially important component of the total global flux to the atmosphere.

The geology and soils of the Marcell Experimental Forest are described by Verry [1975]. Upland soils over slightly calcareous glacial debris constitute 74% of the forest surface area. The upland areas surround lowland organic soils consisting mainly of peat deposits of *Sphagnum* moss near the surface with woody, sedge, and aquatic plant residues at depth. Organic lowland soils are 21% of surface area, with open water making up the remaining 5% of the forest surface. Watersheds at Marcell tend to be small (gen-

erally <100 ha) and well defined. The upland slopes are dominated by quaking aspen (*Populus tremuloides* Michx.) and paper birch (*Betula papyrifera* Marsh.) with a sometimes dense ground cover of hazel (*Corylus* spp.). The peaty lowlands are covered by moss (*Sphagnum* spp.) and sedges (*Carex* spp.) with scattered low shrubs. Black spruce (*Picea mariana* (Mill.) BSP.) is the dominant tree on forested bogs.

The Marcell Experimental Forest averages 766 mm of precipitation annually, 75% as rain. Average annual temperature is 3°C. In comparison to the 25-year record for 1961–1986, 1986 was warmer and wetter (except for a drier May) than average. Average monthly temperature and precipitation for April–June 1986 were 11.7° and 90 mm, respectively, whereas average monthly temperature and precipitation for April–June 1961–1986 were 10.1° and 86 mm, respectively.

Five sites within three watersheds were selected for repetitive CH_4 flux measurements to follow changes as peats warmed from snowmelt in spring to the summer temperature plateau. One was located in a small opening (2 m in diameter) within a speckled alder (*Alnus rugosa* (Du Roi) Spreng.) thicket of a minerotrophic groundwater fen (S-3), that was clear-cut in 1973. As at all sites, the ground is covered with living *Sphagnum* spp. with some sedges and scattered ericaceous shrubs. Four other sites were located in two perched, ombrotrophic bogs (S-2 and S-4, Figure 1). S-2 is entirely forested with a mature 90-year stand of black spruce, whereas S-4 is open in the middle with a small pond at the center of the clearing. The total areas of the watersheds around S-3, S-2, and S-4 are 96, 10, and 34 ha, respectively, and the relative amount of peatland is 26, 30, and 24%, respectively. All three peatlands fill lakes formed in ice block depressions and are representative of small kettle hole bogs scattered across the boreal region. The minerotrophic fen, S-3, is directly influenced by the regional water table; therefore the pore waters exhibited higher pH and conductivity than those of the ombrotrophic bogs. Groundwater influence is also reflected in the vegetation and hydrology [Boelter and Verry, 1977]. In contrast, the perched bogs are ombrotrophic; that is, their nutrients and water are supplied by rain, snow, and dustfall. They are isolated (perched) above the regional water table, resulting in lower pore water conductivity and lower pH from the buildup of organic acids and cation exchange by *Sphagnum* spp. [Gorham et al., 1987; Urban et al., 1987; Clymo, 1987]. The unique hydrology of perched bogs contributes to their distinctive vegetation and chemistry; for example, the central peat dome (8–12 cm high, as measured in the hollows) in S-2 [Verry, 1984] insures runoff toward the edge of the bog where, mixed with runoff from upland mineral soils, a narrow fen margin (lagg) is maintained. The central dome contains distinctly ombrotrophic bog species [Boelter and Verry, 1977]; species characteristic of more minerotrophic environments are found in the lagg.

We used the different vegetation of forested and open ombrotrophic bogs and minerotrophic fens to select and distinguish sites during our August survey of the vast Red Lake peatland [cf. Glaser et al., 1981; Wheeler et al., 1983]. This 1200-km² area is about 130 km northwest of the Marcell Forest. Table 1 lists plant species in 39 plots

Fig. 1. Diagrams of two ombrotrophic bogs in the Marcell Experimental Forest, Itasca County, Minnesota, United States. The region of the present study in north central Minnesota is shown by the solid circle on the inset map. The repetitive collar sites are marked C.1 through C.4. Transects across each bog are shown by solid lines.

at 12 flux sites in the Red Lake peatland; many are also important in Marcell. We included three additional open wetlands in our study. One, the raised Bena bog with a large *Sphagnum* dome covering fen peats, is about 65 km southwest of Marcell and has vegetation resembling that of openings in the bog forests of the Red Lake peatland. Another at Marcell, S-1, is a formerly forested bog clear-cut in 1975. The third, Junction Fen near Marcell, is a 6-ha treeless poor fen transitional to bog, with no stream outlet and characterized by a deep floating mat of *Sphagnum*.

The diverse peatlands studied, ranging in size from 0.01 to 1200 km², are representative of midcontinental peatlands in North America [Glaser and Janssens, 1986] but have far fewer and smaller open pools than more

northerly and more maritime peatlands in North America. The height of their vegetation canopies ranged from 0.1 to 14 m. The pH varied from 3.5 to 7.0. Water table elevations relative to hollows ranged from +15 to -100 cm (0 cm corresponding to *Sphagnum* surface) in these natural, undrained peatlands. Water tables at our sites ranged from +3 to -43 cm.

2.2. Methods

2.2.1. Site selection. In the Marcell Experimental Forest we revisited the exact same spots in each watershed frequently from late April to the end of June. In the perched bogs, aluminum collars were used to minimize

TABLE 1. Plant Species Distributions at the Methane Flux Sites in the Red Lake Peatlands

	Site 1	Site 6	Site 11	Site 2	Site 5	Site 12	Site 3	Site 4	Site 10	Site 7	Site 8	Site 9
	a b c	a b	a b	a b c	a b c	a b c	a b c d	a b c d	a b c	a b c d	a b c d	a b c d
<i>Ledum groenlandicum</i>	2 2 2	2										
<i>Kalmia polifolia</i>	+	2 2	+ 1									
<i>Gaultheria hispidula</i>	2 1 r		1									
<i>Sphagnum fuscum</i>	+ 1	+										
<i>Sphagnum magellanicum</i>	5 4 4	+ 2	4 5	+ +	+ + +	+ + 5						
<i>Sphagnum angustifolium</i>	1 2 2	1 3	3 2	+		+						
<i>Sphagnum capillifolium</i>	+ +	5 3		5 5 5	5 5 4	5 +	+ + + 1					
<i>Polytrichum strictum</i>		+		+ +	2 2 3		1					
<i>Carex oligosperma</i>		1 2		2 2 3	2 2 2		1 1 +					
<i>Carex pauciflora</i>			1 1			+ + 1						
<i>Vaccinium oxycoccos</i>	+ 1 1	1 1	+ +	1 2 1	1 2 1	2 1 1	+ + +				+	+ +
<i>Chamaedaphne calyculata</i>		1 1	+ 2	2 1 1	+ +	1 1 2	+ + + 1					+ 1
<i>Andromeda glaucophylla</i>			+ +	+ + +	+	1 + +	1	+				r + +
<i>Sphagnum papillosum</i>					+		5 5 5 5					
<i>Scheuchzeria palustris</i> var. <i>americana</i>						1 1 +	1 1 1 1	1 + 1 1	1 1 +	+ + +	+ +	
<i>Sarracenia purpurea</i>						r		r				+
<i>Carex limosa</i>							1 1 1 +	+ +	1 2 1	+ 2 +	+ 2 1	
<i>Species Restricted to Fens</i>												
<i>Drosera intermedia</i>							+ + + 1			1 + + 1	+	
<i>Scorpidium scorpioides</i>							4 1		+ +	3 5 5 4	3 4 +	
<i>Rhynchospora alba</i>							1 1 2 1		2	2 2 1 1	+ 1 + +	
<i>Carex lasiocarpa</i> var. <i>americana</i>							3 3 1 1	+ +		2 + 1 2	+ 3 1	3 4 2 2
<i>Menyanthes trifoliata</i>							+ r	+ + r		+ 1 1 +	r +	+ + + r
<i>Carex livida</i> var. <i>grayana</i>									1 + +	+ + + +	1 1 + 1	
<i>Equisetum fluviatile</i>									+ r		r	
<i>Utricularia intermedia</i>									+	+	r	
<i>Utricularia minor</i>									+ +	+ + + +	r +	
<i>Drepanocladus revolvens</i>										3 +	1	
<i>Campyllum stellatum</i>										+	2 3	+ +
<i>Aster junciformis</i>										+		r + +
<i>Potentilla palustris</i>												+ + + r
<i>Sphagnum contortum</i>												+ + 2
<i>Sphagnum warnstorffii</i>												5

Sites 1, 6, and 11 are forested bog; sites 2, 5, and 12 are open bog; site 3 is a transitional poor fen; and sites 4 through 9 are normal fen. The letters a through d refer to plots at each site. Here, r denotes a single occurrence; t, cover of less than 1%; 1, cover of 1–5%; 2, cover of 5–25%; 3, cover of 25–50%; 4, cover of 50–75%; and 5, cover of 75–100%. Species in the upper part are characteristic of bogs (but are also found in fens); those in the lower section are restricted to fens. Plot size was 51 × 51 cm. Nomenclature follows Fernald [1970] for vascular plants, Isoviita [1966] for *Sphagnum*, and Ireland et al. [1981] for other mosses.

disturbance and to ensure a good seal for the flux chamber, which fitted into grooves in the collar that were sealed with water. Collars were placed in the *Sphagnum* peat surface in late April and left for the duration of the study. Boardwalks were built to the collars to limit disturbance.

Bog S-4 is partially forested, but our repetitive sites there were selected in an open portion to contrast with forested sites in S-2. Bog S-4 was always wetter and warmer than S-2 at 10–20 cm below the water table, and its surface was smoother (in the open areas). Collar 1 was located near the center pond (Figure 1). The surrounding bog surface quaked when walked upon, indicating that this portion was floating. Collar 2 was placed near the edge of the spruce forest.

S-2 is completely forested. The entire bog surface is marked by a hummock/hollow microtopography with variations in height as much as 40–50 cm [Verry, 1984]. Collar 3 was placed on top of a hummock, the *Sphagnum* surface of which was approximately 35 cm above surrounding hollows. Collar 4 was placed in a hollow.

The fen site, S-3, was located in an area with alder 2 m high, 15 m off a Forest Service boardwalk. A collar was not available, but the chamber was placed over approximately the same area on each visit. Owing to relatively dense alder thicket this site was only a short distance (20 m) from the fen/upland boundary and 5 m from a site previously studied by our group [Harriss et al., 1985].

2.2.2. Gas analysis. Methane fluxes were measured by two methods. The first employed a continuous sampling chamber technique described in detail elsewhere [Sebach and Harriss, 1982]. An aluminum chamber (51x51x26 cm) was fitted into the collar and sealed with water, or inserted into the soil when there was no collar, or floated on the water surface. On bright days it was covered with a highly reflective Mylar blanket to minimize internal temperature changes. Inside the chamber a flat, brushless fan mixed the air while a blower circulated it via a closed loop of hose through an external infrared detector. The instrument used a gas filter correlation (GFC) technique [Sebach, 1985] to monitor continuously any change in CH_4 concentration of the enclosed air. Bubbles and diffusive CH_4 flux could be distinguished in the output from the detector. Bubbling frequency was found to be very low during our measurements in Minnesota. Minimum detectable flux is $0.1 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ for a typical 15-min measurement.

Fluxes were also measured with air samples grabbed from the head space of the same chamber with 60-mL plastic syringes equipped with plastic stopcocks. The chamber air sample was then analyzed for CH_4 with a Shimadzu Mini-2 gas chromatograph equipped with a flame ionization detector (FID-GC). FID-GC peaks were quantified with a Hewlett-Packard HP-3390A recording integrator. Methane fluxes were determined from the slopes of concentration changes in five samples taken over 20 min. This method yielded a total net CH_4 flux.

Methane concentrations in pore waters of the peat column were determined by sampling a series of depths with 60-mL plastic syringes with stopcocks, attached to a 1/8" stainless steel tube with grooves hack sawed into the bottom 1 cm. A 50-mL water sample could easily be with-

drawn from depths to approximately 50 cm. Difficulties in drawing water only arose in deep samples from more decomposed peats. To analyze for CH_4 , some water was expelled, and an equal volume of room air was introduced into the syringe. The sample was shaken vigorously for 2 min and headspace CH_4 was quantified by FID-GC [McAuliffe, 1971]. The method stripped 98% or more of the CH_4 from the water sample. Concentrations were corrected for temperature and CH_4 in room air. Conductivity of the stripped water sample was measured on a Hach DR/EL-4 conductivity meter.

Methane concentrations in ambient air were also determined by FID-GC. Air samples were taken facing into the wind, with 60-mL plastic syringes (equipped with stopcocks) held as high as possible.

Carrier and standard gases for the gas chromatograph were calibrated with a National Bureau of Standards (NBS) certified standard before shipping to Minnesota. Separate sets of syringes were used for flux, ambient air, and pore water measurements. The water column and flux syringes were disassembled after use so the interior plastic and rubber plunger tip could equilibrate with ambient air before reuse. Samples were usually analyzed within 1–2 hours after collection, but occasionally analysis was delayed for up to 5 hours. The plastic syringes could hold 5 ppm CH_4 for over 2 days with less than 1% loss.

3. RESULTS

3.1. Temporal Variability in Methane Flux

Methane fluxes at the collar sites in the Marcell Experimental Forest are illustrated in Figure 2. Highest fluxes were in the open bog S-4. Collar 2 had the highest fluxes,

Fig. 2. Five-day running averages of CH_4 flux and of temperature measured at 10 cm below the surface of the water table, in the Marcell Experimental Forest.

TABLE 2. Mean, Median, and Range of Methane Flux, With Range of Temperatures Measured at the Same Time at the Long-Term Sites in the Marcell Experimental Forest (April 29 to June 26, 1986)

	Temperature, °C		CH ₄ Flux, mg m ⁻² d ⁻²		
	Surface Water	Range at 10-20 cm	Mean	Median	Range
S-4 ombrotrophic open bog					
collar 1	6.2-28.1	5.9-17.6	148	102	9-601
collar 2	5.8-22.5	4.4-14.5	254	226	9-668
S-3 groundwater fen	5.1-22.1	3.8-12.1	95	80	22-263
S-2 ombrotrophic forested bog					
collar 3	8.4-15.1	4.5-10.7	23	18	6-86
collar 4	6.6-13.4	5.2-12.3	38	29	2-118

which ranged from 9 to 668 mg CH₄ m⁻² d⁻¹ (Table 2). Except for one day, fluxes at collar 2 were always higher than those at collar 1 in the same bog. Even though soil temperatures at collar 1 were slightly warmer, collar 2 was the wetter of the two sites. Lowest fluxes were observed in the forested bog S-2. Similarly, collar 3 (on a hummock and hence drier) had lower fluxes than collar 4 in the hollow except on two occasions. The range for CH₄ flux from bog S-2 was 2 to 118 mg CH₄ m⁻² d⁻¹ (Table 2). S-3 fen fluxes ranged from 22 to 263 mg CH₄ m⁻² d⁻¹, between those in the two bogs.

From late April through mid May, fluxes increased slowly at all five sites, and, except for S-4 collar 2, were well under 100 mg CH₄ m⁻² d⁻¹. Night temperatures above freezing began after May 18. From then until the end of June, fluxes increased substantially, particularly at S-4 (Figure 2).

Daily mean air temperature at all sites ranged from 2° to 23°C between the end of April and the end of June. Temperatures at the water table surface during flux measurements ranged from 6° to 28°C, and at 10 cm beneath the water table from 4° to 18°C. Figure 2 gives a running average temperature at 10 cm depth in the repeatedly sampled Marcell sites.

Water table fluctuations differed among sites. At S-4, collar 1, water table ranged from 3 cm above the peat surface to 10 cm beneath it; at collar 2 from 0 to 9 cm beneath. The range at S-3 was narrow, from 6 to 9 cm beneath the peat surface. At S-2, collar 3, the water table ranged from 35 to 43 cm beneath the peat surface, and at collar 4 the range was 0 to 15 cm beneath the *Sphagnum* surface. Collar 3 had the deepest water table and the lowest flux.

Methane concentrations in peat pore water also increased through the spring. Figure 3 shows profiles of CH₄ concentration for the three watersheds, averaged over the periods shown. In early May, CH₄ concentrations were low within the top 10 cm of peat. Surface depletion was probably due to April snowmelt, which flushed the surface of

each bog. Low temperatures helped to inhibit CH₄ from building up in surface waters. From mid-May to the end of June, pore water CH₄ profiles took on a similar shape in all three watersheds. Concentrations increased rapidly below the water surface and reached their maximum between 5 and 15 cm. For example, in S-2 in early May the average concentration over the top 10 cm of pore water was 6.7 (±3.5, n=6) μmol CH₄ L⁻¹ and 282 (±55, n=7) μmol CH₄ L⁻¹ at depths below 15 cm. By the beginning of June the surface 10 cm of pore water averaged 207 (±15, n=30) μmol CH₄ L⁻¹ compared to 254 (±8, n=30) μmol CH₄ L⁻¹ at depths below 15 cm. The surface averages for the two periods are significantly (at the 95% level) different, and the deep CH₄ concentration averages are not significantly different. Overall, peatlands S-3 and S-4 produced comparable quantities of CH₄; S-2 produced less.

Methane concentrations integrated over the top 30 cm of the water table (Figure 4) increased in early spring until late May to early June, after which they leveled off at 1311 (±46, n=25) mg CH₄ m⁻² in S-4 (average of May 26 to June 26 profiles plus or minus the standard error of the mean), 1050 (±36, n=25) mg CH₄ m⁻² in S-2 and 1485 (±91, n=9) mg CH₄ m⁻² in S-3. This illustrates that CH₄ flux (Figure 2) is controlled by near-surface phenomena and that CH₄ production and accumulation at depth in the soil or sediment may not be directly proportional to the net flux.

3.2. Spatial Variability of Methane Flux

During the summer of 1986 we surveyed CH₄ flux at other sites in northern Minnesota to extend the number and variety of boreal peatlands studied and to place data from the Marcell Experimental Forest in a wider geographical context. Arithmetic means, standard errors of the means, medians, and ranges of CH₄ fluxes measured during the survey in June (Marcell S-1, Junction Fen, Bena) and August (Red Lake), along with fluxes measured at collar sites (late May and June only), during transects

Average Soil CH_4 , Marcell

Fig. 3. Average CH_4 concentration (micromoles per liter of pore water) versus depth for four 3- to 12-day periods.

and during the diel experiment in S-4, are listed in Table 3. Summer (late May through August) fluxes from all peatlands vary over a 80-fold range from 11 to 866 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ with an overall average of $207 (\pm 13) \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ($n=179$). There is a remarkable agreement between the means and the medians over a wide range of fluxes which might suggest that the magnitude of the fluxes approaches a normal distribution.

The summer mean flux in the Marcell area peatlands, $203 \pm 17 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ ($n=120$), was not significantly different ($p < 0.01$) from the mean flux from the Red Lake peatlands, $214 (\pm 25) \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. In the Red Lake peatland, unlike Marcell, open bogs emitted the least CH_4 and fens the most (Table 3). This may be due to degree of wetness (see below). Junction Fen had the highest mean

flux, whereas the open, raised Bena Bog, had a mean flux close to the averages for Marcell and the Red Lake peatland. In general, fens produced higher fluxes than bogs.

4. DISCUSSION

4.1. Effects of Peat Characteristics on CH_4 Flux

Transects for water column CH_4 , temperature, and conductivity were run across bogs S-2 and S-4 in late May and early June and were repeated about two weeks later (see lines across the maps in Figure 1). Methane fluxes were also measured during the later transects. In S-4, transects ran from the marginal spruce forest at either end across the open bog, with stations every 15 m (May 30) or 25 m (June 14) in hollows. In the forested bog S-2, samples were spaced from 5 to 30 m. In both bogs, CH_4 fluxes and concentrations were highest at the edges. This can be seen (Figure 5) at 0 and 105 m in S-2 and 165 to 195 m in bog S-4. The largest flux of the experiment, 866 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, was observed in the edge of S-4, and two of

Fig. 4. Methane concentration in pore water, integrated over the upper 30 cm of the water table at each of the repetitive sites at Marcell and plotted against time of measurement. The repetitive collar sites are marked C.1 through C.4.

TABLE 3. Methane Fluxes From Minnesota Peatlands in June and August 1986

Site	n	Flux, mg CH ₄ m ⁻² d ⁻¹		
		Mean*	Median	Range
Marcell Experimental Forest	120	203 (±17)	138	11-866
S-1, bog (clear-cut 1975)	12	60 (±4)	66	38-85
S-2 forested bog	36	77 (±21)	37	11-694
S-3, fen (clear-cut 1973)	12	142 (±19)	129	68-263
S-4 open bog	44	294 (±30)	261	18-866
Junction Fen, open fen	16	372 (±11)	355	319-462
Bena Bog, open bog	21	218 (±16)	187	151-347
Red Lake peatland	38	214 (±25)	172	24-711
open bog sites	12	85 (±15)	77	24-190
forested bog sites	7	130 (±21)	130	45-214
fen sites	19	325 (±31)	318	152-711
Total	179	207 (±13)	165	11-866

Data include S-2 and S-4 transect data and S-4 diel data.

*Standard error of mean is given in parentheses.

three fluxes over 125 mg CH₄ m⁻² d⁻¹ in S-2 were measured in its fen lagg. In S-2, more CH₄ was measured at each site on June 6 than two weeks later; this was also true at a third of the sites in S-4. Changes in water levels were probably the cause. Both bogs were at a minimum on June 1, and within two weeks the water level had risen between 4 and 6 cm in each bog owing to precipitation. This new water was relatively depleted in CH₄, so that CH₄ standing stocks in surface waters were lower later in the month.

Areas near the edges of S-2 and S-4 not only had higher CH₄ concentrations and fluxes but also higher pore water pH values. Seven stations with pH between 4.6 and 5.0 had an integrated (1-30 cm) CH₄ stock that averaged 1640 mg m⁻², whereas 35 stations with pH between 3.7 and 4.5 averaged 563 mg m⁻² (water table depth was not significantly different in the two groups). Rates of CH₄ production measured from peat slurries [Williams and Crawford, 1984] and from acidophilic microbial communities isolated from bog peats [Goodwin and Zeikus, 1987] have been higher at pH 4.5 - 6.0 than below pH 4.5. The higher pH, CH₄ standing stock, and CH₄ flux near the edges of the bogs are presumably due to the influence of groundwater and/or upland runoff. Observation of enhanced degradation of ¹⁴C-labeled *Sphagnum* when peat slurries were amended with nitrogen or nitrogen plus phosphorus [Williams and Crawford, 1983] and higher CH₄ fluxes measured from fertilized versus unfertilized rice paddies [Cicerone and Shetter, 1981] suggest that the increased nutrient load of minerotrophic waters at bog edges might enhance the efficiency of carbon remineralization and lead to higher CH₄ production. Note that higher CH₄ fluxes from minerotrophic environments were observed in the Marcell (Junction Fen) and Red Lakes areas (Table 3).

4.2. Temperature Effects on Methane Flux

Response to temperature is similar both within bogs and between watersheds. Sites at Marcell showed a strong

dependence of CH₄ flux on temperature (Table 4, Figure 6). The best statistical fits were with temperatures taken 10 cm below the water table surface. Correlations with air temperature improved if daily mean air temperatures were used instead of those at the time of the flux measurement. Figure 6 shows CH₄ flux versus the temperature at 10 cm below the surface of the water table for Marcell sites.

To explore possible short-term variability due to diel temperature variations, on June 17, 1986, CH₄ fluxes were measured every two hours at S-4, collar 1, from 0400 to

Fig. 5. Methane fluxes and concentrations integrated over the upper 30 cm of the water table, plotted as a function of distance along transects in Marcell bogs S-2 and S-4. Transect lines are shown in Figure 1. Fluxes were measured only during the later transect in each bog.

TABLE 4. Effect of Temperature on Methane Flux Within a Variety of Methane-Producing Environments

Environment	Production or Flux	E _a , kJ/mol	Reference
Open bog (S-4, collar 1)	flux	177	this study
Open bog (S-4, collar 2)	flux	174	this study
Fen (S-3)	flux	162	this study
Forested bog (S-2, collar 3)	flux	148	this study
Forested bog (S-2, collar 4)	flux	116	this study
Peat soils	production	111–136	Svensson [1984]
Peat soil, fen	production	92–116	Westermann and Ahring [1987]
Rice paddies	flux	111	Holzappel-Pschorn and Seiler [1986]
Freshwater lake sediments	production	32–119	Kelly and Chynoweth [1981]
Freshwater lake sediments	flux	158	Kelly and Chynoweth [1981]
Coastal marine sediments	production	130–150	Crill [1984]

E_a, the apparent activation energy, is calculated either from the slope of the regression of the logarithm of the flux, or from production rate versus the inverse of absolute temperature, using the integrated form of the Arrhenius reaction rate law discussed in the text. If only a Q₁₀ is given in the reference, E_a is calculated using the given temperatures.

2000 LT. Fluxes ranged from 164 to 290 mg CH₄ m⁻² d⁻¹; averaging 238 (±15) mg CH₄ m⁻² d⁻¹. The standard error, by encompassing variability over a 16-hour period, may represent a total precision of 6% for flux measured over one day. Ambient air temperatures ranged from 0° to 20.1°C. The wide range did not affect CH₄ flux strongly, but it did affect near-surface water temperature. Surface pore water temperature varied 7° over the course of the day, with the effect damping out by 10 cm depth (variation <1%). Mean temperature at the surface (13.3°) was 0.3° warmer than at 10 cm, and was 0.5° warmer than the mean air temperature. These data were used to select the 10-cm depth for measuring temperature trends.

Table 4 lists Arrhenius activation energies (E_a) calculated for Marcell and for other sites. For a temperature increase from 10° to 20°C at 10–20 cm, CH₄ fluxes increased from 5.4 to 13 times at Marcell; apparent activation energies ranged from 116 to 177 kJ/mol. These values compare well with those from other studies, which ranged from 32 to 158 kJ/mol. Svensson's [1984] incubation experiments with peats are perhaps the most directly comparable, with E_a values of 111–136 kJ/mol. The apparent activation energies listed in Table 4 are similar to the values, 67–113 kJ/mol, for other biologically mediated anaerobic processes such as ammonium production and sulfate reduction [Aller and Yingst, 1980]. These E_a values are empirical temperature/rate expressions, whose physical meaning remains unclear in most cases because they gloss over a number of variables in the delicate balance between biological activity and substrate supply. For example, Figure 2 shows a lag period in early spring before flux rates increase. This may be due to cool temperatures.

The subsequent increase could reflect rising temperatures or, at least in part, exponential regrowth of populations of methanogenic bacteria decimated by spring freeze-thaw cycles [cf. Chapin et al., 1978].

4.3. Methane Flux and Hydrology

Fluxes listed in Table 3 are similar to those measured during a preliminary survey from northern Minnesota in August 1983, 3–1943 mg CH₄ m⁻² d⁻¹ [Harriss et al., 1985]. The range of fluxes measured at Marcell in 1983, 3–866 mg CH₄ m⁻² d⁻¹, is similar to that measured in Marcell in June 1986, 11–866 mg CH₄ m⁻² d⁻¹. Mean fluxes from both years (152 and 203 mg CH₄ m⁻² d⁻¹ for 1983 and 1986, respectively) are not significantly different at the 95% confidence level. The only significant difference was observed in watershed S-3 (WS-3 in Harriss et al. [1985]). S-3 fluxes in 1983 were very low, 3–5 mg CH₄ m⁻² d⁻¹, in contrast to 68–263 mg CH₄ m⁻² d⁻¹ in 1986. The difference is probably due to variations in hydrology at different sites and times within the fen. In 1983 the S-3 site had "visible water flow in surface peat derived from active groundwater input," whereas in 1986 the study site lacked visible flow. The high variability of the flux from watershed S-3, the low fluxes as compared to fen sites in the Red Lake peatland and Junction Fen, and the fact that S-3 is a transitional peatland with both bog and fen characteristics make extrapolations from the S-3 data to other fens uncertain. Junction Fen and the richer groundwater fens visited in the Red Lake peatland are probably more typical of northern fens.

As illustrated above in the discussion of transect data,

Fig. 6. Methane flux data from each repetitive site in the Marcell Forest plotted against temperature.

water flow through surface peat can have a direct effect on CH_4 flux at a given site. In early May, when the water table was highest in the Marcell Experimental Forest, water was moving across bog surfaces through the living *Sphagnum* layer. This top layer behaved like a saturated porous sponge. The result of high-water flood conditions is slightly higher pH and lower CH_4 concentrations in near-

surface pore waters such as those of early May in Figure 3. The relatively short residence time of the surface water in the watersheds during high discharge leaves little time for CH_4 to accumulate, and CH_4 fluxes are correspondingly lower. Once the water table falls and the residence time of bog water increases, CH_4 accumulates in the pore water (Figures 3 and 4) and fluxes increase.

A crude estimate of the influence of water flow through bogs S-2 and S-4 to their respective CH_4 fluxes can be made by regressing the log of the CH_4 flux against 5-day running averages of daily mean streamflow exiting the bogs and mean air temperature. The use of streamflow data is rather crude, because it does not take into account actual flow across the slightly domed centers of the bogs, residence time of the bog water, or losses of water via evaporation and transpiration. In both bogs, streamflow and temperature make statistically significant contributions to the methane flux ($p < 0.05$, $n = 24$). Together these parameters explain 78% and 74% of flux variation in S-2 and S-4, respectively, with streamflow contributing only 4% and 8%. Higher streamflows are associated with lower fluxes as discussed above. Although the effect of streamflow on flux is significant, it is a second-order effect. Other water-related parameters such as residence time may have a greater effect.

Seasonal changes in water table make it difficult to separate the effects of the degree of decomposition of water-logged peat from the effects of temperature on CH_4 flux. The degree of decomposition of a peat soil is frequently indicated by the von Post humification scale [Korpikajko and Woolnough, 1977]; the larger the index number, the greater the decomposition. However, the following comparison suggests that the role of decomposition deserves study in this context. When changes in spring temperature began to slow in late May and early June, the top of the water table under the hollow site in S-2 (collar 4) fluctuated between zones in the peat column where the humification index was H-2 and H-3. In August at Red Lake, about half the fen sites had surface water in H-2 peats, the other half in H-3 peats. Methane fluxes from both environments were higher when the tops of the flooded soils were more decomposed. Fluxes averaged $27 (\pm 2.3)$ and $53 (\pm 6.5) \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ for H-2 peats at the top of

TABLE 5. Methane Flux Along a Latitudinal Gradient

Site	Latitude, °N	Methane Flux,* $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$	n
Corkscrew swamp, Florida	26	128 ± 78	11
Okefenokee swamp, Georgia	30	141 ± 41	12
Mountain bogs, West Virginia	39	251 ± 78	14
This study, Minnesota	47	207 ± 13	179
Fen and marsh, Alaska	62	196 ± 28	13

Measurements are from soils with surface peat layers greater than 50 cm and no permafrost. All but the Alaska and Florida sites are *Sphagnum* peats. The measurements were made by the Langley Research Center group using techniques described in section 2.2.

*Plus or minus standard error.

the water table in S-2 and the Red Lake fens, respectively. When more decomposed H-3 peats were the topmost waterlogged layers, fluxes averaged $47 (\pm 8.9)$ and $154 (\pm 14.7)$ $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ for S-2 and the Red Lake fens.

Fluxes in the Red Lake fens were significantly higher ($p < 0.01$), averaging about 3 times those in the Red Lake bogs. Water table in the fens averaged 8 cm above the peat surface, whereas in the bogs it averaged 18 cm below the living moss surface, providing a considerable depth of well-aerated surface to support the activities of CH_4 -oxidizing bacteria. However, the flux difference may equally well have been caused by a better nutritional status for methanogenic bacteria in the circumneutral, minerotrophic fen peats than in the strongly acid, ombrotrophic bog peats (see section 4.1). The rather deep water table in the S-3 fen (about 8 cm beneath the peat surface) may help to explain why its fluxes are lower than those from the Red Lake fens.

4.4. Comparison With Other Sites

Although the peat-filled ice block depressions in the Marcell Experimental Forest are common in the boreal zone, they are probably less important (in total area) than the large raised bogs characteristic of glacial outwash and old glacial lake plains, of which the Bena Bog is an example. Most important are the vast paludified and patterned peatlands of the Hudson/James Bay lowland [Martini, 1982]; the smaller Red Lake peatland resembles them

but exhibits much less open water. The other major peatland complex in the boreal zone (with generally similar vegetation) is that of the West Siberian Plain between the Ob and the Yenisei Rivers [Walter, 1977].

Summer CH_4 fluxes from all the sites ranged 80-fold overall from 11–866 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (Table 3). The distribution was such that 68% of the fluxes were between 100 and 1000 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (61% between 100 and 500 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$). The highest rates were from open sites at the Marcell S-4 bog and Junction Fen and from circumneutral fen sites in the Red Lake peatland. Differences between average and median CH_4 flux rates only vary by 6–65 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ across the wide range of peatlands sampled (Table 3). Forested bog sites in Marcell S-2 and the Red Lake peatland were consistently low.

There are few comparable data on CH_4 flux from northern areas. Methane emissions from 0.3 to 950 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ were reported from ombrotrophic and minerotrophic peatlands in Sweden [Svensson, 1974, 1980; Svensson et al., 1975; Svensson and Rosswall, 1984]. Moore and Knowles [1987] reported fluxes of 0–112 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ from subarctic fens. Sebacher et al. [1986] observed average fluxes (plus or minus the standard errors) of 106 ± 5 and 289 ± 14 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ from Alaskan boreal marsh and fen, respectively. Table 5 shows average CH_4 flux rates (plus or minus the standard errors) that we have measured in a variety of peatlands from 26.5°N to above 62°N ; they range between 128 and 251 $\text{mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. The sites in Florida, Georgia and West Virginia were very wet.

In order to model annual CH_4 fluxes, average values should be weighted to include the effects of parameters observed to affect CH_4 flux, for example, temperature, wetness, and mineral content of pore waters. A simple example, using seasonal temperature observations at the Marcell forested bog S-1 [Brown, 1976] and the empirical temperature/flux relationship observed in bogs S-2 and S-4 during this study, is shown in Figure 7. The solid line is the modeled flux rate for each bog using the temperature 30 cm beneath the peat surface in bog S-1 during 1970 (it was then forested). The 30-cm peat depth is roughly that at which our temperature measurements were made, 10 cm below the water table surface. The fluxes observed in 1986 fit the estimated fluxes quite well, particularly in S-2 (also a forested bog). The fact that S-4 warmed more quickly after snowmelt is obvious from the earlier increase in fluxes in 1986. Integrating under the derived flux curve from spring thaw, around April 15, to autumn freeze, around November 15, gives annual emission of 12 g $\text{CH}_4 \text{ m}^{-2}$ in S-2 and 58 g $\text{CH}_4 \text{ m}^{-2}$ in S-4. We can compare these estimates to annual fluxes calculated by multiplying the June means for S-2 and S-4 (Table 3) by an assumed season of 150 days. The results are annual fluxes of 12 and 44 g $\text{CH}_4 \text{ m}^{-2}$ for S-2 and S-4, respectively, quite similar to the modeled fluxes.

4.5. Relationship of CH_4 Flux to Primary Production, Decomposition, and Peat Accumulation

The mean flux plus or minus the standard error of the mean for all sites in northern Minnesota during June and

Fig. 7. Methane fluxes (J) for Marcell bogs S-2 and S-4, modeled for an entire year using the temperature (T) response of the flux illustrated in Figure 7 and temperature data of Brown [1976] measured 30 cm below the peat surface in the nearby ombrotrophic Marcell bog S-1. The equations are $J = \exp[-15257.9(1/T)] + 57.2$ for S-2 and $J = \exp[-17893.0(1/T)] + 67.9$ for S-4. The 1986 flux measurements, and the mean and range for our August 1983 flux measurements in the same bogs, are included.

August including the transect and diel data in Marcell ($n=179$) is $207 \pm 13 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. That CH_4 flux over 150 days would give an annual methane flux of about $23 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$, 7.5% of estimated net primary production by northern peatland plants, $307 \text{ g C m}^{-2} \text{ yr}^{-1}$, and equal to the estimated rate of peat accumulation in undrained northern peatlands, $24 \text{ g C m}^{-2} \text{ yr}^{-1}$ [Gorham, 1988]. If we assume that anaerobic $\text{CH}_4\text{-C}$ production is balanced by an equal amount of anaerobically produced $\text{CO}_2\text{-C}$, and that net primary production minus peat accumulation equals total aerobic plus anaerobic decomposition, then anaerobic losses of carbon, about $46 \text{ g C m}^{-2} \text{ yr}^{-1}$, are about 19% of the estimated aerobic losses, $237 \text{ g C m}^{-2} \text{ yr}^{-1}$.

4.6. Boreal Peatlands as a Source of Methane to the Troposphere

Our measured flux rates indicate that boreal peatlands are a significant source of biogenic CH_4 to the troposphere. The average flux reported here, $207 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, if it occurred over the total area of peatlands north of 40° for 120 days of the year, would yield $72 \text{ Tg CH}_4 \text{ yr}^{-1}$ to the atmosphere. Using a larger estimate for undrained northern peatlands, $3.56 \times 10^{12} \text{ m}^2$ [Gorham, 1988], that yield becomes $88 \text{ Tg CH}_4 \text{ yr}^{-1}$. These fluxes are 24–46% of Ehhlalt and Schmidt's [1978] estimates of total wetland CH_4 flux, 190–303 $\text{Tg CH}_4 \text{ yr}^{-1}$, and are higher than Matthews and Fung's [1987] estimate of 62 $\text{Tg CH}_4 \text{ yr}^{-1}$ from peatlands between 50° and 70°N . Given that a molecule of CH_4 is about 20 times as effective as a CO_2 molecule in "greenhouse" warming [Mooney et al., 1987; cf. Ramanathan et al., 1987], $75\text{--}90 \text{ Tg CH}_4 \text{ yr}^{-1}$ ($=56\text{--}67.5 \text{ Tg CH}_4\text{-C yr}^{-1}$) would have an effect equivalent to $1125\text{--}1350 \text{ Tg CO}_2\text{-C yr}^{-1}$, or 22–26% of the 5200 $\text{Tg CO}_2\text{-C}$ emitted to the atmosphere annually by fossil fuel combustion [Bolin et al., 1983].

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