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LETTER

Radiocarbon evidence for the substrates supporting methane formation within northern Minnesota peatlands

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Abstract—Bogs and fens from northern Minnesota produce large quantities of CH_4, which may be either emitted to the atmosphere or stored in below-ground reservoirs. The identity of the organic materials that support CH_4 production has been uncertain, but we present evidence that a significant fraction of surface emission and below-ground CH_4 is derived from recently fixed organic compounds. First, the CH_4 emitted from both bogs and fens has a ^{14}C signature equivalent to contemporary values for atmospheric CO_2. Second, in flooded fens rates of CH_4 emission are linearly related to rates of CO_2 exchange and to the $\delta^{13}C$ of emitted CH_4. Third, peat-porewaters as deep as several meters below the surface contain mixtures of CH_4 derived from both modern and older organic substrates. The source of the modern organic substrates is most likely dissolved organic compounds produced from the decay of recently produced litter, roots and root exudation products and transported into deeper layers of the peat. These data indicate that CH_4 emissions are closely linked to the living vegetation and hydrology of northern peatlands and less dependent on the lability and decomposition of peat within the deeper layers of the catotelm.

1. INTRODUCTION

Wetlands are major contributors to the atmospheric CH_4 budget (Cicerone and Oremland, 1988). Their greatest areal extent is at northern latitudes (Aselman and Crutzen, 1989). Peatlands make up 85% of Canadian wetlands (Roulet et al., 1993) and most of the wetlands above 45°N (Matthews and Fung, 1987). The Glacial Lake Agassiz peatlands cover over 20,000 ha of northwestern Minnesota, USA, forming one of the largest semicontinuous peatlands in North America (Wright et al., 1992). These peatlands contain massive raised bogs and patterned fens and are noted because their rates of CH_4 emission (Crill et al., 1992, 1988; Dise, 1993) are 5 to 15 times higher than those reported for nearby Canadian peatlands of the Hudson Bay lowlands (Moore and Knowles, 1990; Moore et al., 1990, 1994; Roulet et al., 1994; Klinger et al., 1994). The porewaters of the Minnesota bogs and fens also contain high concentrations of CH_4 that accumulate during droughts and apparently are released in episodic pulses following the return of normal precipitation patterns (Romanowicz et al., 1993, 1995). Similar seasonal changes involving lower concentrations of porewater CH_4 have been reported from other northern peatlands (Moore et al., 1990; Windsor et al., 1992). The source of the higher values for emitted and porewater CH_4 from the Minnesota peatlands has been unknown, but radiocarbon and emission data support the hypothesis that a significant proportion of CH_4 in these peatlands is produced from organic compounds recently fixed by photosynthesis.

2. METHODS

During July and August, 1991, we sampled bogs and fens throughout a 7,680 km^2 study area within the Glacial Lake Agassiz region of northern Minnesota. Access to these areas was obtained via helicopter. The differing peat landforms are characterized by their distinctive water chemistry and vegetation patterns (Glaser et al., 1981; Glaser, 1992). The bogs have convex profiles in cross section and receive all of their surface water from precipitation. Specific conductivity is low (<100 μmhos cm^{-1}), pH is low (3.8 to 4.2) and dissolved calcium is less than 2 mg L^{-1} (Glaser et al., 1990). The bog vegetation is dominated by *Sphagnum* with *Picea mariana* in forested areas and *Carex oligosperma* in non forested lawns. The water table is generally below the peat surface in bogs and above the surface in fens or water tracks. Due to the addition of groundwater, conductivity, Ca concentrations and pH are higher in fens (>200 μmhos cm^{-1}, >2 mg L^{-1}, and 5.5–6.5, (Romanowicz et al., 1995). Fens are dominated by the sedges *Carex lasiocarpa*, *C. livida* and *Rhynchospora alba*.

Gas exchange measurements for CH_4 and CO_2 were performed in clear Plexiglas chambers placed upon aluminum frames (collars). Air within the chamber was stirred with a 12 volt fan. Samples of chamber air were collected at 5 min intervals by syringe for CH_4 analysis, injected into evacuated hypovials with butyl rubber stoppers, pressurized to 2 atmospheres and analyzed within 7 days on a Shimadzu mini-2 gas chromatograph with a flame ionization detector. Standards and ambient air were packaged similarly and run along with the samples. Some CH_4 emission measurements were made in a metal cham-

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Table 1. ^{14}C content of emitted methane collected in chambers. The term pMC, percent modern carbon, is calculated as ($\Delta^{14}C$/1000+1)*100)

site	$\delta^{13}C$ o/oo	$\Delta^{14}C$ o/oo	pMC
BOGS			
Fairland	-71.9	+160.6 (8.7)	116
Red Lake 4	-62.3	+139.6 (7.7)	114
Sturgeon	-73.5	+135.4 (6.9)	114
Mean of 3 bogs		+145.2 ± 13.5	
FENS			
Western water tract	-63.5	+149.1 (10)	115
Western water tract	-65.6	+154.8 (8.8)	115
Red Lake 4 water Tract	-69.0	+141.8 (6.9)	114
Mean of 3 fen samples		+148.6 ± 6.5	
Mean of 6 samples		+146.9 ± 9.7	

ber, but systematic differences between the two chamber types were not observed (see also Chanton et al., 1992, 1993). Emitted CH_4 was sampled from chambers for isotopic analysis following the methods described in Chanton et al. (1992). Carbon dioxide exchange was determined by measuring CO_2 concentration within the clear chamber every second over 30 to 45 second intervals using a LICOR model 6200 photosynthesis system (Whiting et al., 1991; Whiting and Chanton, 1992). Because of helicopter time constraints, only full sun and respiration CO_2 exchange measurements were made. Total system respiration was measured by shrouding the chamber with a black out cloth.

Porewaters were sampled from piezometers installed at 0.5 m sampling intervals from the water table surface to the underlying mineral soil. Water was pumped from depth with a peristaltic pump at the minimum speed necessary to draw a continuous column of bubble free water. Porewater CH_4 for isotopic analysis was collected in 50 mL syringes, extracted twice with ambient air, and transferred to vials fitted with butyl rubber stoppers.

Methane samples were prepared for isotopic analysis as described in Chanton et al. (1992), by combustion of CH_4 over copper oxide at 800°C in a helium gas stream and cryogenic trapping of produced CO_2. Samples were sealed into 6 mm diameter breakseals and run on a Finnigan MAT Delta E isotopic ratio mass spectrometer. Selected samples of CH_4, collected and combusted to CO_2 as described above, were further converted to graphite (Vogel et al., 1987) for ^{14}C analysis conducted by AMS (accelerator mass spectrometry) at the Lawrence Livermore National Laboratory Center for AMS. Peat cores were collected with a modified Livingstone peat sampler (Wright et al., 1984) and the ^{14}C activity in bulk peat samples was determined by conventional counting procedures (Beta Analytic Inc.). All C-14 data were corrected for fractionation effects by measuring the sample $^{13}C/^{12}C$ ratio and normalizing the C-14 results to a common $\delta^{13}C$ of −25‰.

3. RESULTS AND DISCUSSION

Three lines of evidence indicate that a significant proportion of the CH_4 in these peatlands is derived from recently fixed organic compounds. First, the CH_4 emitted to the atmosphere was always modern ($\Delta^{14}C$, +146.9 ± 9.7‰, n = 6, 114–115 % modern carbon, pMC, Table 1) in agreement with other studies (Wahlen et al., 1989; Quay et al., 1991). The $\Delta^{14}C$ content of the CH_4 emitted from the surface in both bogs and fens was statistically equivalent. Analysis of trends in the $\Delta^{14}C$ of atmospheric CO_2 yields a value of +155‰ at several northern hemisphere locations in the beginning of 1990 (Levin et al., 1992). Extrapolating linearly, from a mean rate of decrease of $\Delta^{14}C$ of −9.7‰ y^{-1} (Levin et al., 1992), yields an estimated value for the $\Delta^{14}C$ content of atmospheric CO_2 of +140‰ (114 pMC) for the time of sampling, in the summer of 1991. The similarity of the $\Delta^{14}C$ values for contemporaneous atmospheric CO_2 and CH_4 emitted from the Lake Aggasiz peatland is consistent with the hypothesis that the CH_4 was produced from recently fixed organic materials. It is even possible that some coupling between organic production and decomposition to CH_4 occurs within the same season. Recent results of pulse labeling experiments in rice have shown that during periods of peak production up to 72–100% of methane emitted from rice was from carbon fixed via photosynthesis within the same season (Minoda and Kimura, 1994). However, while the observed ^{14}C content of emitted methane is consistent with our hypothesis, other explanations can be derived.

Additional support to the hypothesis is offered by the relationship of CH_4 emission to CO_2 exchange (Fig. 1). In the

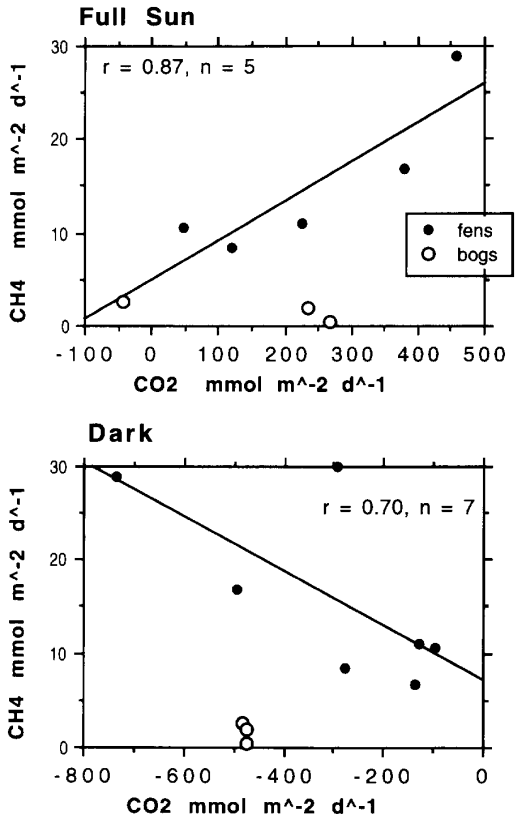

FIG. 1. Methane emission rate (y axis, mmol CH_4 m^{-2} d^{-1}) vs. the exchange of CO_2 (x axis, mmol m^{-2} d^{-1}) under full sun (upper panel) and dark (shrouded, lower panel) conditions. Filled symbols represent fens (water table above the surface), while open symbols represent bogs (water table was below the surface). Positive values for CH_4 denote emission from the surface to the atmosphere, positive values for CO_2 denote surface uptake and negative values denote surface CO_2 release. Carbon dioxide release under dark conditions was due mostly to vascular plant respiration rather than to heterotrophic microbial respiration, for the sites that exhibited the strongest CO_2 uptake under sunlit conditions also exhibited the strongest CO_2 release under dark conditions. More dark measurements were made than full sun measurements due to several cloudy days.

flooded-fen sites, CH_4 emission was related linearly with CO_2 uptake under light conditions and with CO_2 release under dark conditions, indicating that CH_4 emission was related to living plant biomass. These results are similar to those reported from a variety of flooded wetlands (Whiting et al., 1991; Whiting and Chanton, 1992, 1993). Bog sites, in contrast, emitted little CH_4 during the 1991 sampling period because the water table was depressed below the peat surface following the end of an extreme multi-year drought. Seasonal droughts have had a similar effect on CH_4 emissions and water-table elevations in other peatlands (Roulet et al., 1993; Bubier et al., 1993). At these sites lower CH_4 emission was attributed to CH_4 oxidation within an unsaturated peat-layer through which CH_4 must transit on its way to the atmosphere from the deeper saturated sites of production (Flechner and Hemond, 1992). Lower water tables may also accelerate the decomposition of labile carbon substrates through aerobic respiratory pathways, with the result that less carbon substrates are available for methanogenesis. As will be discussed below, this factor may be responsible for dramatic differences in the ^{14}C content of porewater CH_4 between bogs and fens.

Although our sampling in 1991 was conducted at the end of a drought, porewater chemistry at depth primarily reflected a recharge (downwelling) pattern caused by precipitation that occurred during the previous wet years (Siegel et al., 1995). Apparently there is a lag phase of about 4 years in groundwater flow patterns in response to local rainfall. Our hydrologic data indicate that the modern DOC in the deeper pore fluids must be very recent origin (<10 years, Siegel et al., 1995). In 1981–1982, circumneutral groundwater had completely flushed the pore fluids from the peat profile (except for the uppermost meter of peat where groundwater was still mixing with precipitation). During the next decade (1983–1990) the bog's flow system reversed from a prevailing discharge to a recharge flow-regime. Meteoric waters then penetrated deeply into the peat profiles and slowly flushed the pore fluids. Modern DOC was probably advected downward during this time. It should take 8–10 years to completely flush the pore fluids in the deeper peat (Siegel et al., 1995; Siegel and Glaser, 1987).

Methane emission rates were also related to the $\delta^{13}C$ of emitted CH_4 at flooded fen sites (Fig. 2). As CH_4 emission rates increased, the CH_4 became increasingly enriched in ^{13}C. Relationships between $\delta^{13}C$ and emission rates have been observed previously on a seasonal basis (Tyler et al., 1994; Kelley et al., 1992; Chanton and Martens, 1988; Martens et al., 1986) and have generally been attributed to seasonal variations in CH_4 production mechanism. Increasing the importance of acetate fermentation (relative to CO_2 reduction, which is the main alternative methane generation pathway) leads to ^{13}C enriched CH_4 (Whiticar et al., 1986; Burke et al., 1988). The observed relationship (Fig. 2) between increasing ^{13}C and CH_4 emission rate indicates the importance of living plant biomass in controlling CH_4 emission, because in the degradation of fresh organic matter, the acetate cleavage pathway of methane production is thought to dominate over CO_2 reduction (Sugimoto and Wada, 1993; Schoell, 1988). The greater importance of acetate fermentation in vegetated wetlands has also been inferred in lake edge environments in Alaska (Martens et al., 1992).

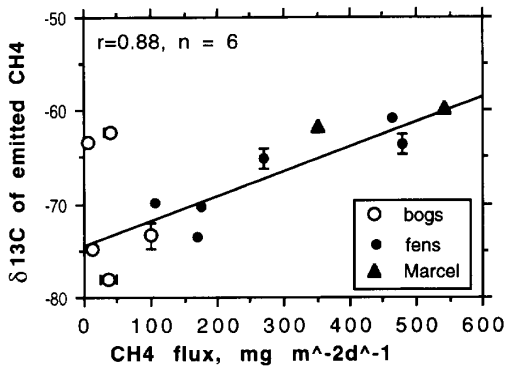

FIG. 2. Methane emission rate (x axis, mg CH_4 m^{-2} d^{-1}) vs. the $\delta^{13}C$ of emitted CH_4 captured in chambers. Filled symbols represent fens and open symbols represent bogs. The linear regression is through the filled circles only. Bog sites and Marcell fen data (data from July and August, Kelley et al., 1992) are shown for comparison only. At three bog sites, the ^{13}C composition of emitted CH_4 fit the trend exhibited by the flooded fen sites; at low flux rates the CH_4 was depleted in ^{13}C. Methane relatively enriched in ^{13}C was released at low rates from two bogs suggesting the occurrence of CH_4 oxidation in the unsaturated zone.

The third factor supporting the hypothesis is that porewater CH_4 in bogs and fens was enriched in ^{14}C relative to peat at the same depth horizon (Fig. 3) (Aravena et al., 1993; Charman et al., 1994). In fens, the CH_4 had a ^{14}C age of less than 500 years to depths of 2 m and was 1000 to 2000 years younger than the surrounding peat for each sample. Bog porewater CH_4 was also consistently 1000–1500 years younger than the surrounding peat. These data can be explained best if the CH_4 pool at any depth contains a mixture derived from both "old" peat carbon and recently fixed organic compounds transported downward from surficial sites of production. Using a mixing model (Bowman, 1990) with the ^{14}C activity of the peat at each depth and the emitted CH_4 as endmember values for old and modern carbon respectively, we calculated that the fraction of the porewater CH_4 produced from recently fixed organic carbon ranged from surficial (1 m) values of 50 to 75% in fens to 35 to 45% in bogs (Fig. 4). Even at depths of 3 m in both types of peatland, porewater CH_4 still contained 10 to 25% recently fixed carbon . While the steady state methane emissions we observed from these peatlands was composed of modern carbon, somewhat older methane could be released on occasion from the deeper layers of the peat in episodic pulses (Romanowicz et al., 1995).

These findings suggest that the evolution of methane from the deeper anaerobic layers of the peat (catotelm, Ingram, 1983) is not indicative of the decay rate of peat within the catotelm because labile organic compounds (presumably as DOC, Charman et al., 1994) may be advected (or diffuse) from the acrotelm (upper layer) to the catotelm. Decomposition rates of catotelm peat are of great interest, because it has been assumed that peat accumulation will eventually cease, as the catotelm becomes thicker and decomposition within it eventually matches input to its surface (Clymo 1984, 1991). Our findings indicate that gas evolution from the catotelm

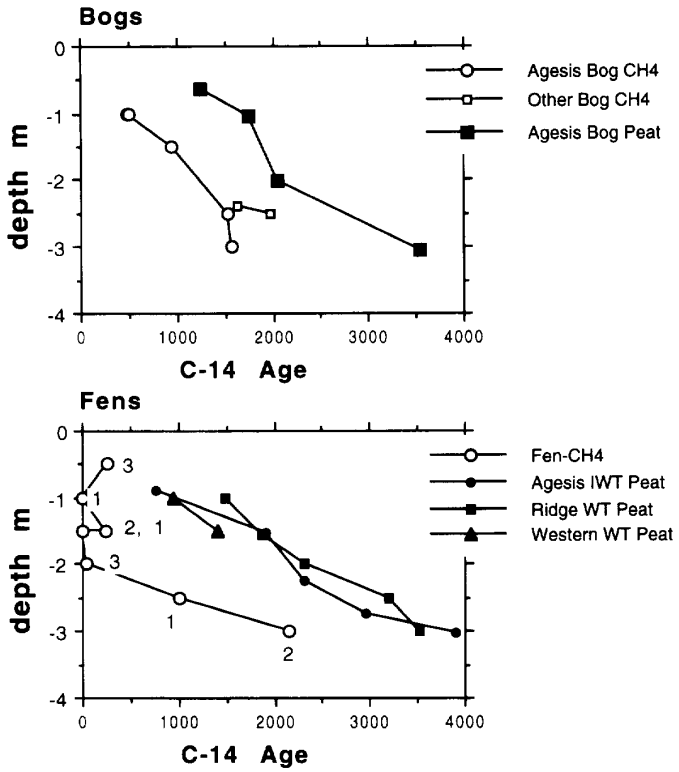

FIG. 3. The ^{14}C age of dissolved porewater CH_4 (open circles) and peat (filled symbols). Methane extracted from bog porewaters (upper panel) yielded apparent ages of 500 y at 1 m depth ($\Delta^{14}C$ −59 to −62‰) and increased to 1500 to 2000 years ($\Delta^{14}C$ −170 to −235‰) at depths from 2.5 to 3 m. Fen porewater CH_4 (lower panel) varied in age between modern and 500 y to depths of 2 m before increasing in age. Methane is significantly enriched in ^{14}C relative to peat at similar depths. Above 2 m depth, fen CH_4 is enriched in ^{14}C relative to bog CH_4. The sites for the fen samples are 1 Agesis Internal Water Track, 2 Ridge Water Track and 3 Western Water Track. IWT represents internal water track and WT represents water track.

may overestimate decomposition of catotelm peat. Alternatively, it is also possible that the ^{14}C enrichment in methane we observed in catotelm methane could be derived from the advection or diffusion of young methane from the acrotelm to the catotelm. Different isotopes diffuse according to their own gradients, independent from one another and from the bulk compound (Chanton et al., 1987).

Because the fens were characterized by the lateral flow of pore fluids in 1991 (Romanowicz et al., 1993), recently fixed organic compounds were either advected downward into the peat profile from upslope recharge zones or else the ^{14}C enriched CH_4 diffused downward. In bogs, the porewater chemistry indicates deep penetration of dilute acidic surface water during 1991 (Romanowicz et al., 1993). The concentration of Ca, for example, remained less than 3 mg l^{-1} from the water table to depths of 3 m, indicating that the pore fluids had been completely flushed by surface waters recharging downward into the peat profile. The striking difference between the radiocarbon profiles for bogs and fens indicates that a greater proportion of the recently fixed substrates were consumed by aerobic respiration within the wider oxic zone of the bogs. These data also may reflect the greater hydraulic conductivity of sedge peats (fens) relative to *Sphagnum* peats (Badmen and Eggelsmann, 1963; Chason and Siegel, 1986) or greater production of labile dissolved organic carbon in fens.

4. CONCLUSIONS

Methanogenesis in large peatlands may be more closely linked to the living vegetation and hydrology than to the litter quality of the underlying peat itself. A significant fraction of the methane produced, emitted and stored within these peatlands is derived from recently fixed organic carbon. The results of this study justify the application of remote-sensing technology to the estimation of methane emissions based upon relationships between CO_2 exchange, vegetation, and water inundation (Aselman and Crutzen 1989, Whiting and Chanton, 1993) at least in wet inundated peatlands dominated by vascular plants (fens). In bryophyte-dominated systems (bogs), where the depth of the water table below the surface exerts a major control on rates of methane emission, remote sensing may be more difficult to apply. While the supply of

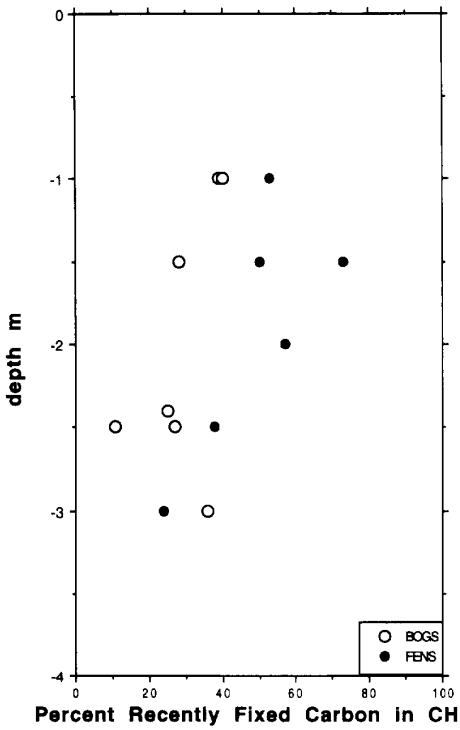

FIG. 4. The fraction of methane at depth in the peat which was formed from recently fixed carbon. The ^{14}C activity of the peat at each depth and the activity of emitted CH_4 were used as end member values for old and modern carbon respectively in a mixing model. Open symbols represent bogs while filled symbols represent fens.

the compounds supporting methane formation ultimately depends on net primary productivity, the hydrology of these peatlands determines their downward transport into the peat profile. In addition to water-table fluctuations, flow reversals from recharge (downward flow) to discharge (upward flow) or the reverse will determine the supply of these compounds within the deeper peat (Siegel and Glaser, 1987; Charman et al., 1994; Romanowicz et al., 1993).

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REFERENCES

Aravena R., Warner B. G., Charman D. J., Belyea L. R., Mathur S. P., and Dinel H. (1993) Carbon isotopic composition of deep carbon gases in an ombrogenous peatland, northwestern Ontario, Canada. *Radiocarbon* **35**, 271–276.

Aselman I. and Crutzen P. J. (1989) Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions. *J. Atmos. Chem.* **8**, 307–358.

Baden W. and Eggelsman R. (1963) Zur Durchlassigkeit der Moorboden. *Z. Kulturtech. Flurbereinig* **4**, 226–254.

Bowman S. (1990) *Radiocarbon Dating*. British Museum Publications.

Bubier J. L., Moore T. R., and Roulet N. T. (1993) Methane emissions from wetlands in the midboreal region of northern Ontario, Canada. *Ecology* **74**, 2240–2254.

Burke R. A., Martens C. S., and Sackett W. M. (1988) Seasonal variations of D/H and $^{13}C/^{12}C$ ratios of microbial methane in surface sediments. *Nature* **332**, 829–831.

Chanton J. P. and Martens C. S. (1988) Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary. *Global Biogeochem. Cycles* **2**, 289–298.

Chanton J. P., Martens C. S., and Goldhaber M. B. (1987) Biogeochemical cycling in an organic-rich coastal marine basin. 8. A sulfur isotopic budget balanced by differential diffusion across the sediment-water interface. *Geochim. Cosmochim. Acta* **51**, 1201–1208.

Chanton J. P., Whiting G. J., Showers W. J., and Crill P. M. (1992) Methane flux from *Peltandra Virginica:* stable isotope tracing and chamber effects. *Global Biogeochem. Cycles* **6**, 15–31.

Chanton J. P., Whiting G. J., Happell J. D., and Gerard G. (1993) Contrasting rates and diurnal patterns of methane emission from emergent aquatic macrophytes. *Aquatic Botany* **46**, 111–128.

Charman D. I. Aravena, R. A., and Warner B. G. (1994). Carbon dynamis in a forested peatland in northeastern Ontario, Canada. *J. Ecol.* **82**, 55–62.

Chason D. B. and Siegel D. I. (1986) Hydraulic conductivity and related physical properties of peat, Lost River peatland, northern Minnesota. *Soil Sci.* **142**, 91–99.

Cicerone R. J. and Oremland R. (1988) Biogeochemical aspects of atmospheric methane. *Global Biogeochem. Cycles* **2**, 299–327.

Clymo R. S. 1984. The Limits of Peat Bog Growth. *Phil. Trans. Royal. Soc. London* **303B**, 605–654.

Clymo R. S. (1991) Peat growth. In *Quaternary Landscapes* (ed. E. J. Cushing and L. C. Shane), pp. 76–112. Univ. Minnesota Press.

Crill P. M., Bartlett K. B., Harriss R. C., Gorham E., Verry E. S., Sebacher D. I., Madzar L., and Sanner W. (1988) Methane flux from Minnesota peatlands. *Global Biogeochem. Cycles* **2**, 371–384.

Crill P. M., Bartlett K. B., and Roulet N. (1992) Methane flux from boreal peatlans. *Suo* **43**, 173–182.

Dise N. B. (1993) Methane emissions from Minnesota peatlands: Spatial and seasonal variablility. *Global Biogeochem. Cycles* **7**, 371–384.

Flechner E. J. and Hemond H. F. (1992) Methane transport and oxidation in the unsaturated zone of a *sphagnum* peatland. *Global Biogeochem. Cycles* **6**(1), 33–44.

Glaser P. H. (1992) Raised bogs in eastern North America - regional controls for species richness and floristic assemblages. *J. Ecol.* **80**, 535–554.

Glaser P. H., Wheeler G. A., Gorham E., and Wright H. E., Jr. (1981) The patterned peatlands of the Red Lake peatland, northern Minnesota: vegetation, water chemistry, and landforms. *J. Ecol.* **315**, 575–599.

Glaser P., Janssens J. A., and Siegel D. (1990) The response of vegetation to chemical and hydrological gradients in the lost river peatland, Northern Minnesota. *J. Ecol.* **78**, 1021–1048.

Ingram H. A. P. (1983) Hydrology. In *Ecosystems of the World, 4A, Mires: Swamp, Bog, Fen and Moor* (ed. A. J. P. Gore), pp. 67–158. Elsevier.

Kelley C. A., Dise N. B., and Martens C. S. (1992) Temporal variations in the stable carbon isotopic composition of methane emitted from Minnesota peatlands. *Global Biogeochem. Cycles* **6**, 263–269.

Klinger L. F., Zimmerman P., Greenberg J. P., Heidt L. E., and Guenther A. B. (1994) Carbon trace gas fluxes along a successional gradient in the Hudson Bay lowland. *J. Geophys. Res.* **99**, 1469–1494.

Levin I., Bosinger R., Bonani G., Francey R. J., Kromer B., Munnich K. O., Suter M., Trivett N. B. A., and Wolfli W. (1992) Radiocarbon in atmospheric carbon dioxide and methane: global distribution and trends. In *Radiocarbon After Four Decades* (ed. R. E. Taylor et al.), pp. 503–518. Springer.

Martens C. S., Blair N. E., Green C. D., and Des Marais D. J. (1986) Seasonal variations in the stable carbon isotopic signature of biogenic methane in a coastal sediment. *Science* **233**, 1300–1303.

Martens C. S., Kelley C. A., and Chanton J. P. (1992) Carbon and hydrogen isotopic characterization of methane from wetlands and lakes of the Yukon-Kuskokwim Delta, western Alaska. *J. Geophys. Res.* **97**, 16,689–16,701.

Matthews E. and Fung I. (1987) Methane emission from natural wetlands: Global distribution, area, and environmental characteristics of sources. *Global Biogeochem. Cycles* **1**, 61–86.

Minoda T. and Kimura M. (1994) Contribution of photosynthesized carbon to the methane emitted from paddy fields. *Geophys. Res. Lett.* **21**, 2007–2010.

Moore T. R. and Knowles R. (1990) Methane emissions from fen, bog and swamp peatlands in Quebec. *Biogeochemistry* **11**, 45–61.

Moore T. R., Roulet N., and Knowles R. (1990) Spatial and temporal variations of methane flux from subarctic/northern boreal fens. *Global Biogeochem. Cycles* **4**, 29–46.

Moore T. R., Heyes A., and Roulet N. T. (1994) Methane emissions from wetlands, southern Hudson Bay lowland. *J. Geophys. Res.* **99**, 1455–1467.

Quay P. D., King S. L., Stutsman J., Wilbur D. O., Steele L. P., Fung I., Gammon R. H., Brown T. A., Farwell G. W., Grootes P. M., and Schmidt F. H. (1991) Carbon isotopic composition of atmospheric CH_4: Fossil and biomass burning source strengths. *Global Biogeochem. Cycles* **5**, 25–47.

Romanowicz E. A., Siegel D. I., Chanton, J. P., and Glaser P. H. (1995) Temporal variations in dissolved methane deep in the Lake Agassiz Peatlands, Minnesotsa. *Global Biogeochem. Cycles* **9**, 197–212.

Romanowicz E. A., Siegel D. I., and Glaser P. H. (1993) Hydraulic reversals and episodic methane emissions during drought cycles in mires. *Geology* **21**, 231–234.

Roulet N. T., Ash R., and Moore T. R. (1992) Low boreal wetlands as a source of atmospheric methane. *J. Geophys. Res.* **97**, 3739–3749.

Roulet N. T., Ash R., Quinton W., and Moore T. (1993) Methane flux from drained northern peatlands: effect of a persistent water table lowering on flux. *Global Biogeochem. Cycles* **7**, 749–769.

Roulet N. T., Jano A., Kelly C. A., Klinger L. F., Moore T. R., Protz R., Ritter J., and Rouse W. (1994) Role of the Hudson Bay lowland as a source of atmospheric methane. *J. Geophys. Res.* **99**, 1439–1454.

Schoell M. (1988) Multiple origins of methane in the earth. *Chem. Geol.* **71**, 1–10.

Siegel D. I., Reeve A. S., Glaser P. H., and Romanowicz E. A. (1995) Climate-driven flushing of pore water in peatlands. *Nature* **374**, 531–533.

Siegel D. I. and Glaser P. H. (1987) Groundwater flow in a bog/fen complex, Lost River peatland, northern Minnesota. *J. Ecol.* **75**, 743–754.

Sugimoto A. and Wada E. (1993) Carbon isotopic composition of bacterial methane in a soil incubation experiment: contributions of acetate and CO_2/H_2. *Geochim. Cosmochim. Acta* **57**, 4015–4027.

Tyler S. C., Brailsford G., Yagi K., Minami K., and Cicerone R. J. (1994) Seasonal variations in methane flux and $\delta^{13}CH_4$ values for rice paddies in Japan and their implications. *Global Biogeochem. Cycles* **8**, 1–12.

Vogel J. S., Southon J. R., and Nelson D. E. (1987) Catalyst and binder effects in the use of filamentous graphite for AMS. *Nucl. Instrum. Methods Phys.Res.* (Sect. B) **29**, 50–56.

Wahlen M., Tanaka N., Henry R., Deck B., Zeglen J., Vogel J. S., Southon J., Shemesh A., Fairbanks R., and Broecker W. (1989) Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon. *Science* **245**, 286–290.

Whiticar M., Faber G., and Schoell (1986) Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation—isotopic evidence. *Geochim. Cosmochim. Acta* **50**, 693–709.

Whiting G. J. and Chanton J. P. (1992) Plant-dependent CH_4 emission in a subarctic Canadian fen. *Global Biogeochem. Cycles* **6** (3), 225–231.

Whiting G. J. and Chanton J. P. (1993) Primary production control of methane emission from wetlands. *Nature* **364**, 794–795.

Whiting G. J., Chanton J., Bartlett D., and Happell J. (1991) Relationships between CH_4 emission, biomass, and CO_2 exchange in a subtropical grassland. *J. Geophys. Res.* **96**, 13,067–13,071.

Windsor J., Moore T. R., and Roulet N. T. (1992) Episodic fluxes of methane from subarctic fens. *Canadian J. Soil Sci.* **72**, 44–452.

Wright H. E., Mann D. H., and Glaser P. H. (1984) Piston corers for peat and lake sediment. *Ecology* **65**, 657–659.

Wright H. E., Jr., Coffin B. A., and Aaseng N. E. (1992) *The Patterned Peatlands of Minnesota*. Univ. Minnesota Press.