Controls on CH_4 emissions from a northern peatland

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Abstract. We examined the controls on summer CH_4 emission from five sites in a peatland complex near Thompson, Manitoba, Canada, representing a minerotrophic gradient from bog to rich fen at wet sites, where the water table positions ranged from -10 to -1 cm. Average CH_4 flux, determined by static chambers on collars, ranged from 22 to 239 mg CH_4-C m^{-2} d^{-1} and was related to peat temperature. There was an inverse relationship between water table position and CH_4 flux: higher water tables led to smaller fluxes. The determination of anaerobic CH_4 production and aerobic CH_4 consumption potentials in laboratory incubations of peat samples was unable to explain much of the variation in CH_4 flux. Average net ecosystem exchange of CO_2 ranged from 1.4 to 2.5 g CO_2-C m^{-2} d^{-1} and was strongly correlated with CH_4 flux; CH_4 emission averaged 4% of CO_2 uptake. End-of-season sedge biomass was also strongly related to CH_4 flux, indicating the important role that vascular plants play in regulating CH_4 flux. Determination of isotopic signatures in peat pore water CH_4 revealed average $\delta^{13}C$ values of between -50 and -73‰ and δD of between -368 and -388‰. Sites with large CH_4 emission rates also had high CO_2 exchange rates and enriched $\delta^{13}C$ CH_4 signatures, suggesting the importance of the acetate fermentation pathway of methanogenesis. Comparison of δD and $\delta^{13}C$ signatures in pore water CH_4 revealed a slope shallow enough to suggest that oxidation is not an important overall control on CH_4 emissions at these sites, though it appeared to be important at one site. Analysis of ^{14}C in pore water CH_4 showed that most of the CH_4 was of recent origin with percent of modern carbon values of between 112 and 128%. The study has shown the importance of vascular plant activities in controlling CH_4 emissions from these wetland sites through influences on the availability of fresh plant material for methanogenesis, rhizospheric oxidation, and plant transport of CH_4.

1. Introduction

Methane (CH_4) emissions from wetlands are controlled by several factors, including water table position, which determines the degree of aerobism/anaerobism in wetland sediments [e.g., *Moore and Roulet*, 1993]; peat temperature, which controls the rates of microbial CH_4 production and oxidation [e.g., *Crill et al.*, 1993]; and substrate quality, which affects carbon mineralization [e.g., *Moore and Dalva*, 1997; *Svensson and Sundh*, 1992; *Updegraff et al.*, 1995; *Valentine et al.*, 1994]. In a boreal peatland complex, *Bubier*

et al. [1995a] were able to relate average summer CH_4 emissions to the average temperature at the water table for over 100 sites, though there was 28% unexplained variance in the regression, primarily at the wetter sites. Over shorter timescales, *Kuttunen et al.* [1996] have also shown that variations in CH_4 flux can be related to water table position and temperature.

There is also a link between plant cover and CH_4 flux. Plant communities, especially bryophytes, are good predictors of CH_4 flux, because their distribution in wetlands closely follows water table position, a major control on CH_4 production and oxidation [*Bubier et al.*, 1995b]. In addition, vascular vegetation may play an active and passive role in CH_4 emission. Carbon exuded from plant roots can act as a labile substrate which enhances methanogenesis, and some plants may act as a conduit of CH_4 from the wetland sediments to the atmosphere, bypassing oxidation in the aerobic zone [e.g., *Chanton et al.*, 1992a, b; *Dacey*, 1981; *Kelker and Chanton*, 1997; *Schimel*, 1995; *Sebacher et al.*, 1985; *Waddington et al.*, 1996; *Whiting and Chanton* 1992;

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Yavitt and Knapp, 1995]. *Whiting and Chanton* [1993] proposed that net ecosystem productivity (NEP) may be an important variable that can be used to model CH_4 flux from wetlands, based on their finding of a strong NEP:CH_4 relationship among sites ranging from northern Canada to Florida. In Finnish and Swedish mires, *Alm et al.* [1997] and *Waddington et al.* [1996] also found a relationship between net CO_2 exchange and CH_4 emission at the scale of microsites, particularly at the wetter sites.

The purpose of this study was to examine the controls on CH_4 flux from five sites at the wet end of the hydrological gradient (water table depths from -10 to -1 cm) in a diverse peatland complex within the discontinuous permafrost region of northern Canada. Several different types of measurement were used to address the issue, including (1) measurements of peat temperature, water table position, and peat water chemistry; (2) incubation experiments to compare the potential of the peat profiles to produce CH_4 under anaerobic conditions and consume CH_4 under aerobic conditions; (3) a full growing season of net ecosystem exchange (NEE) of CO_2 and CH_4 flux measurements in clear, static chambers from different plant communities within the peatland; and (4) ^{13}C and ^{14}C isotope measurements of pore water CH_4 to assess the origin and age of the CH_4. The study proposed to develop a hierarchy of factors that control CH_4 emission and to put the NEP-CH_4 flux relationship into the overall context of interacting environmental variables within a peatland environment with high water tables.

2. Methods

2.1 Study Area and Sites

This study was conducted in a large peatland complex 30 km west of Thompson, Manitoba, Canada (55°40'N, 97°52'W), in the Northern Study Area (NSA) of the Boreal Ecosystem and Atmosphere Study (BOREAS). Found within the discontinuous permafrost zone of boreal northern Manitoba, the study area contains a broad range of peatland types, including both ombrotrophic bogs and minerotrophic fens. Permafrost, while absent in the wetlands, is present in the surrounding elevated peat plateaus. The degradation of this permafrost continues to expand the wetland, creating "collapse" areas which can develop into bogs or fens, depending on the importance of groundwater influence on the site [*Zoltai*, 1993]. The climate of continental, interior Thompson is characterized by low temperatures (mean annual temperature -3.9°C) and low precipitation (mean annual precipitation 585 mm yr^{-1}). During 1994, the May to September period received 66% of the long-term precipitation, while the temperature was 1.3°C warmer than average.

Five sites within the peatland were chosen for study, representing a productivity gradient where the water table was near the surface. Major features of each site are as follows:

2.1.1. Collapse bog (CB). This is an open graminoid bog (see *Bubier et al.* [1995a] for site classification). This site was located near the margin of a collapse scar formed by the thaw of a palsa, and it has been separated from the regional ground water table. It was dominated by *Sphagnum riparium* (average 99% cover), with *Carex paupercula* and

Vaccinium oxycoccus (14 and 5% cover, respectively). Seasonal water table position averaged -1 cm, and the peat pore water had a pH of 4.0.

2.1.2. Poor fen (PF1 and 2). Two open graminoid poor fen sites were located in a collapse scar connected to the regional water table. *S. riparium* dominated at both sites (100% cover), with *Carex aquatilis* (average 27 and 22% cover in PF1 and PF2, respectively) and *Carex limosa* (average 11 and 1% cover in PF1 and PF2, respectively). Average water table depths were -10 and -8 cm, and pore water pH values were 4.3 and 4.4 for PF1 and PF2, respectively.

2.1.3. Intermediate fen (IF). The open graminoid intermediate fen had a rich growth of sedges (*C. rostrata* and *C. limosa* with average 49 and 10% cover, respectively) and *S. riparium* (10% cover). Water table position averaged -6 cm, and the pore water pH was 5.8.

2.1.4. Rich fen (RF). The open low-shrub rich fen was located adjacent to the boardwalk serving the micrometeorological tower [*Lafleur et al.*, 1997]. There was a diverse flora, with *Andromeda glaucophylla* (35% cover), *Menyanthes trifoliata* (31% cover), *Campylium stellatum* (29% cover), *Calliergon stramineum* (15% cover), *Carex chordorrhiza* (9%), and the brown mosses *Limprichtia revolvens*, *Meesia triquetra*, and *Scorpidium scorpioides* (13, 15, and 6% cover, respectively) being the main species present. Average water table position was -5 cm (though there was great seasonal variation) and the pH of pore water was 6.8. More detailed site descriptions can be found in *Bellisario* [1996] and *Bubier et al.* [1995a].

2.2. CH_4 Production and Consumption Potentials

Peat samples were taken at 10 cm increments from the peat surface to a depth of 50 cm at the five sites in August 1993 and stored in double Ziplock bags at 4°C. Anaerobic incubations were conducted by placing 5 g of wet peat from a given depth and 5 mL of distilled water in a 50 mL Erhlenmeyer flask, which was stoppered and flushed with N_2 for 25 min at a rate of 60 mL min^{-1}. The flasks were incubated under dark conditions at 21°C for 5 days. The headspace was sampled initially and then sampled after 12 and 24 hours and daily for the remaining 4 days [*Moore and Dalva*, 1997]. Triplicates of each sample were incubated, along with a control of distilled water. The CH_4 production potential was calculated from the mean increase in headspace CH_4 over the 5 days. Aerobic CH_4 consumption potential was determined by incubating samples as above, using air to which CH_4 had been added to create an initial concentration of 10,000 ppmv CH_4.

2.3. CO_2 and CH_4 Flux Measurements

A closed system was used to determine NEE of CO_2 at each of four to five collars in the five sites. The system consisted of two parts: a sampling chamber and collar arrangement and a sensor system, similar to that used by *Whiting et al.* [1992]. The chamber was a 35 cm cube, with a single open side, composed of 3 mm clear polycarbonate plastic which transmits approximately 87% of incident photosynthetically active radiation (PAR) (0.4 - 0.7 μm). During sampling, the chamber rested on polycarbonate

collars, which were cut into the peat to a depth of 10 cm in May, with 2 cm protruding above the peat surface. Sampling was conducted from boardwalks with a water seal between chamber and collar.

Instantaneous NEE was determined from changes in CO_2 concentration inside the chamber over a 2 min period. A fan inside the enclosure circulated the air, and a pump and flow regulator continuously drew gas from the enclosure through an infrared gas analyzer (LICOR 6252) at a rate of 1 L min^{-1}. CO_2 concentrations (ppmv) were recorded every 3 s with a data logger, along with temperature and relative humidity both inside and outside the enclosure, and PAR was recorded with an external quantum sensor (LICOR 190SA).

NEE measurements were made across a range of natural and induced (using neutral density films) PAR intensities, as well as under dark conditions. Relative humidity in the enclosure tended to increase rapidly during the sampling under light conditions, necessitating the measurement of CO_2 exchange within the first 30-60 s, using a minimum of five points. Linear regression of these points versus time produced the instantaneous NEE rate; if the r^2 of these data points was less than 0.87, the sampling data were discarded.

NEE measurements were made during three 10-14 day periods in 1994, coinciding with the BOREAS intensive field campaigns (IFCs). The IFC-1 measurement period fell between Julian day (JD) 157 and 166 (early June); IFC-2 period fell between JD 183 and 208 (mid-July), and IFC-3 period fell between JD 237 and 245 (late August). NEE and incident PAR measurements were fit with a rectangular hyperbola model, and separate relationships were developed to model site respiration, based on air temperature and water table position [*Bellisario et al.*, 1998]. NEE-PAR and respiration relationships were then used to model net ecosystem production (NEP), the integrated daily ecosystem production, at each collar.

CH₄ fluxes were measured once a week under dark conditions (the chamber was shrouded), independently of NEE measurements. The CO_2 sampling ports were closed, and 50 cm of 6 mm Tygon tubing was attached to a CH₄ sampling port with a 3-way stopcock, attached to a 60 ml syringe. A 10 mL sample of air from the chamber was collected four times over 12 min, with the syringe being pumped. Sites were normally sampled on the same day, coinciding with manual measurements of water table depth and peat temperature.

Analysis of the CH₄ samples took place within 8 hours of collection on a Shimadzu Mini-2 flame ionization detector, using CH₄ standards of 2 and 200 ppm. The CH₄ flux was determined from the change in CH₄ concentration over the 12 min sampling period: the minimum r^2 value for significance was 0.87, and any data which fell below this value were rejected. A positive CH₄ flux means a transfer of CH₄ from the peat surface to the atmosphere. A positive CO_2 flux represents uptake by the plants, and a negative flux indicates respiration from the site.

2.4. Biotic and Abiotic Variables Monitored

Air temperature, peat temperature, and water level position were recorded continuously at each site, and PAR was also recorded continuously at the micrometeorological tower located in the BOREAS NSA fen [*Lafleur et al.*,

1997]. Water samples for major cation analysis and pH were taken in mid-July at the same time as plant species identification and percent cover. In early September, aboveground vascular biomass was clipped from each collar and sorted into three categories: (1) *Carex* and other sedge material, (2) woody vascular leaf material, and (3) herbaceous vascular plant material. The clippings were oven dried at 60°C for 48 hours and weighed.

2.5 Carbon Isotope Sampling and Analysis

Sampling for pore water CH₄ isotopes took place once a month at selected sites by extracting water from depths of 15 and 50 cm using a 60 mL syringe attached to a stainless steel tube. In the laboratory, pore water CH₄ was then extracted into an equal volume of nitrogen (N₂) by headspace equilibration. The N₂-CH₄ gas sample was transferred into an inverted 160 mL Pierce hypovial by displacement of water and stoppered with Belco butyl rubber stoppers. About 2 - 3 mL of water was left in each vial, and the vials were then inverted and frozen until processed. Where CH₄ concentrations were too low to obtain sufficient CH₄ for analysis using the hypovial method, pore water was collected in several 60 mL syringes and transferred directly to evacuated 1 L bottles via a needle/stopcock assembly inserted into a rubber stopper in the bottle's mouth. The bottles contained 15 g of potassium hydroxide which acted as a preservative and were kept at 4°C until analyzed.

Pore water CH₄ was prepared for isotopic analysis (δD, $\delta^{13}C$, and $\delta^{14}C$) as described by *Chanton et al.* [1992a] by combustion of CH₄ over copper oxide at 800°C in a He gas stream and cryogenic trapping of produced CO_2. Samples were sealed into 6 mm diameter break seals. CH₄ samples for δD were processed with $\delta^{13}C$ samples. Water resulting from the combustion of CH₄ was trapped on an 3 mm stainless steel trap containing seven turns into and out of a pentane slush trap at approximately -130°C. This water was transferred to glass tubes containing zinc reagent purchased from Indiana University, and the tubes were sealed [*Coleman et al.*, 1982; *Kendall and Coplen*, 1985]. Reaction of the water with the zinc to form H_2 was accomplished by heating the tubes in a block heater at 500°C for 30 min. Both CO_2 and H_2 were run on a Finnigan MAT Delta S isotopic ratio mass spectrometer at Florida State University. Selected samples of CH₄, collected and combusted to CO_2 as described above, were further converted to graphite for ^{14}C analysis by accelerator mass spectrometry (AMS) at the Lawrence Livermore National Laboratory Center for AMS. All ^{14}C data were corrected for fractionation effects by measuring the sample $^{13}C/^{12}C$ ratio and normalizing the ^{14}C results to a common $\delta^{13}C$ of -25‰.

3. Results and Discussion

3.1. CH₄ Flux Summary

Seasonal average CH₄ fluxes from the five sites ranged from 10 to 500 mg CH₄-C m^{-2} d^{-1} (Figure 1), similar to or higher than those observed in other areas with the same peatland communities [e.g., *Bubier et al.*, 1993, 1995a; *Moore et al.*, 1990, 1994], despite the latter half of the 1994 summer being unusually dry. CH₄ fluxes measured along a
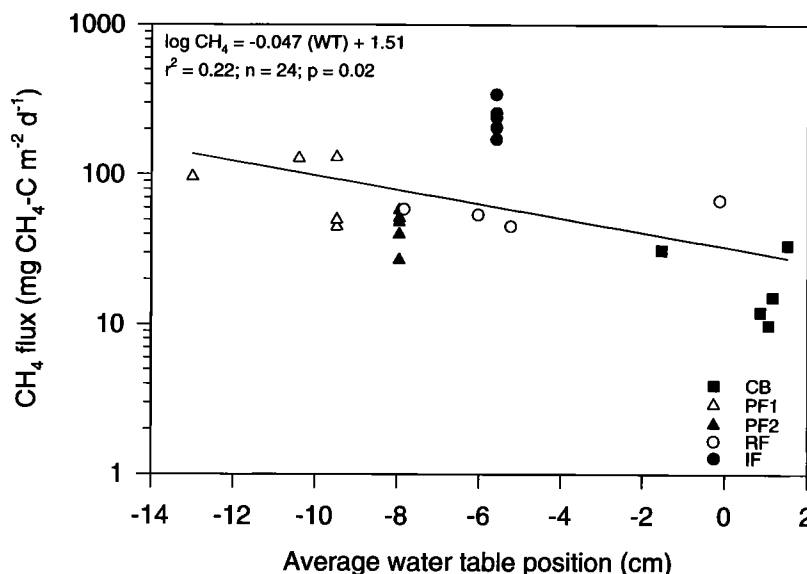
Figure 1. Seasonal average CH_4 flux as a function of average water table position for each collar, June - August 1994.

peatland productivity gradient in Alberta were closer to those measured in Thompson, ranging from 0 to 700 mg CH_4 m^{-2} d^{-1} (J. Chanton and G. Whiting, oral communication, 1995).

Within the Thompson sites, neither pore water nutrient status nor pH were significant predictors of CH_4 emissions, but the correlation between average peat temperature at 10 cm and CH_4 flux was consistent with that found by others (r^2 = 0.38, p = 0.001, and n = 24). However, the relationship between water table position and CH_4 flux was inverse to that typically observed, with a decrease in CH_4 with a water table closer to the peat surface. Although an increase in CH_4 flux occurs with a rise in water table position when a wide range of peatlands is considered (e.g., see *Bubier et al.* [1995a] for the Thompson area), these results suggest that controls other than water table position or temperature may be important in determining variations in CH_4 flux at wetland sites where the water table is close (<-15 cm) to the surface.

3.2. CH_4 Production and Consumption Potentials

Anaerobic CH_4 production potentials of peat samples to a depth of 50 cm ranged from <0.01 to >100 μg CH_4 g^{-1} d^{-1}, with the variation among sites generally greater than the variation with depth in individual profiles (Figure 2). Aerobic CH_4 consumption potentials of four profiles ranged from 4 to 58 μg CH_4 g^{-1} d^{-1}, and generally decreased with depth in the profile (Figure 2). These results are similar to those obtained by *Moore and Dalva* [1997] for a wide range of northern peatlands.

An estimate of the importance of CH_4 production in controlling field CH_4 flux was made, assuming a bulk density of the top 10, 20, and 30 cm of the profiles to be 0.05, 0.10, and 0.15 g cm^{-3}, respectively, CH_4 production

potentials only for those depths at or below the water table and exclusion of the CH_4 consumption data. A comparison of predicted and observed fluxes from four of the five sites is made in Figure 2 for CH_4 fluxes in August 1994. In general, the predicted fluxes from the CH_4 production potentials are larger than the observed field CH_4 fluxes, as may be expected because the peat samples were mixed and exposed during the incubation, the incubation temperature of $21°C$ is higher than the peat profile temperatures (except for the top 10 cm [*Bubier et al.*, 1995a]), and the CH_4 consumption capacity of the upper layers, especially above the water table, has not been included. Variations in CH_4 production potential appear to be unable to account for much of the variation in observed CH_4 flux from these peat sites at the wet end of the transect.

3.3. CH_4 Flux and Plant Productivity

Average CH_4 fluxes from each collar were regressed against modeled NEP for each IFC period and showed a strong relationship between CH_4 and NEP during IFC-1 (Figure 3). During IFC-2, most collars showed an increase in NEP, while the water table at all sites dropped, but the relationship between NEP and CH_4 remained significant. During IFC-3, the water table declined further NEP decreased as plants began to senesce, but the NEP:CH_4 flux relationship was maintained. On the basis of measurements made during the three IFC periods and interpolation based on PAR and temperatures, the seasonal average NEP of each site fell between 1.4 and 2.5 g CO_2-C m^{-2} d^{-1} [*Bellisario et al.*, 1998]. NEP values rose during the first half of the summer and then fell, with some sites (notably CB and RF) becoming an atmospheric source, rather than sink, of CO_2 by the end of August. For each collar, seasonal average NEP values ranged from 0.8 to 3.2 g CO_2-C m^{-2} d^{-1} (Figure
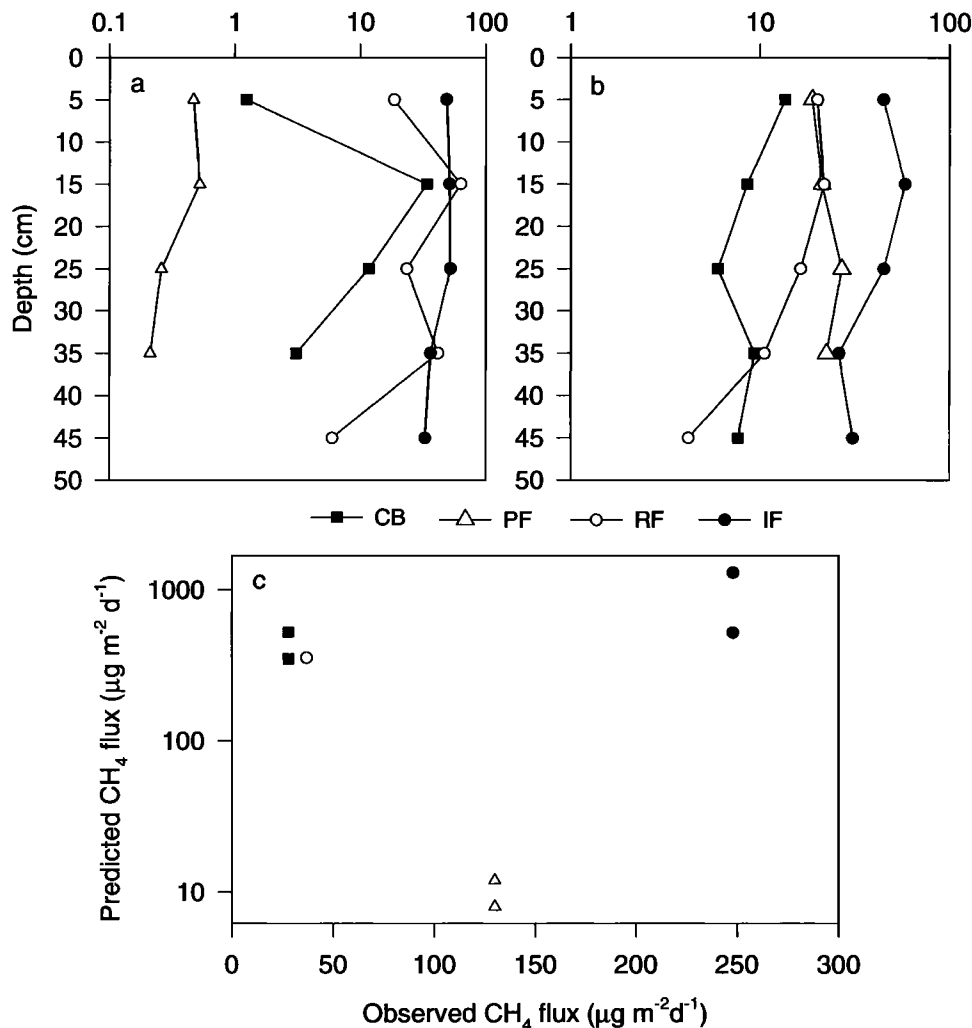
Figure 2. (a) Anaerobic CH_4 production and (b) aerobic CH_4 consumption potentials (ug CH_4 g^{-1} d^{-1}) at four sites, derived from laboratory incubations of peat samples collected to a depth of 50 cm. (c) The relationship between observed flux at the four sites and that predicted from the anaerobic incubations to a depth of 30 cm.

4). When taken as the mean seasonal values, CH_4 represented between 1.7 and 4.4% of the NEP at each site, except for the IF site, where the figure was 10.4%.

The seasonal average NEP and CH_4 fluxes for each site fell close to the overall relationship between NEP and CH_4 flux established by *Whiting and Chanton* [1993] for a wider range of wetlands in North America and by *Waddington et al.* [1996] for four lawn sites in Sweden (Figure 5). At four Finnish peatland sites, ranging from hummock to flark and lawn, *Alm et al.* [1997] also found a strong relationship between CH_4 flux and NEP during the peak production period, though the CH_4 emissions were greater for a given NEP value than found in this study and reported by *Waddington et al.* [1996] and *Whiting and Chanton* [1993]. This difference may be related to the restriction of Finnish measurements to a 4 week midsummer period. For all of the data sets, there is a strong relationship between CH_4 flux and

NEP, which represents an average of 4% of NEP (Figure 5). All sites have a high water table, except the hummocks in the *Alm et al.* [1997] work, and *Waddington et al.* [1996] note that the CH_4:NEP relationship developed in a Swedish boreal peatland held only for the lawn sites.

The end-of-season aboveground vascular plant biomass also showed a strong relationship with seasonal average CH_4 flux, especially when the sedge biomass was separated, explaining 80% of the variation in CH_4 flux among the 24 collars (Figure 6). No other vascular plant group was a significant predictor of CH_4 flux.

In clipping experiments conducted at the IF site under flooded conditions, higher fluxes were observed in the nonclipped sites, suggesting that plant-enhanced CH_4 transport was occurring [*Waddington et al.*, 1996]. Clipping of sedges close to the peat surface or water table has been observed to affect CH_4 emission rates at other sites as well
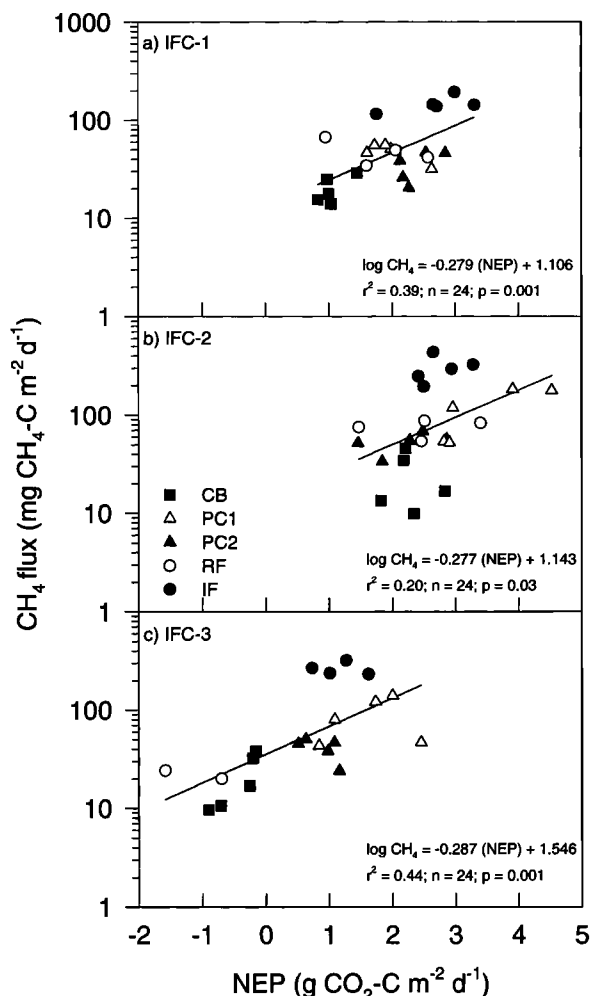
Figure 3. Relationship between CH_4 flux and mean daily modeled net ecosystem productivity (NEP) for all sites during (a) IFC-1, (b) IFC-2, and (c) IFC-3.

[e.g., *Kelker and Charlton*, 1997; *Waddington et al.*, 1996; *Whiting and Chanton*, 1992]. There are a number of reasons for the link between CH_4 flux and plant activity. It may be related to the ability of some vascular plants, such as *Carex*, to act as a conduit for CH_4 between the porewater and the atmosphere, bypassing oxidation pathways encountered by CH_4 diffusing to the peat surface. In *C. aquatilis* and *C. rostrata*, *Kelker and Chanton* [1997] have recently suggested that CH_4 transport is not limited by aboveground portions, such as leaves and stomata, but that the main limitations are belowground, at the pore water-root or root-shoot boundaries. Alternatively, plant root exudates may be suitable substrates for methanogenesis, meaning sites with higher primary productivity could support higher fluxes of CH_4 through increased belowground substrate production [e.g., *Chanton et al.*, 1995; *Holzapfel-Pschorn and Seiler*, 1986; *Seiler et al.*, 1984]. To clarify the relative importance of these possible controls, isotope analysis of pore water CH_4 was done at four of the five Thompson sites.

3.4. Stable CH₄ Isotopes

Stable CH_4 isotope signatures obtained from peat pore water samples at four sites did not show any seasonal trend within sites but did vary significantly among sites (Table 1). The CB site had the most depleted $\delta^{13}C$ signature in terms of both average (-73.3‰) as well range (-80.4 and -68.6‰). The IF site exhibited the most enriched ^{13}C signatures, with a mean of -50.0‰ and a range of -52.9 and -46.5‰. The other two sites sampled (PF1 and RF) showed intermediate $\delta^{13}C$ signatures, with means of -61.9 and -56.0‰, repectively.

These differences in $\delta^{13}C$ signatures at the extreme ends of the productivity gradient may be attributable to differences in CH_4 production pathways. Enrichment of ^{13}C in CH_4 from wetlands has generally been associated with the acetate fermentation pathway of methanogenesis, which dominates in vegetated sites [*Burke et al.*, 1988; *Blair and*
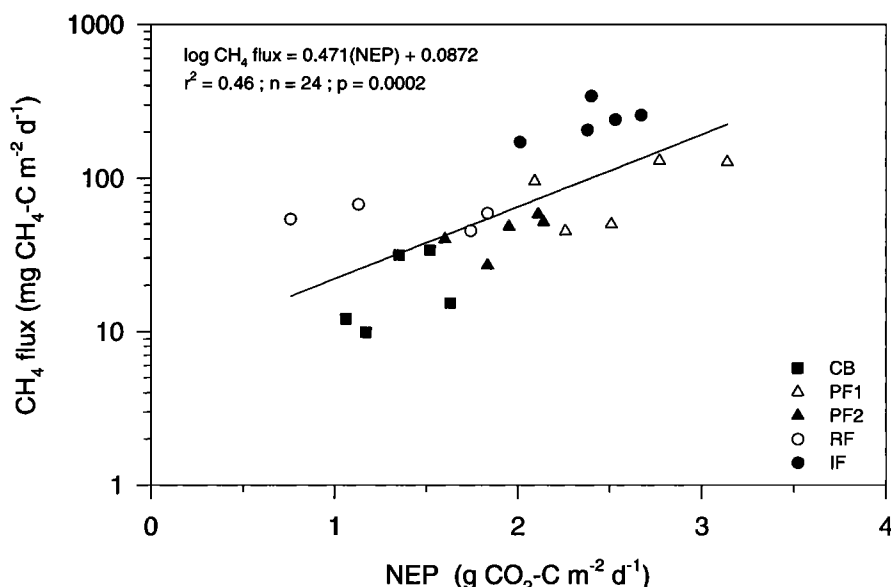

Figure 4. Seasonal average CH_4 and CO_2 (net ecosystem production) flux for collars at each of the five sites.

log CH$_4$ = 0.754 (log NEP) + 1.66
r^2= 0.47; n = 22; p < 0.0005

CH$_4$ (mg CH$_4$-C m^{-2} d^{-1})

NEP (g CO$_2$-C m^{-2} d^{-1})

▲ Thompson   □ Whiting and Chanton [1993]
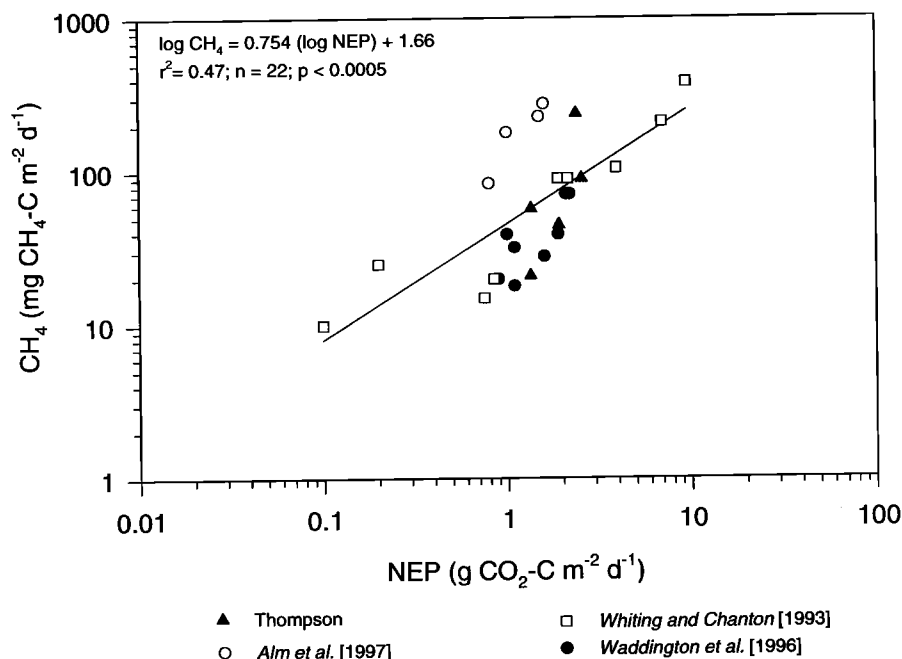○ Alm et al. [1997]   ● Waddington et al. [1996]

Figure 5. Relationship between mean seasonal CH$_4$ flux and mean seasonal NEP for the five Thompson sites. Also shown are the results of *Whiting and Chanton* [1993] for measurements made at a variety of wetland sites in North America, the mean seasonal values at four Swedish lawn sites over 2 years [*Waddington et al.*, 1996], and those made by *Alm et al.* [1997] during the peak production period at four sites in Finland.

Carter, 1992; *Sugimoto and Wada*, 1993] and with oxidation processes, which preferentially consume the lighter C and H isotopes [*Coleman et al.*, 1982; *Happell et al.*, 1993]. The acetate fermentation pathway is thought to dominate over CO$_2$ reduction when fresh organic material is utilized, as in sites with high plant productivity [*Schoell*, 1988; *Martens et al.*, 1992; *Sugimoto and Wada*, 1993]. Less productive plant

communities with more recalcitrant material tend to use the CO$_2$ reduction pathway. For example, at King's Bog, Washington state, where *Sphagnum* spp. dominate and sedges are scarce, CH$_4$ production was dominated by CO$_2$ reduction, and the δ^{13}C signature of CH$_4$ was very depleted (-74 ± 5‰) [*Lansdown et al.*, 1992].

Comparison of δD and δ^{13}C in pore water CH$_4$ for those

log CH$_4$ = 0.007 (*Carex*) + 1.22
r^2 = 0.80; n = 24; p = 0.0000

CH$_4$ flux (mg CH$_4$-C m^{-2} d^{-1})

■ CB
△ PF1
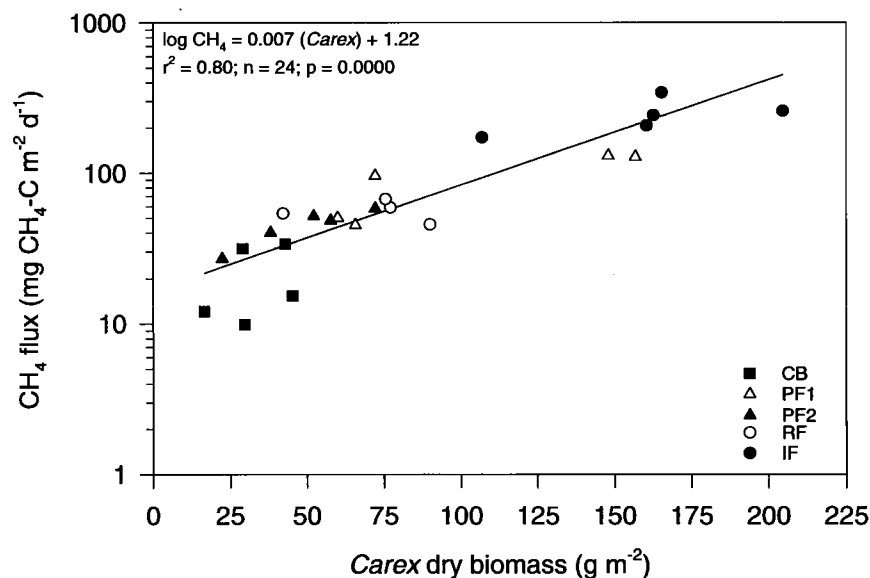▲ PF2
○ RF
● IF

Carex dry biomass (g m^{-2})

Figure 6. Relationship between seasonal mean CH$_4$ flux and end-of-season, aboveground sedge biomass for each collar at the five sites.

Table 1. Pore Water CH_4 Isotope Analyses With Sample Size and Standard Deviations and the Range of Signatures Observed (Most Depleted and Enriched)

Site	$\delta^{13}C$		δD	
	Average (n, s.d.)	Depleted (Enriched)	Average (n, s.d.)	Depleted (Enriched)
CB	-73.3 (11, 4.8)	-80.4 (-68.6)	-387.7 (11, 16.3)	-402.6 (-350.3)
PF-1	-61.9 (11, 4.8)	-70.8 (-56.4)	-378.6 (10, 11.1)	-402.9 (-364.5)
IF	-50.0 (14, 1.8)	-52.9 (-46.5)	-372.0 (13, 14.0)	-381.2 (-337.5)
RF	-56.0 (10, 5.5)	-63.0 (-52.0)	-368.1 (4, 23.1)	-407.9 (-350.3)

Values are given in per mil. Variable n denotes sample size; s.d. is standard deviation. Abbreviations are as follows: CB, collapse bog; PF, poor fen; IF, intermediate fen; and RF, rich fen.

samples with a large enough volume allows an assessment of the importance of CH_4 oxidation as a control of CH_4 emission (Figure 7). The regression of δD against $\delta^{13}C$ produced an overall slope of 0.97, much smaller than observed in other studies in which CH_4 oxidation was important. *Coleman et al.* [1981] reported slope values of 8.5 - 13.5 in laboratory incubation studies, while *Happell et al.* [1994] observed a value of about 5 for a field study. Negative $\delta D:\delta^{13}C$ slopes have been interpreted to indicate differences in CH_4 production pathways, such as acetate fermentation as opposed to CO_2 reduction [*Whiticar et al.*, 1986; *Burke et al.*, 1988]. The overall slope suggests a mixture of both oxidation and production effects: however, within sites one process may be important. For example, the

slope of $\delta D:\delta^{13}C$ at the IF site is much steeper than the other sites and suggests an important control of CH_4 oxidation (Figure 7).

Enriched $\delta^{13}C$ isotopic signatures are associated with sites exhibiting large CH_4 fluxes (Figure 8). This suggests that abundant fresh organic material at the sites with the greatest plant productivity stimulated larger CH_4 emissions via the acetate fermentation pathway. A similar pattern was found in northern Minnesota peatlands, where larger CH_4 emissions and ^{13}C enrichment were found at sites with higher plant productivity [*Chanton et al.*, 1995].

At the Thompson sites, as NEP and sedge biomass increased, we suggest that all of the following occurred: (1) there was increasing importance of acetate fermentation, relative to CO_2 reduction, in the production of CH_4; (2) there was an increase in rhizospheric CH_4 oxidation; (3) there was an increase in the ability of the plant cover to transport and emit CH_4 to the atmosphere; and (4) the combination of these processes resulted in an increase in CH_4 emission rates.

3.5. Radiocarbon

Analysis of $\delta^{14}C$ in CH_4 collected from peat pore water reveals that CH_4 was systematically enriched in bomb radiocarbon (Table 2). Analysis of trends in the $\delta^{14}C$ of atmospheric CO_2 yields a value of $+155‰$ at several Northern Hemisphere locations at the beginning of 1990 [*Levin et al.*, 1992]. Extrapolating linearly from a mean rate of decrease of ^{14}C of -9.7‰ yr^{-1} [*Levin et al.*, 1992] yields an estimated value for the $\delta^{14}C$ content of atmospheric CO_2 of $+121$ to $+111‰$ (111 to 112 percent modern carbon) for the time of sampling in the summers of 1993 and 1994, respectively. All of the Thompson peat pore water samples were enriched in radiocarbon relative to contemporaneous atmospheric CO_2, indicating the dominantly recent origin of
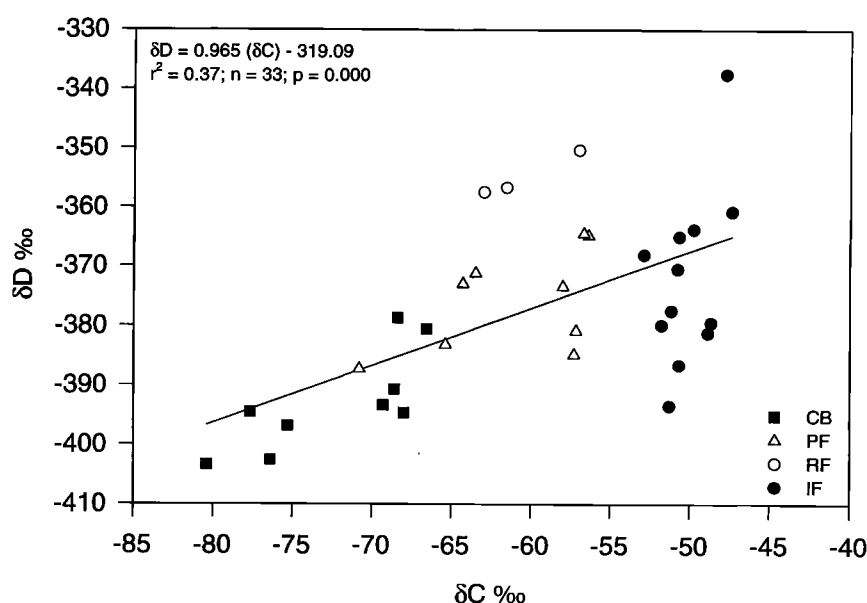

$\delta D = 0.965 \, (\delta C) - 319.09$
$r^2 = 0.37; n = 33; p = 0.000$

Figure 7. Relationship between $\delta^{13}C$ and δD for all pore water CH_4 samples containing >45 μmol CH_4 collected at the sites.
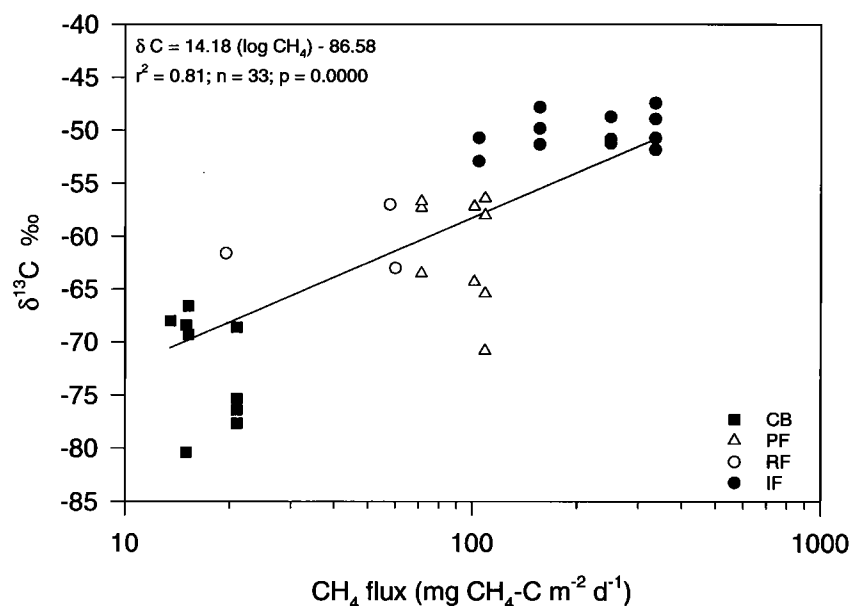
Figure 8. Relationship between $\delta^{13}C$ and mean CH_4 flux for collars at the sites.

C in CH_4. This is in agreement with other studies [e.g., *Aravena et al.*, 1993; *Chanton et al.*, 1995; *Charman et al.*, 1994; *Quay et al.* 1991; *Wahlen et al.*, 1989]. *Chanton et al.* [1995] observed that the ^{14}C content of CH_4 emitted from the glacial Lake Agassiz peatland was similar to the ^{14}C content of atmospheric CO_2. They reported ^{14}C ages for CH_4 of 0 - 350 years for samples collected at depths ranging from 0.5 to 1.0 m depth in Minnesota fens. *Aravena et al.* [1993] and *Charman et al.* [1994] reported that CH_4 collected at depths of 65-85 and 93-95 cm in Ontario peatlands had radiocarbon ages of 640 and 3440 years, respectively. When radiocarbon measurements have been conducted on CO_2 and CH_4 at the same depth in peatlands, they have been of similar age and have been thought to represent the same gas pool, or the CO_2 has been slightly older than the CH_4 [*Aravena et al.*, 1993; *Charman et al.*, 1994]. The CH_4 samples collected in our study contain higher radiocarbon contents than CH_4 samples collected in other northern peatlands.

Table 2. Radiocarbon Content of CH_4 Collected From the Peatlands

Site	Characteristics of Sample	$\delta^{13}C$, %	pMC (±)
RF moat 1	unvegetated, bubble	-68.7	118.1 (0.8)
RF moat 2	unvegetated, bubble	-68.7	119.4 (0.7)
RF moat 1	vegetated, bubble	-55.4	117.9 (0.7)
RF moat 2	vegetated, bubble	-55.4	115.3 (0.8)
RF	pore water 50 cm depth	-58.0	126.0 (0.8)
CB	vegetated, pore water, 50 cm depth	-68.9	112.2 (0.6)
CB moat	pore water, 50 cm depth	-77.0	127.5 (1.1)
PF	vegetated, pore water, 50 cm depth	-60.0	114.8 (0.7)
PF moat	pore water, 50 cm depth	-57.0	117.1 (0.8)
IF	pore water, 50 cm depth	-50.8	121.4 (1.0)

Percent modern carbon (pMC) is calculated as $[(D^{14}C/1000) + 1]/100$.

4. Conclusions

Environmental controls of CH_4 fluxes from five peatland sites at the wet end of the hydrologic gradient were examined using several different approaches. Peat temperature at a depth of 10 cm was positively correlated with CH_4 flux, but average water table position, ranging from +1 to -13 cm, revealed an increase in CH_4 flux with lower water tables, contrary to expectation. Peat profile CH_4 production and consumption potentials were unable to explain differences in flux among the sites. Significant relationships between CH_4 flux and net ecosystem production (NEP) indicated a strong link with plant-mediated activities in these *Carex*-dominated peatland communities, either through increased vascular transport or the stimulation of methanogenesis. CH_4 flux represented between 2 and 10% of NEP, with an average of 4%, similar to that found in other northern peatlands where the water table is close to the surface. The relationship between aboveground vascular plant biomass, especially sedges, suggested that *Carex* spp. play an important role in determining CH_4 flux regulation. The $\delta^{13}C$ analyses of pore water CH_4 revealed that plant production affected CH_4 emissions, as sites with large CH_4 fluxes have enriched $\delta^{13}C$ pore water CH_4 signatures. This tendency for sites with high rates of plant production to be enriched in ^{13}C is at least partly the result of differing CH_4 production pathways, as more productive sites utilize new organic C as a substrate for CH_4 production via the acetate fermentation pathway. The ^{14}C analysis of pore water CH_4 also revealed enrichment with bomb C, indicating a recent substrate origin for much of the CH_4 that has been produced in these peatlands. This study is consistent with the findings of *Whiting and Chanton* [1993] and others on the importance of plant activities in regulating CH_4 fluxes at peatland sites with high water tables. A better understanding of the role of site plant productivity as a regulator of CH_4 flux dynamics

is the first step to being able to utilize remotely sensed vegetation indices to predict CH_4 emissions now and under climate change scenarios.

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