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Winter fluxes of methane from Minnesota peatlands

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Abstract. Winter fluxes of methane were investigated in northern Minnesota during 1988—89 and 1989—90. Two bogs and a fen emitted methane throughout the snow-covered season (November through March). Fluxes decreased to a low level of 3—16 mg CH_4 m^{-2} d^{-1} in late March, reflecting decreasing peat temperatures and (in 1989—90) increasing depth of frost in the peat. Winter fluxes calculated by integration for an open poor fen, an open bog, a forested bog hollow, and a hummock site in the forested bog averaged 49, 12, 13, and 5 mg m^{-2} d^{-1}, respectively, in 1989—90 (the year most measurements were made). These comprised 11%, 4%, 15%, and 21% of total annual flux.

Introduction

The concentration of atmospheric methane has been increasing by about 1% per year (Khalil & Rasmussen 1990a). Methane is an important greenhouse gas that has, per molecule, approximately 20 times the warming effect of CO_2, and is increasing at about double the rate of CO_2 (Ramanathan 1988; Mooney et al. 1987). During the last decade it contributed about 12% to total greenhouse warming (Hansen et al. 1989). Reasons for the rapid rise in concentration are not known, but may involve a combination of an increase in human-caused sources (rice paddy agriculture, livestock, biomass burning, venting during coal and natural gas exploration), and a decrease in the main atmospheric sink, the hydroxyl radical (Cicerone & Oremland 1988; Khalil & Rasmussen 1985, 1990b). Stabilizing atmospheric methane concentration will require better information about the current sizes of sources and sinks, as well as some estimate of how environmental changes such as global warming would affect them.

Natural wetlands may comprise the largest single source of methane to the atmosphere, about 80—115 $\times$ 10^{12} g CH_4 yr^{-1}, or 15—20% of the total (Aselmann & Crutzen 1989; Matthews & Fung 1987). Estimates of flux used to compile these figures assume that methane is released only

over a 'productive season' roughly equivalent to the frost-free or snow-free period in mid- to high-latitudes, and the inundation season in the tropics and subtropics. No methane release is postulated in late fall or winter from temperate and boreal wetland regions.

This paper reports the occurrence of significant winter releases of methane from peatlands in northern Minnesota, estimates the relative contribution of winter flux to total annual flux, and suggests hypotheses to account for the observed pattern of winter release. It is part of a larger study on the annual flux of methane from Minnesota peatlands (Dise 1991; 1992). A more complete discussion of the spatial and seasonal variability in flux during a two-year period may be found in these papers. This report focusses on the unexpectedly high amounts of methane released in the winter from this area.

Study sites

The study was made at peatlands under the jurisdiction of the US Forest Service within the Marcell Experimental Forest (47° 32′ N, 93° 28′ W) in Itasca county, Minnesota. The region is a complex of small upland watersheds and kettle-hole bogs, the latter mostly forested with black spruce (*Picea mariana*) and tamarack (*Larix laricina*). Average annual temperature (1961—1990) is 3 °C and average annual precipitation is 77 cm, about 30% of which falls as snow.

The three peatlands selected for flux measurements were bogs within watersheds S2 and S4, and Junction fen. S2, the driest site, is a very slightly domed, ombrotrophic bog that is 3 ha in area and completely forested with black spruce. Porewater pH (0—40 cm) measured over a two year period averaged 3.9, with a range of 3.7—5.3 (Dise 1991). Understory vegetation is dominated by *Sphagnum angustifolium, Sphagnum magellanicum* (on drier hummocks) and *Ledum groenlandicum* (labrador tea), with *Chamaedaphne calyculata* (leatherleaf), *Eriophorum spissum* (cottongrass), *Sarracenia purpurea* (pitcher plant), and *Smilacina trifolia* (three-leafed false Solomon's seal) occurring in abundance. Methane was measured from both a hummock and a hollow in the bog; the former was the same site used by Crill et al. (1988). A third site in S2, a fen lagg surrounding the bog, released significant amounts of methane over a relatively short period in the summer only (Dise 1992), probably through the stems and leaves of macrophytes (*Calla palustris*).

S4 is a partially open 8 ha bog with a small central pond. Vegetation in the open bog area, where flux measurements were made, is dominated by *Chamaedaphne calyculata* over *Sphagnum capillifolium*, with *Carex*

oligosperma, Eriophorum virginicum and *Rhynchospora alba* the most prevalent sedges. *Larix laricina* and small *Picea mariana* are scattered, *Sarracenia purpurea* and *Menyanthes trifoliata* (buckbean) are also common. Porewater pH (0—80 cm) averaged 4.6, with a range of 3.9—6.0. Methane was measured from two hollows, one of which (collar 1) was the same site used in an earlier study (Crill 1988).

Junction fen is an open poor fen dominated by *Carex oligosperma* with some *Scheuchzeria palustris* (arrowgrass) and *Vaccinium oxycoccus* (cranberry) over *Sphagnum angustifolium, Sphagnum capillifolium,* and *Sphagnum fuscum.* Because it has no outlet and receives some runoff from surrounding uplands, it is wetter than the other two peatlands. Average porewater pH, 4.5, was similar to S4, but the 2-year range was smaller (4.1—5.6). Methane flux was measured from a slight hummock. More complete descriptions of the vegetation, hydrology and porewater chemistry of the three peatlands and the five sites are found in Crill et al. (1988), Verma et al. (1992) & Dise (1991).

The winter of 1988—89 followed the wettest year recorded since measurements began at Marcell in 1962. The snowpack at time of maximum water accumulation (early March) reached 64.5 cm., the deepest in 14 years. Heavy snowfall in late October and mid-November insulated the peat surface so that it never froze fully in bog S2 or S4, and only froze lightly (maximum depth 5 cm) in Junction fen. The winter of 1989—90 was dry, with the maximum snowpack of 42.5 cm 18% below the 1962—90 average of 52 cm. Snow cover was light through November and December, and by early December the peatlands were frozen to a depth of about 13 cm. Frost depth increased to a maximum in mid-March of ca. 25 cm in S2, 28 cm in S4, and 30 cm in Junction fen. Lenses of frost were not completely gone from the peat until May in Junction fen and S4 and June in S2.

Methods

This paper defines 'winter flux' as occurring throughout the snow-covered season, November through March. During this period in 1988—89 23 methane flux measurements were made at Marcell. The effort was nearly doubled in 1989—90, with 40 measurements made. Flux was measured with an open-bottomed aluminum chamber of dimensions 64 cm × 64 cm × 37 cm. At snow depths less than about 20 cm, the chamber was placed on aluminum collars preset in the peat and sealed with water or packed snow. Snow inside the collar over the surface was not disturbed. Later in the season when the snow was deeper it was gently removed by shovel to

about 20 cm over the peat. The chamber was then sunk to the peat surface and the edges were sealed with packed snow.

Flux was measured by sampling air from the chamber headspace with 60 cc plastic syringes, using the method described by Crill et al. (1988). Samples were taken every four minutes over a 20 minutes period (total of five syringes). Methane concentrations was measured within a few hours in the laboratory with a Shimadzu Mini 2 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard HP-3390A integrator. Flux was calculated from the slope of the concentration change over time, corrected to the surface area covered by the chamber and the 'effective volume' of the chamber (total volume of chamber reduced by the volume occupied by the peat surface and the water equivalent of the snow in the chamber). The sensitivity of this method is 0.01 ppmv CH_4 and the minimal detectable flux is 0.3 mg CH_4 m^{-2} d^{-1} (Barlett et al. 1988). Linear regressions of concentration over time were highly significant: 80% of the measurements had regression coefficients (r^2) greater than 0.99, and none were below 0.93.

Porewater samples were extracted by fitting a hollow stainless steel tube (100 cm long) onto the stopcock of a 60 cc plastic syringe with a piece of tubing. Solution was drawn at the desired depth into the syringe through a slit cut one cm above the sealed bottom of the tube. In the lab, all but 30 cc of the porewater was expelled, and 30 cc of room air was introduced into the syringe. The sample was shaken for 5 minutes, thereby stripping the methane from the water into the headspace. Crill et al. (1988) found this method effectively removed over 98% of the porewater methane within 2 minutes. The headspace sample was analyzed for CH_4 by gas chromatograph, with concentrations corrected for CH_4 in the room air. To minimize the risk of contamination, porewater syringes were rinsed thoroughly after use, and syringes used for porewater samples were not used for any other kind of sampling. Porewater methane concentration was measured in four replicate profiles (0—80 cm, 10 cm intervals) in Junction fen and S4 every 1—2 months. The amount of methane stored in the top 80 cm was estimated by multiplying concentrations by soil porosity and integrating over depth.

Long-term linearity of fluxes was tested in bog S2 and Junction fen in November and February by leaving the chamber on the snow-covered peat surface for 4—24 hours. Concentrations of methane in the chambers built up to 40—150 ppm CH_4 over this time period (20—80 times background), and flux was estimated through linear regression of methane concentration at the beginning and at the end of chamber placement. In two cases, these measurements were comparable to a 20 minute flux measurement, and in one case (in S2) the long-term estimate was roughly

double that of the 20 minute estimate on the nearest date. The reason for this unexpected higher flux is not known, but may be due to episodic releases of methane (Whalen & Reeburgh 1988), making the 20 minutes fluxes conservative estimates. This flux was the most divergent of 10 sets of such comparisons made in S2 and Junction over two years (Dise 1991).

Five flux measurements (2 in S2, 2 Junction, 1 in S4) were made by setting the chamber directly atop the snowpack in November, February and March (chamber sunk in 20—30 cm snow) to detect CH_4 release from the snow surface after emission from the bog or fen surface. The snow flux measurements were not used in other calculations, because an adequate seal could not be expected. The chamber was also set over an upland site in November 1988 to confirm that methane was emitted from the bog surface and not from air pockets in the snow. Methane concentration of air within the snow was also measured in all three wetlands throughout the winter of 1988—89. The data set for the entire study may be found in Dise (1991).

Results

All 3 peatlands emitted methane through the winter (Fig. 1, Table 1), with the highest fluxes in November and the lowest (3—16 mg CH_4 m^{-2} d^{-1}) in late March. Of the 63 measurements, one zero value was detected on 27 Feb 1990 in Bog S4 (it is not possible, with the techniques used, to distinguish a true zero flux from an inadequate seal on the chamber). No net methane consumption was detected, i.e. there were no negative fluxes. Methane flux was highest in Junction fen, lowest in the relatively dry hummock site at S2, and intermediate in the S2 hollow site and S4, following the same order as during the rest of the year (Table 2, also Dise 1992; Crill et al. 1988).

Paired *t*-tests between measurements made on the same date (+/− 4 days) in the two winters showed significantly higher fluxes in 1989—90 ($N = 13$ pairs, $t = -2.45$, $p < 0.04$). Integrating for the five months November 1989 through March 1990 (the year during which the most flux measurements were made) gave a total methane flux of 7.3 g CH_4 m^{-2} for Junction fen, 2.0 g m^{-2} for bog S2-hollow, 1.8 g m^{-2} for bog S4 (two sites averaged), and 0.7 g m^{-2} for bog S2-hummock. Mean methane fluxes for these months were 49, 13, 12 and 5 mg m^{-2} day^{-1}, respectively, comparable to mean summer (June—August) flux from the relatively dry S2 hummock site (21 mg m^{-2} day^{-1}; Table 2).

Other measurements provided corroborative evidence that these data represent actual methane release from the bog surface through the snow

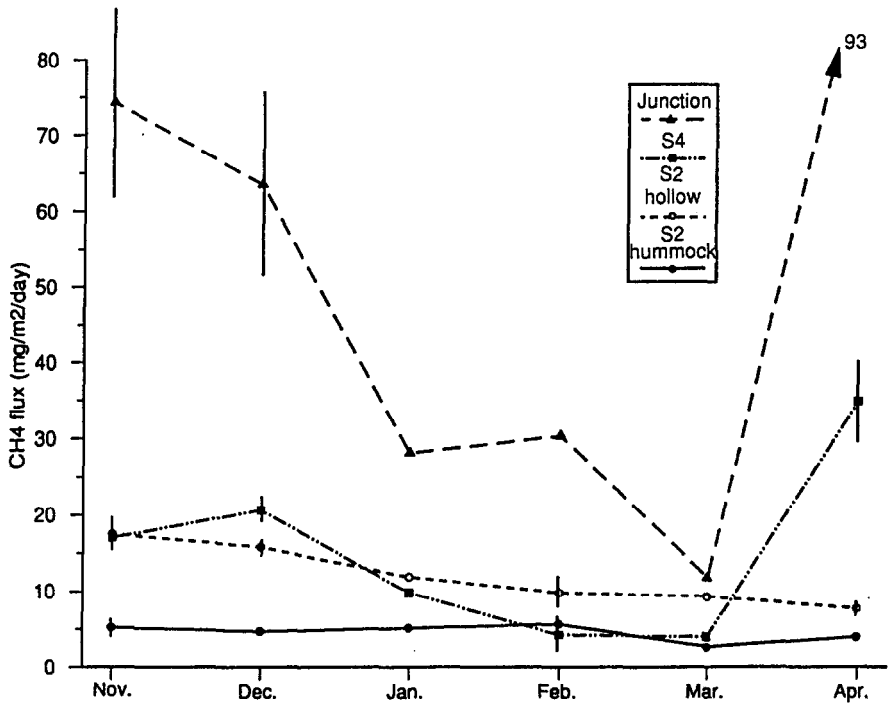

Fig. 1. Average monthly methane flux, November to April (1988–89 and 1989–90 data pooled), peatland sites in Marcell Experimental Forest (+/– 1 std. error shown for points with > 2 measurements). Values are arithmetic averages.

and into the atmosphere. There was no detectable flux from the upland site measured on November 21, 1988, although fluxes from the peatland sites in the days before and after ranged from 9 to 50 mg CH_4 m^{-2} day^{-1}. Linear buildup of methane concentration was recorded in all five chambers set atop the deep snow, and fluxes calculated from these were similar to fluxes from the peat surface measured on the same days (Dise 1991). Methane concentrations from ten samples of air trapped in the snowpack (measurements made November 1988–April 1989) averaged 2.17 ppmv, a slight elevation from ambient air methane measured on the same dates (1.82 ppmv).

Porewater methane concentrations were highest in winter, then declined in early spring (Fig. 2). The ratio between monthly flux and stored methane (units: $month^{-1}$) compares the balance of methane production/consumption with release of the gas. At Marcell the ratio indicated a rapid net production of methane in the summer months (*flux/stored* ranged from 1–10 'net turnovers' per month) and a winter slowdown so that, by

Table I. November—March methane flux measurements (mg CH_4 m^{-2} d^{-1}), Marcell Experimental Forest peatlands. Mean values shown are arithmetic averages and, in 1989—90, average fluxes calculated by integration

1988—89

Site	Mean flux	Std. dev.	Range	N.
S2, hummock	5	1	4—6	3
S2, hollow	14	7	6—26	7
S4	15	3	11—20	7
Junction	46	22	8—70	6

1989—90

Site	Mean flux	Std. dev.	Range	N.	Integrated Mean
S2, hummock	5	2	3—8	8	5
S2, hollow	14	4	9—19	8	13
S4	13	9	0—26	16	12
Junction	59	41	11—118	8	49

February, monthly flux accounted for only a tenth to a hundredth of stored methane (Fig. 3). Although the lowest fluxes were in March, the lowest ratio of flux to stored methane was in February.

Discussion

Winter fluxes of methane from northern peatlands can comprise an important part of the yearly budget. During 1989, when most measurements were made, winter fluxes from Junction fen, S2-hollow, and S2-hummock were 11%, 15%, and 21%, respectively, of annual flux (Table 2). In contrast, the winter component of the two sites in bog S4 was only 4% of the total flux. These differences in the relative importance of winter flux reflect differences in the annual distribution of fluxes. Whereas bog S2 emitted relatively low amounts of methane all year, and Junction fen fairly high amounts, bog S4 had low flux in the winter, fall and spring (similar to S2), but high flux in the summer (similar to Junction). Although methane emission increased in all five sites in July, the increase in S4 was a more pronounced 'pulse'. The reason for the differences in yearly flux regimes is

Table 2. Daily, summer (June—August, 92 days), winter (November—March, 151 days), annual and estimated annual[1] methane flux, Marcell Experimental Forest (April 1989—April 1990)

Site	Daily flux (mg CH_4 m^{-2} d^{-1})			Summer, winter flux		Annual flux (g CH_4 m^{-2} yr^{-1})	
	Integrated mean	Range	N.	Integrated mean (mg CH_4 m^{-2} d^{-1})	Total (g CH_4 m^{-2})	Calculated	[1]Estimated
Bog S2, hummock	10	2—48	36	21, 5	1.9, 0.7	3.5	3.2
Bog S2, hollow	38	6—246	36	93, 13	8.5, 2.0	13.8	13.9
Bog S2, fen lagg	35	−1—482	27	121, 0	11.2, 0	12.6	18.2
Bog S4	118	0—1056	68	356, 12	32.8, 1.8	43.1	53.4
Junction fen	180	11—767	37	402, 49	37.0, 7.3	65.7	60.3

[1] Estimated annual flux calculated as (average summer flux)*(number of frost-free days), using 150 as the approximate number of frost-free days in this region.

unknown and, because so few annual studies on methane release from peatlands have been done, it is not clear if a specific pattern of flux (e.g. evenly distributed all year or showing a summer pulse) is consistent in any given peatland from year to year. Clearly, the importance of winter fluxes to the global budget of methane from northern peatlands will not be resolved until we are able to identify which peatlands behave like S2 and Junction (where winter flux is significant) and which behave like S4 (where winter flux is not significant). To do this, more must be known about the physical, chemical and biological factors that control methane flux.

Annual flux of methane has been estimated in previous studies by multiplying average summer flux (usually 2—3 months) by a production season equivalent to the frost-free or snow-free period, about 150 days in this region. Comparing annual flux (April 1989—April 1990) estimated by this method to that calculated by integration resulted in underestimates of annual flux of about 10% for Junction and S2-hummock, near exact agreement for S2-hollow, and overestimates of about 24% for S4 (Table 2). Sufficient data exist only for S2-hollow and Junction fen to compare two different years: 1988—89 and 1989—90 (beginning and ending in mid-September instead of April as above). Although there are fewer data

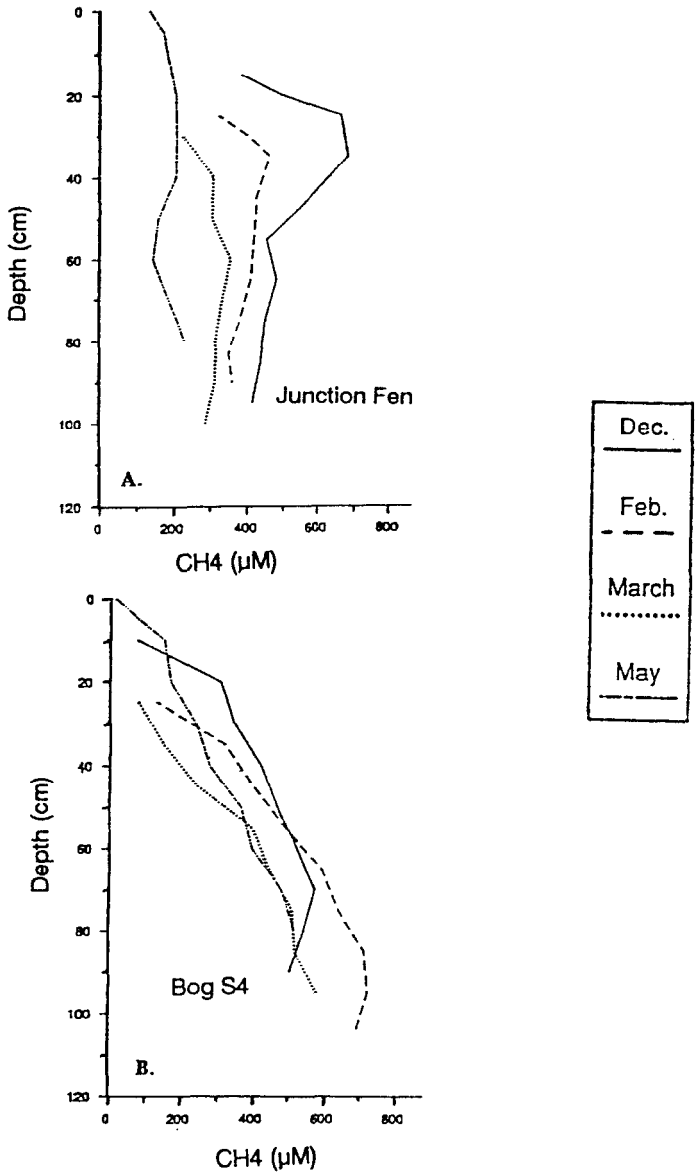

Fig. 2. Porewater methane concentration profiles, December 1989—May 1990. Each point is the average of four measurements. From Dise, 1992.

points for the 1988—89 winter and the 1990 summer than at other times, a two-year comparison is important because the years differ: peak summer flux in 1990 was about half that of 1989, and no July spike was detected in 1990. Reflecting this, the winter component of yearly flux increased

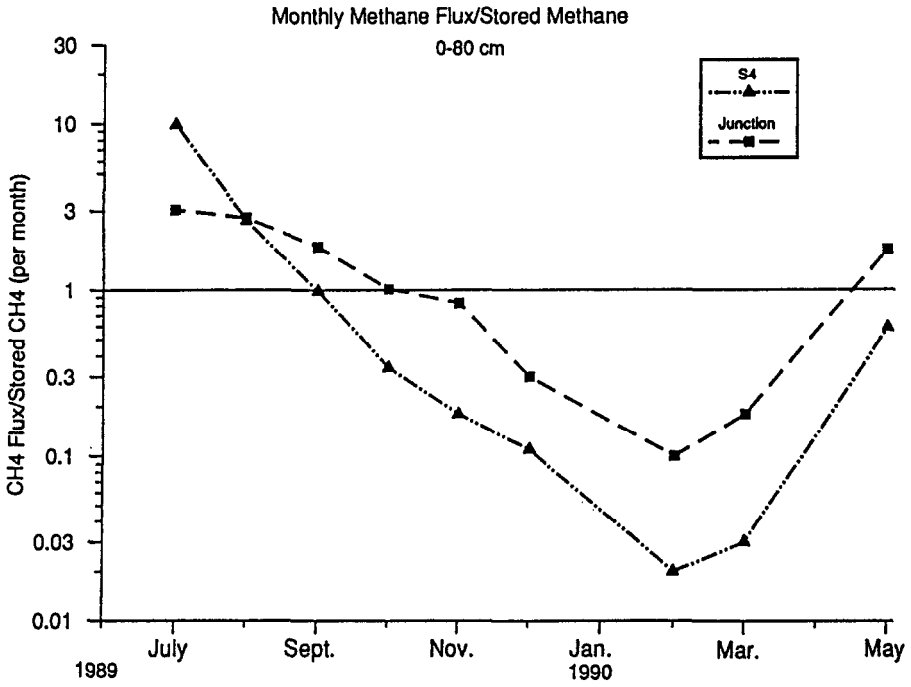

Fig. 3. Monthly flux: storage ratios of methane, 0—80 cm, S4 bog and Junction fen. From Dise, 1992.

from 8% to 17% in Junction fen and from 12% to 20% in S2-hollow from 1988—89 to 1989—90 (Table 3), and the error in the 150-day annual flux estimate changed from a slight overestimate for both sites to a 12.5% underestimate in S2-hollow and a 30% underestimate in Junction fen.

It is clear that time, resources and logistics dictate that few peatlands will be measured through the winter. In some cases, however, winter flux can be highly significant and cause errors in annual estimates of (in this study) up to 30%. It is possible that this problem may be resolved by making one or two flux measurements at the time of lowest flux to suggest whether the peatland emits significant amounts of methane in the winter. A rough estimate of the pattern of annual flux at a site is the ratio of the highest summer emission (in Marcell, average July flux) and the lowest winter emission (average March flux). Sites with relatively even emission — S2-hummock, S2-hollow and Junction fen — had ratios ranging from 10—30, while those with pulses in summer had ratios over 100. The importance of winter fluxes at a site may be estimated by the inverse of this ratio. In this data set an excellent empirical relationship was found between % winter flux and [March flux/July flux] (Fig. 4), with a regres-

Table 3. Comparison of winter and summer methane fluxes and proportion of annual flux for two years (23 Sept. 88—22 Sept. 89, 23 Sept. 89—22 Sept. 90). Units are g CH_4 m^{-2} over November—March (winter) or June—August (summer).

	1988—89		1989—90	
	Bog S2, hollow	Junction fen	Bog S2, hollow	Junction fen
Winter flux	1.7	4.8	2.0	7.3
(% of annual)	(12)	(8)	(20)	(17)
Summer flux	8.5	37.0	5.5	18.9
(% of annual)	(64)	(63)	(54)	(43)
Annual flux	13.4	58.9	10.2	43.9
[1]Estimated annual flux	13.9	60.3	8.9	30.7

[1] Calculation described in Table 2.

sion coefficient (r^2) of 0.99. Ratios such as the March/July flux may be useful as indicators of potentially high winter fluxes in other ecosystems, although more field data are needed to evaluate the worth of any such 'predictor' (which may be site-specific). One yearly study on methane flux from Alaska (Whalen & Reeburgh 1988) suggests that winter flux is not a significant component of the total methane budget in tundra ecosystems. This may be due to freezing of the entire peat profile in winter, and thus lack of a porewater reservoir. Peatland sites without permafrost, and with late winter-early spring fluxes that are more than 1% of peak fluxes may well be sites with high winter methane emissions.

Improving annual estimates of methane emission from peatlands without resorting to all-year measurements will require more knowledge about the mechanisms underlying the release of methane in winter months. One hypothesis to explain winter emission of methane is that rates of production in the most active zone (ca 0—50 cm, Williams & Crawford 1984) decline through the winter (following decreasing peat temperatures), but do not cease entirely. Alternatively, CH_4 production may stop, so that winter fluxes represent the steady loss of 'old' methane from deep peat (Clymo 1984) through cracks and fissures in frozen surface layers. Most likely, both new production and emission from stored sources occur simultaneously and the balance shifts over the course of the winter: active production and consumption become less important relative to passive loss as peat temperatures drop and peat freezes. The *methane flux/stored methane* ratio, which drops below the 1:1 level in early fall, suggests that

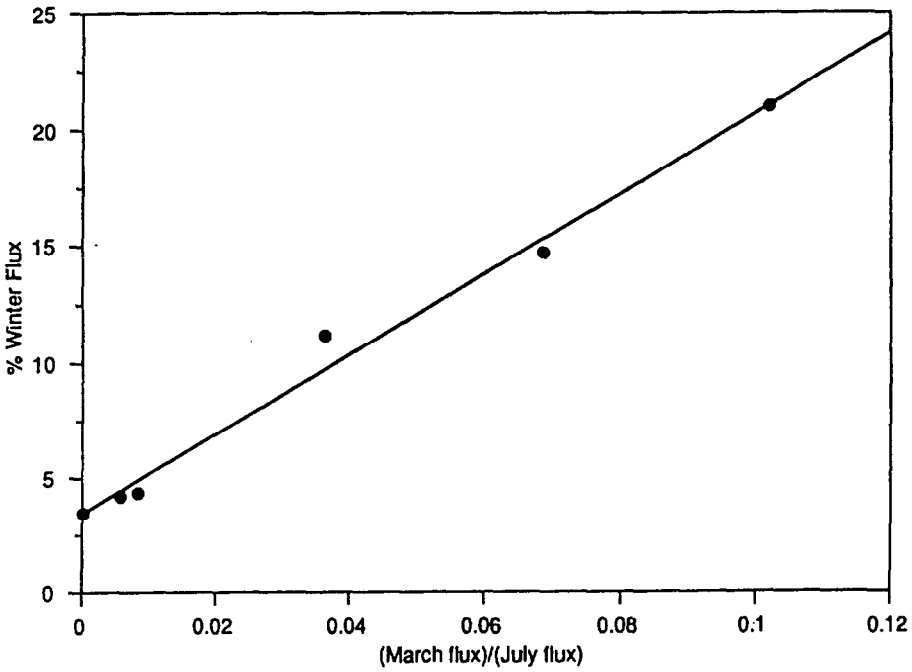

Fig. 4. Ratio of mean March flux to mean July flux as a predictor of the winter fraction of annual flux, Marcell Experimental Forest peatlands, 1989—1990. Values are calculated by integration, and include the fen lagg site in S2.

Regression equation:
% winter flux = 172.5 (March flux/July flux) + 3.5
$r^2 = 0.99$

winter fluxes mostly reflect the release of methane produced in the summer and stored in the peat. The observation that flux in the 1990 winter (when peat was frozen to 30 cm) was slightly higher than flux in 1989 (when the peat was unfrozen all winter) argues for at least some release from deep peat. Data on winter methane production and oxidation, and on the ^{14}C age of winter and summer emissions are necessary to begin to answer these questions.

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