

Soil chemistry versus environmental controls on production of CH₄ and CO₂ in northern peatlands

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Summary

Rates of organic carbon mineralization (to CO₂ and CH₄) vary widely in peat soil. We transplanted four peat soils with different chemical composition into six sites with different environmental conditions to help resolve the debate about control of organic carbon mineralization by resource availability (e.g. carbon and nutrient chemistry) versus environmental conditions (e.g. temperature, moisture, pH). The four peat soils were derived from *Sphagnum* (bog moss). Two transplant sites were in mid-boreal Alberta, Canada, two were in low-boreal Ontario, Canada, and two were in the temperate United States. After 3 years in the field, CH₄ production varied significantly as a function of peat type, transplant site, and the type–site interaction. All four peat soils had very small rates of CH₄ production (< 20 nmol g⁻¹ day⁻¹) after transplant into two sites, presumably caused by acid site conditions (pH < 4.0). One peat soil had small CH₄ production rates regardless of transplant site. A canonical discriminant analysis revealed that large rates of CH₄ production (4000 nmol g⁻¹ day⁻¹) correlated with large holocellulose content, a large concentration of *p*-hydroxyl phenolic compounds in the Klason lignin, and small concentrations of N, Ca and Mn in peat. Significant variation in rates of CO₂ production correlated positively with holocellulose content and negatively with N concentrations, regardless of transplant site. The temperature response for CO₂ production varied as a function of climate, being greater for peat formed in a cold climate, but did not apply to transplanted peat. Although we succeeded in elucidating some aspects of peat chemistry controlling production of CH₄ and CO₂ in *Sphagnum*-derived peat soils, we also revealed idiosyncratic combinations of peat chemistry and site conditions that will complicate forecasting rates of peat carbon mineralization into the future.

Introduction

Most wetlands between 50°N and 70°N latitude have developed organic soil (peat) at least 30 cm deep (Kivinen & Pakarinen, 1981). The reason is that shed plant biomass decomposes slowly in these systems (Clymo, 1983). Two proximate factors that limit decomposition rates have been implicated. One is unfavourable environmental conditions for decomposer microorganisms, i.e. cold, waterlogged peat and inherently acid pH. The other factor is little availability of resources for decomposer microorganisms, which has two facets: (i) complex organic compounds and (ii) deficiency of nutrient elements. We explore the relative strength of these controls on decomposition of peat soil from several ecosystems in North America.

Cold limits biological activity, although microorganisms adapted to extreme cold might show greater respiratory

response to warm temperature than ones adapted to warmer temperature (Lloyd & Taylor, 1994). Saturated conditions limit aerobic processes, although they facilitate anaerobic CH₄ production (Yavitt *et al.*, 1997). Fluctuating waterlogged versus aerated conditions might stimulate organic matter decomposition (Belyea, 1996). The pH in many northern peatlands is buffered (Mullen *et al.*, 2000) at less than the pH optimum for many microbial processes (Goodwin *et al.*, 1988). Even under favourable environmental conditions, the most common peatland plants *Sphagnum* (bog moss) and ericaceous shrubs are notoriously decay-resistant, nutrient-poor plants (van Breemen, 1995). As peat accumulates, the input of new nutrients relies increasingly on rainfall with dilute nutrient concentrations, rather than drainage water. Indeed, rates of CH₄ production have been correlated with concentrations of N (Valentine *et al.*, 1994) and trace metals (Basiliko & Yavitt, 2001).

The result is a wide range of poorly understood CH₄ and CO₂ production rates in peat soils (Segers, 1998). We

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addressed the variation in gas production rates by separating the effects of environmental conditions and peat chemistry using a field transplant experiment. We used the 'common garden' approach in which portions of four peat soils with different chemical composition were transplanted into six different sites with contrasting environmental conditions before being retrieved and analysed for production of CH₄ and CO₂.

Methods

The four peat soils were taken from three peatlands (Table 1). All of the collections were made in July 1994. Two were taken from within the Bleak Lake peatland complex, in central Alberta, Canada (54°41'N, 113°28'W, altitude 625 m), specifically in an ombrotrophic treed bog with a nearly continuous *Sphagnum* ground layer, dominated by *S. fuscum*. The site has a mixture of ericaceous shrubs and trees, including *Ledum groenlandicum*, *Vaccinium oxycoccos*, *Smilacina trifolia*, *Rubus chamaemorus* and scattered *Picea mariana* trees (Vitt *et al.*, 1995). One soil sample was taken 5–15 cm below the surface vegetation, and thus it was less decomposed than the other sample taken 35–45 cm below the vegetation. The second site was a treed bog in the Experimental Lakes Area (ELA) in northwestern Ontario, Canada (49°40'N, 93°48'W, altitude 400 m). This site has a ground cover of *Sphagnum fallax* and *S. magellanicum* and dense cover of *L. groenlandicum* and scattered *P. mariana* (Dyck & Shay, 1999). The soil sample was taken 35–45 cm below the surface vegetation. The fourth peat soil was taken from the Big Run peatland complex in the Appalachian Mountain region of West Virginia, USA (39°07'N, 79°35'W, altitude 970 m). Big Run is an open (non-treed) peatland with a continuous cover of *Sphagnum recurvum* and a mixture of sedges, including *Eriophorum virginicum*

(Wieder, 1985). The soil was collected 35–45 cm below the vegetation.

We collected peat samples by pounding five replicate PVC tubes (10 cm diameter), open at both ends, into the peat deposit, being careful to avoid peat compaction within the tube. The tube and peat within were removed, and peat from the specific 10 cm depth intervals was retained. The five replicates were combined into one bulk sample before thirty-five 100 cm³ portions were taken as quickly as possible. Thirty portions were placed into individual 5 cm-diameter by 5 cm-long plastic tubes (i.e. 'peat traps', Wieder & Yavitt, 1991). Nylon stocking was placed over each end and secured in place with perforated end caps. Five replicate traps were placed into a plastic bag, which was placed within another bag to reduce exposure to air, sealed and flown to the transplant site. This took 2 days to complete. The remaining five portions of peat soil were used to determine initial chemical composition.

We chose six contrasting transplant sites (i.e. common gardens) in which previous studies had characterized aspects of environmental conditions (Table 2). Two of the transplant sites were in the Bleak Lake peatland complex. One was the bog, described above. The other was a non-forested poor fen water track dominated by *Carex tenuiflora*, *Sphagnum angustifolium* and *S. teres* (Vitt *et al.*, 1995). Two transplant sites were at ELA. One site was a low-density treed bog, designated L979, which was flooded to simulate a hydroelectric reservoir. The other was a poor fen portion of peatland, designated L632, which was not flooded. The fifth site was a treed bog in the Marcell peatland complex in north-central Minnesota, USA (47°30'N, 93°30'W, altitude 625 m) designated S-2. The bog is dominated by ground cover of *Sphagnum magellanicum* and *S. angustifolium*, with a nearly complete canopy of *P. mariana* (Grigal, 1991). The sixth incubation site was Big Run.

Table 1 Characteristics of the peat soils before transplant. Values shown are means ± 1 standard error

	Bleak Lake 5–15 cm	Bleak Lake 35–45 cm	ELA 35–45 cm	Big Run 35–45 cm
Bulk density /g cm ⁻³	0.041 ± 0.003	0.07 ± 0.01	0.04 ± 0.01	0.04 ± 0.01
Loss on ignition /%	99.3 ± 0.4	98.6 ± 0.4	91.4 ± 0.7	75.3 ± 1.3
N /mg g ⁻¹ ash-free mass	4.8 ± 0.1	7.2 ± 0.3	13.5 ± 0.3	16.3 ± 0.2
P /mg g ⁻¹ ash-free mass	0.28 ± 0.01	0.43 ± 0.01	0.59 ± 0.01	0.74 ± 0.01
Ca /mg g ⁻¹ ash-free mass	1.33 ± 0.01	1.46 ± 0.01	3.39 ± 0.04	1.82 ± 0.01
Mg /mg g ⁻¹ ash-free mass	0.27 ± 0.01	0.60 ± 0.01	0.57 ± 0.01	0.31 ± 0.01
Na /mg g ⁻¹ ash-free mass	0.07 ± 0.01	0.13 ± 0.01	0.06 ± 0.01	0.06 ± 0.01
Fe /mg g ⁻¹ ash-free mass	0.45 ± 0.01	1.05 ± 0.01	1.67 ± 0.01	3.54 ± 0.02
Mn /μg g ⁻¹ ash-free mass	140.1 ± 0.6	47.0 ± 0.1	40.5 ± 0.3	116.6 ± 0.5
Co /μg g ⁻¹ ash-free mass	12.8 ± 0.2	30.1 ± 0.3	49.3 ± 0.2	102.3 ± 0.6
Ni /μg g ⁻¹ ash-free mass	0.8 ± 0.1	0.8 ± 0.1	1.8 ± 0.1	5.2 ± 0.1
Soluble fats, oils, waxes /mg g ⁻¹ ash-free mass	55 ± 3	51 ± 6	62 ± 3	73 ± 3
Total hot-water soluble /mg g ⁻¹ ash-free mass	124 ± 4	138 ± 8	106 ± 5	84 ± 2
Holocellulose /mg g ⁻¹ ash-free mass	580 ± 60	492 ± 30	458 ± 32	241 ± 27
Klason lignin /mg g ⁻¹ ash-free mass	240 ± 20	322 ± 32	369 ± 42	600 ± 82

Table 2 Characteristics of the transplant sites

	Wetland type	Peat pH	Water table depth ^a /cm
Bleak Lake (54°30'N, 113°30'W; MAT ^b = 1.4°C; MAP ^c = 490 mm)			
Bog	Forested bog	3.9	-35
Water track	Poor fen	5.4	0
ELA (49°40'N, 93°48'W; MAT = 1.8°C; MAP = 678 mm)			
Control	Poor fen	No data	-20
Flooded	Forested bog	4.12	0
Marcell (47°30'N, 93°30'W; MAT = 4.0°C; MAP = 762 mm)			
S-2	Forested bog	3.6	-25
Big Run (39°07'N, 79°35'W; MAT = 7.9°C; MAP = 1330 mm)			
	Poor fen	4.2	-5

^aWater table depth is mean depth below the surface vegetation in summer.

^bMAT, mean annual temperature.

^cMAP, mean annual precipitation.

All of the traps were placed 15 cm below the surface vegetation by making an incision in the peat deposit, placing the peat trap at the appropriate depth, and allowing the incision to close. The traps were marked with a permanent flag to aid retrieval. We retrieved all of the traps in July 1997. They were placed in plastic bags in the field and shipped to Cornell University, and analyses began within 2 days of collection. In the laboratory, we divided the peat in each trap into two equal-sized portions. One portion was used to measure production rates of CH₄ and CO₂. The other portion was used for chemical analyses.

For the production measurements, we placed a 30-g portion of field-moist peat into a preweighed 350-ml Mason jar. Each jar was sealed immediately with a lid that had a septum through it to allow us to sample headspace gas concentrations, and the headspace was exchanged three times with O₂-free N₂ to establish anoxic conditions. We incubated each jar without agitation at 22°C for 7 days. We chose this standard temperature for all of the incubations to make comparison of production rates among transplant sites without the confounding effect of temperature differences. Therefore, our analysis measures acclimation to a warm peat temperature rather than effect of temperature *per se*. Every day during this period, we took a 5-ml gas sample from the jar headspace for analyses of CH₄ and CO₂ and immediately added 5 ml of N₂ to maintain gas pressure. Samples were analysed within 4 hours of collection by gas chromatography using a flame ionization detector for CH₄ and a thermal conductivity detector for CO₂. The gas chromatograph had a 2.75 m × 3.18 mm column of Poropak Q (80/100 mesh, Waters Chromatography, Milford, MA) maintained at 50°C to separate the gases. The flow rate of the He carrier gas was 30 ml minute⁻¹. Injector temperature was 110°C. We used certified CH₄ standards (1.0, 9.8, 102, 10 400 μmol mol⁻¹ CH₄ in O₂-free N₂) and CO₂ standards (1024, 10 000 μmol mol⁻¹ CO₂ in O₂-free N₂) for calibration, and calculated concentrations of CH₄ and CO₂ by comparing peak areas for samples and standards.

After the last gas sample, the volume of the jar headspace was determined by filling the jars with water and weighing the volume added. The water was then poured off and the peat was dried and weighed. Potential production rates for CH₄ and CO₂ were calculated from a linear regression of the change in gas production versus time during the 7-day incubation period. We also accounted for produced CO₂ that dissolved in the peat matrix, which was calculated using Henry's law (Flett *et al.*, 1976) and the temperature-dependent Bunsen solubility coefficient for CO₂ (Wilhelm *et al.*, 1977). The final rates are expressed as moles of gas per gram of dry peat per day.

The second set of material per trap was divided into several portions for chemical analyses. One portion was used to quantify organic fractions according to the method of Wieder & Starr (1998). In this scheme, different fractions are removed sequentially from a peat sample and their contribution is determined gravimetrically. The sum of four fractions (soluble fats, oils, waxes; total hot-water soluble; holocellulose; lignin) equals the total organic content. The bulk of the so-called lignin fraction is vascular plant lignin, but it also can contain variable amounts of acid-insoluble carbon from bryophytes as well as cutins and tannins (Preston *et al.*, 1997). Therefore, we refer to the fraction as Klason lignin. Total organic matter content was determined by dry-ashing 2 g of peat at 600°C for 4 hours. (To facilitate comparisons with other data sets some results are expressed on a per gram organic C basis, which was estimated as 50% of the organic matter content.) The ash was dissolved in nitric acid and used for analysis of metals and P by inductively coupled plasma spectroscopy (ICP). Nitrogen was determined by a modified semi-micro Kjeldahl method.

Alkaline CuO oxidation (Hedges & Ertel, 1982) was used to further characterize the Klason lignin fraction. A 50-mg portion was reacted with a mixture of 7 ml 8% (by weight) NaOH, 100 mg Fe(NH₄)₂(SO₄)₂·6H₂O (an O₂ scavenger) and 1 g CH₂Cl₂-extracted CuO under O₂-free N₂ for 3 hours at 150°C. The phenolic reaction products were extracted from

the reaction digest using disposable 6 ml solid-phase extraction tubes filled with a reversed-phase C-18 packing (Supelco, Bellefonte, PA). The retained phenolics were eluted from the tubes with ethyl acetate, which was then evaporated under a continuous stream of O₂-free N₂ gas. The organic residue was dissolved in high-performance liquid chromatography (HPLC) grade CH₃OH and then analysed by reversed-phase HPLC (Rainin C-18 microsorb column, 250 mm × 4 mm) with detection by ultraviolet (280 nm) spectrometry. Individual phenolic compounds were quantified by peak area, after calibration with standards of known concentration.

The alkaline CuO oxidation releases phenolic monomers from the uncondensed structures of the lignin molecule. The resulting phenolics can be used as a plant source indicator in unhumified organic matter as well as a measure of diagenetic state in highly humified organic matter (Hedges *et al.*, 1988). Twelve predominant phenolic monomers are produced, which can be categorized into distinct families on the basis of chemical substitution: mono-methoxyl substituted vanillyl phenols (ΣV : vanillin, vanillic acid, acetovanillone); dimethoxyl substituted syringyl phenols (ΣS : syringaldehyde, syringic acid, aceto-syringone); non-methoxyl substituted *p*-hydroxyl phenols (ΣP : *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, *p*-hydroxyacetophenone); and cinnamyl phenols (ΣC : ferulic acid, *p*-coumaric acid). Weight ratios are sums of phenols of individual families (e.g. $\Sigma C:\Sigma V$, $\Sigma S:\Sigma V$, $\Sigma P:\Sigma V$) and are used to understand lignin origin. Gymnosperm lignin produces primarily vanillyl phenols when reacted with CuO, whereas angiosperm lignin produces both vanillyl and syringyl phenols. Lignin from non-woody plants releases significantly more cinnamyl phenols than other plant lignin. Although *Sphagnum* does not have lignin *per se*, CuO oxidation releases large amounts of *p*-hydroxyl phenols. There are several ways to assess the degree of lignin diagenesis. For instance, an increase in the phenolic acid to aldehyde ratio is taken as a measure of increasing decomposition.

Statistical analyses

We used analysis of variance (ANOVA) to determine whether rates of CH₄ production and CO₂ production differed among the four peat types and six incubation sites. Methane data were log_n transformed before analysis.

We used canonical discriminant analysis (CDA) to examine aspects of peat chemical composition that most likely contributed to the differences in CH₄ production rates. CDA is a multivariate statistical technique that identifies linear combinations of observation variables (canonical variables) that differentiate among groups. We assigned peat samples into one of three groups: (i) large production rates, > 500 nmol g⁻¹ day⁻¹, (ii) moderate production rates, between 10 and 500 nmol g⁻¹ day⁻¹, and (iii) small production rates, < 10 nmol g⁻¹ day⁻¹. CDA is sensitive to data with a non-normal distribution. Therefore, we used log_n (value) and

square root (value + 1)⁻¹ transformations before analyses. This prevented interference by differences in units, magnitude or dimension of variables. CDA also is very sensitive to non-significant variables (Brown & Wicker, 2000), and thus we eliminated variables from the final analysis that did not explain data structure among groups.

Results

Bulk peat sample, preincubation

Chemical composition of the four peat soils ranged from more holocellulose than Klason lignin and small concentrations of N, P and trace metals (Bleak Lake surface peat) to large concentrations of Klason lignin and nutrient elements (Big Run peat) (Table 1). The other two peat soils had intermediate holocellulose:Klason lignin ratios and nutrient element concentrations. As a result, the C:N ratio ranged from 93:1 in Bleak Lake surface peat to 21:1 in Big Run peat. The C:P ratio (mass basis) ranged from 1600:1 to 458:1. There was no significant difference in Ca concentration among the four peat soils.

Production rates for CH₄ and CO₂

Rates of CH₄ production ranged from 1 to 4500 nmol g⁻¹ day⁻¹ (Figure 1). The ANOVA indicated significant ($P < 0.05$) effects of peat type and transplant site, as well as the peat type–site interaction. All of the peat samples retrieved from Bleak Lake bog and Marcell had very small rates of CH₄ production (< 50 nmol g⁻¹ day⁻¹). Big Run peat also had small rates of CH₄ production rates regardless of the transplant site. Excluding samples transplanted in Bleak Lake bog and Marcell, both of the Bleak Lake peat samples had mean CH₄ production rates of > 1000 nmol g⁻¹ day⁻¹ versus a mean rate of 180 nmol g⁻¹ day⁻¹ for ELA peat.

Rates of CO₂ production measured under anoxic conditions ranged from 2 to 35 μmol g⁻¹ day⁻¹ (Figure 1). Analysis of variance indicated significant ($P < 0.05$) differences among peat types, but no difference in rates as a function of transplant site. Big Run peat consistently had the smallest CO₂ production rates. Carbon dioxide production was correlated positively with holocellulose (Pearson correlation coefficient $r = 0.79$, $P < 0.001$) and negatively with N concentrations (Pearson $r = -0.82$, $P < 0.001$).

CDA analysis

The variation in CH₄ production was discriminated by two canonical functions (Figure 2). The first function separated the group with large CH₄ production rates from the other two groups. Large CH₄ production rates were positively related to acid-soluble carbohydrates (holocellulose) and non-methoxyl substituted *p*-hydroxyl (ΣP) phenols in the Klason lignin. This

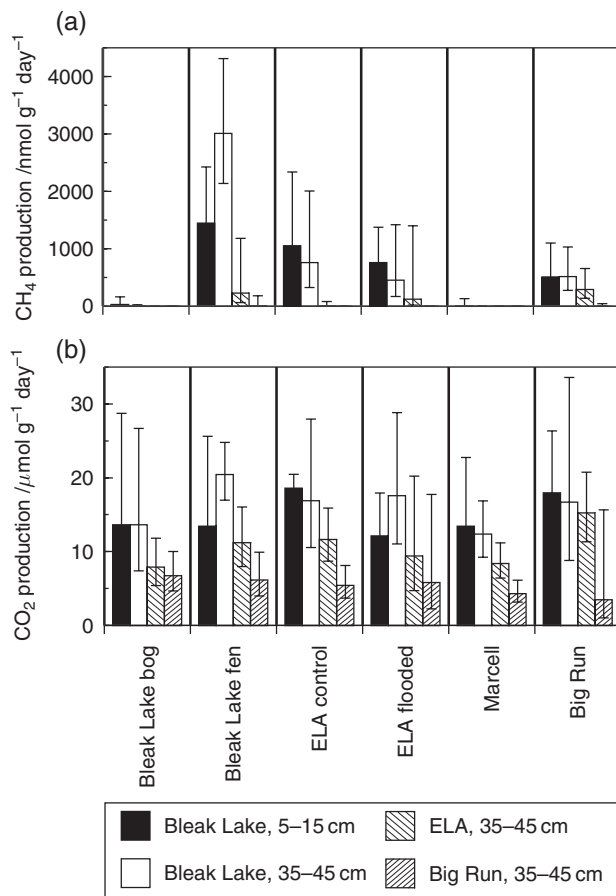


Figure 1 Mean rates of (a) CH₄ production and (b) CO₂ production in four different peat samples after separate portions of each sample were incubated for 3 years in six different sites. Vertical bars represent 99% confidence intervals.

group also was negatively related to peat with large N, Ca and Mn concentrations. The second canonical function separated the groups with moderate and small CH₄ production rates, with the smallest rates related to a large ratio of vanillic acid to vanillin aldehyde among the mono-methoxyl substituted V phenols.

Chemical analysis of peat after incubation

Some chemical characteristics of peat changed markedly during transplant, whereas others did not (Table 3). Bleak Lake peat, with small N concentrations, showed greater N concentrations after transplant in all sites, whereas ELA peat and Big Run peat with large N concentrations showed no change after transplant (Table 4). Phosphorus concentrations behaved differently, showing no change after transplant for Bleak Lake surface peat (small P concentration) and Big Run peat (large P concentration), otherwise P concentrations decreased (Table 4). Calcium, Mg and Na concentrations behaved similarly, with large increases in concentration after transplant in Bleak

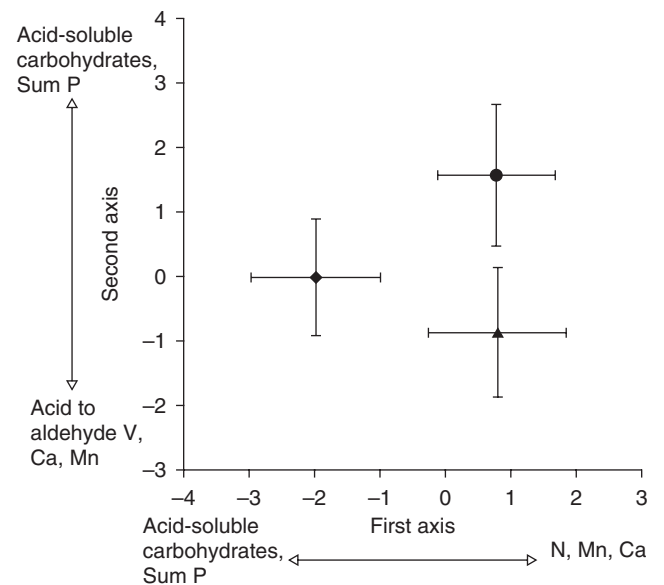


Figure 2 Canonical discriminant analysis plot illustrating the discrimination of peat samples grouped according to mean CH₄ production rates: ♦, > 500 nmol g⁻¹ day⁻¹; ●, 10–500 nmol g⁻¹ day⁻¹; ▲, < 10 nmol g⁻¹ day⁻¹. Also indicated along each axis are the variables measured on the peat samples that discriminated the groups significantly. Plot differences are Mahalanobis distances. Vertical and horizontal bars represent 95% confidence intervals.

Lake water track and ELA flooded (Table 4). Iron, Co and Ni showed a trend of increasing concentrations when initial concentrations were small (Bleak Lake peat) to smaller concentrations when initial values were large (Big Run peat). The greatest concentrations occurred after transplant in ELA control and in Big Run. Manganese concentrations behaved more like the base cations (Ca, Mg, Na) than like trace metals (Fe, Co, Ni).

Although the organic matter content and relative amounts of holocellulose versus Klason lignin changed by less than 10%, CuO oxidation revealed marked changes in the composition of the Klason lignin fraction (Table 5). For example, the yield of ΣV, ΣS, ΣP and ΣC phenols increased by 20–70% in Bleak Lake surface and ELA peat. The yields were much greater in Bleak Lake deep peat, especially when transplanted into Bleak Lake water track and Big Run, whereas Big Run peat had smaller yields in some cases. The diagenetic acid/aldehyde ratios increased by 30–70%, including those for Big Run peat, indicating increased decomposition.

Discussion

Knowing the control of CH₄ production and CO₂ production in peat will help us to assess the impact of environmental change (e.g. climatic changes) on carbon mineralization rates and the implications for atmospheric concentrations of CO₂ and CH₄. The debate is similar to that in ecology about the

Table 3 Percentage change of nutrient element concentrations in peat following transplant. Values shown are means \pm 1 standard deviation across the six incubation sites

Element	Bleak Lake 5–15 cm	Bleak Lake 35–45 cm	ELA 35–45 cm	Big Run 35–45 cm
N	+39 \pm 2	+29 \pm 9	-3 \pm 5	+2 \pm 3
P	-5 \pm 9	-21 \pm 16	-18 \pm 6	-15 \pm 21
Ca	+233 \pm 240	+191 \pm 239	+29 \pm 65	+10 \pm 90
Mg	+347 \pm 446	+94 \pm 167	+57 \pm 147	+28 \pm 142
Na	+37 \pm 39	-6 \pm 68	+111 \pm 166	+63 \pm 104
Fe	+840 \pm 650	+235 \pm 159	+120 \pm 110	-22 \pm 31
Co	+652 \pm 427	+196 \pm 112	+81 \pm 69	-27 \pm 24
Ni	+153 \pm 95	+147 \pm 56	+72 \pm 66	-27 \pm 25
Mn	-3 \pm 32	+130 \pm 117	+135 \pm 161	-42 \pm 39

importance of nature (genes) versus nurture (environment). The classic approach to separate the two effects is transplanting soil (or organisms) to new environments. Our study used a

'common garden' design in which soils were transplanted to a different site, i.e. a common garden (Clausen *et al.*, 1948). A variation involves transplanting reciprocally using the same sites for collection and transplanting. We previously did a reciprocal transplant experiment with peat (Yavitt *et al.*, 2000), which led to this study using peat soils with a wider range of chemical composition and subjecting them to a wider range of environmental conditions. While our experimental design might seem unbalanced, especially in the choice of transplant sites (Table 2), the purpose was not an experiment with few replicated treatments, but rather to subject peat soils to a wide range of environmental conditions that might reveal idiosyncratic responses.

The four soils in our study were characteristically *Sphagnum*-derived peat. They had the requisite small concentrations of Ca (Grigal, 1991). The Bleak Lake peat samples had the typical small concentrations of Klason lignin, given that *Sphagnum* mosses are non-vascular plants with a different type of polyphenolic network than 'true' lignin produced by vascular plants (van Breemen, 1995). *Sphagnum* mosses also

Table 4 Summary of selected changes in nutrient element concentrations before incubation and after transplant in each site

Peat type, depth and transplant site	N	P	Ca	Fe	Mn
	/mg g ⁻¹				
Bleak Lake, 5–15 cm	4.8 ^a	0.29 ^a	1.33 ^a	0.45 ^a	0.14 ^a
In BL bog	6.7 ^b	0.25 ^a	2.05 ^c	1.90 ^c	0.10 ^a
In BL water track	6.7 ^b	0.27 ^a	8.81 ^e	1.25 ^b	0.19 ^a
In ELA control	6.7 ^b	0.28 ^a	3.51 ^d	8.12 ^e	0.10 ^a
In ELA flooded	6.6 ^b	0.24 ^a	8.12 ^e	3.45 ^d	0.17 ^a
In Marcell	6.6 ^b	0.30 ^a	1.60 ^b	3.06 ^d	0.10 ^a
In Big Run	6.7 ^b	0.31 ^a	2.48 ^c	7.62 ^e	0.16 ^a
Bleak Lake, 35–45 cm	7.2 ^a	0.43 ^c	1.47 ^b	1.05 ^a	0.05 ^a
In BL bog	8.9 ^{b,c}	0.36 ^{b,c}	2.33 ^c	1.75 ^b	0.11 ^b
In BL water track	9.2 ^{b,c}	0.39 ^{b,c}	8.63 ^e	1.98 ^b	0.20 ^c
In ELA control	8.2 ^{a,b}	0.34 ^b	3.49 ^d	6.36 ^d	0.09 ^a
In ELA flooded	10.0 ^c	0.39 ^{b,c}	8.67 ^e	3.31 ^c	0.15 ^b
In Marcell	9.5 ^c	0.38 ^{b,c}	1.63 ^b	4.41 ^d	0.06 ^a
In Big Run	9.8 ^c	0.21 ^a	0.86 ^a	3.66 ^c	0.05 ^a
ELA, 35–45 cm	13.5 ^a	0.60 ^b	3.39 ^b	1.67 ^a	0.04 ^a
In BL bog	13.7 ^a	0.54 ^{a,b}	2.23 ^a	2.47 ^b	0.06 ^{a,b}
In BL water track	12.7 ^a	0.46 ^a	7.68 ^d	1.41 ^a	0.19 ^c
In ELA control	13.5 ^a	0.50 ^{a,b}	4.28 ^c	4.80 ^c	0.06 ^{a,b}
In ELA flooded	13.8 ^a	0.44 ^a	6.39 ^d	4.21 ^c	0.16 ^c
In Marcell	12.4 ^a	0.52 ^{a,b}	2.45 ^a	2.69 ^b	0.03 ^a
In Big Run	12.5 ^a	0.48 ^a	3.28 ^b	6.50 ^d	0.07 ^{a,b}
Big Run, 35–45 cm	16.3 ^a	0.74 ^b	1.82 ^b	3.54 ^b	0.12 ^b
In BL bog	16.7 ^a	0.67 ^b	1.04 ^b	1.93 ^a	0.04 ^a
In BL water track	15.6 ^a	0.74 ^b	4.57 ^c	1.92 ^a	0.12 ^b
In ELA control	17.4 ^a	0.68 ^b	1.43 ^b	2.92 ^b	0.04 ^a
In ELA flooded	16.8 ^a	0.66 ^b	3.45 ^c	3.66 ^a	0.13 ^b
In Marcell	16.5 ^a	0.71 ^b	0.93 ^{a,b}	4.43 ^c	0.03 ^a
In Big Run	16.7 ^a	0.32 ^a	0.52 ^a	1.68 ^a	0.04 ^a

Statistical analysis was done separately for each peat soil before transplant and following transplant in each site; separate analyses with the same letter are not significantly different at $P < 0.05$.

Table 5 Summary of lignin oxidation products in peat before incubation and after transplant in each site

Peat type, depth and transplant site	ΣV	ΣS	ΣP	ΣC	ac/al _V ^a	ac/al _S ^b
	/mg g ⁻¹ peat C					
Bleak Lake, 5–15 cm	2.94	2.56	12.08	2.20	0.43	0.34
In BL bog	4.80	4.08	23.05	3.34	0.23	0.06
In BL water track	4.19	3.94	18.49	3.48	0.80	0.34
In ELA control	3.33	2.77	14.07	1.34	0.85	0.35
In ELA flooded	7.28	6.20	31.72	5.04	0.29	0.08
In Marcell	6.78	3.58	24.57	0.89	0.52	0.18
In Big Run	3.25	3.15	13.17	1.83	0.64	0.32
Bleak Lake, 35–45 cm	2.18	2.48	7.88	0.06	0.33	0.08
In BL bog	7.37	6.09	6.78	2.67	0.56	0.36
In BL water track	16.87	12.04	23.87	7.50	0.57	0.35
In ELA control	12.54	6.66	7.89	1.77	0.59	0.38
In ELA flooded	10.43	9.87	13.85	5.47	0.53	0.38
In Marcell	6.02	4.18	10.35	1.10	0.54	0.33
In Big Run	10.89	6.84	13.37	3.61	0.65	0.42
ELA, 35–45 cm	7.97	8.15	12.19	0.74	0.40	0.31
In BL bog	10.24	9.77	8.08	4.79	0.56	0.40
In BL water track	23.50	18.74	42.52	15.98	0.56	0.36
In ELA control	8.96	9.15	11.14	3.39	0.56	0.39
In ELA flooded	8.99	7.60	10.01	3.33	0.38	0.30
In Marcell	10.38	10.77	11.87	4.69	0.50	0.34
In Big Run	8.63	7.97	9.70	4.96	0.54	0.41
Big Run, 35–45 cm	31.16	14.65	5.82	1.41	0.55	0.34
In BL bog	13.87	11.11	12.88	4.39	0.62	0.39
In BL water track	59.78	37.38	10.32	9.75	0.57	0.32
In ELA control	8.32	7.49	3.95	2.80	0.93	0.46
In ELA flooded	33.28	17.24	6.31	6.78	0.67	0.46
In Marcell	16.06	10.32	3.08	3.83	0.75	0.43
In Big Run	15.28	8.21	3.14	2.96	0.83	0.48

^aac/al_V, ratio of acid to aldehyde for V phenols.

^bac/al_S, ratio of acid to aldehyde for S phenols.

For explanation of ΣV, ΣS, ΣP, ΣC see text.

have a higher yield of ΣP phenolics relative to ΣS and ΣC phenols (Williams *et al.*, 1998), owing to the lack of mono- and di-methyl substituted phenyl propane monomers in the poly-phenolic network. This serves as an organochemical ‘fingerprint’ of *Sphagnum* residue. The slightly greater Ca concentration in ELA peat was still within levels found in *Sphagnum*-derived peat (Grigal, 1991). The greater concentration of Klason lignin in the ELA and Big Run peat reflects decomposition of the holocellulose fraction leaving the more decay-resistant Klason lignin in the residue (Williams *et al.*, 1998). The large amounts of ΣC, ΣS and ΣV phenolics in Big Run peat are unusual for *Sphagnum*-derived peat (Williams & Yavitt, 2003). We have speculated that their contribution reflects a richer diversity of vascular plants that grew on the site in the past, and their legacy has been recorded in peat chemistry (Williams & Yavitt, 2003).

Soil C:N ratios were within the range of values commonly found in *Sphagnum*-derived peat (Kuhry & Vitt, 1996). The threefold difference in C:N ratio of subsurface Bleak Lake

peat versus Big Run peat taken from the same depth interval again indicates greater decomposition of Big Run peat, i.e. more C than N loss (Kuhry & Vitt, 1996). The C:P ratio of Bleak Lake surface peat was similar to the value that Bridgham *et al.* (2001) reported for fresh *Sphagnum*-derived peat, and the small ratio of Big Run peat confirms greater decomposition.

Trace metals in *Sphagnum* peat have received much less attention, but are an important consideration since all methanogens require Fe, Ni and Co for growth (Whitman, 1985). Specific concentrations required for growth are not known, but concentrations in Bleak Lake peat appear to be small enough to limit growth (Basiliko & Yavitt, 2001). The Fe, Co and Ni concentrations in Big Run peat are about typical of amounts found in peatlands in North America impacted by atmospheric pollution (Cole *et al.*, 1990). The Mn content of peat is important, in particular, for fungi which have Mn-containing phenol oxidase enzymes that degrade lignin (Berg *et al.*, 1996). Indeed, the very large concentration of Klason lignin in Big Run peat

might be related to the Mn concentration that is 10 times smaller than the value reported by Berg *et al.* (1996) that retards lignin decay in leaf litter in boreal forests.

Transplant revealed a few specific patterns in nutrient concentrations. For example, changes in N and P concentrations were largely a function of initial concentration, with only a few subtle site differences. This result is interesting in the light of threefold greater N deposition in rain in Big Run than in Bleak Lake (Berner & Berner, 1996). Bleak Lake water track and ELA flooded imparted large increases in Ca (Mg and Na) concentrations, suggesting that base-cation rich groundwater infiltrates the peat in these sites. In contrast, large increases in Fe (Ni and Co) concentrations were evident in peat (except Big Run peat) transplanted in ELA control and Big Run. Soil dust is the largest source of trace metals in these areas (Berner & Berner, 1996), suggesting that site-specific characteristics distinguished atmospheric deposition at these two sites.

Production rates for CH₄ and CO₂

We initiated laboratory incubation of transplanted soil samples within 48 hours after retrieval. Since the incubations were done at one temperature and under anoxic conditions, they do not represent production rates *in situ*. However, because they were done on freshly collected samples, and incubated for only 7 days, they represent production rates by the endogenous populations of anaerobic microorganisms, without temperature and aeration limiting their activity during the incubation. We chose anoxic conditions for all of the incubations to assess potential CH₄ production, even though we realize that aerobic bacteria are responsible for some of the CO₂ production *in situ*.

Environmental conditions limited CH₄ production but not CO₂ production in Bleak Lake bog and in Marcell. Whether the cause was just one unfavourable condition or several conditions is unclear. From previous studies, we know that Bleak Lake bog and Marcell had the most acid peat pH values (Table 1), whereas all of the known methanogens grow at a pH range of 5.6–8 (Garcia *et al.*, 2000). There has been some debate (Dunfield *et al.*, 1993) about the way that acid pH affects methanogens in peat. One is direct toxicity *per se*, similar to that for rumen methanogens (Van Kessel & Russell, 1996). The other is an indirect effect of acidity on H₂ production that subsequently fuels CH₄ production, similar to that in lake sediments (Goodwin *et al.*, 1988). Our data support direct toxicity since anaerobic microbial activity (CO₂ production) was not impeded.

Bleak Lake peat supported the greatest rates of CH₄ and CO₂ production, even though it was derived mostly from *Sphagnum fuscum*. It has been suggested that this species decomposes very slowly (Johnson & Damman, 1991), and it has been associated with small rates of CH₄ emission into the atmosphere (Bubier *et al.*, 1995). However, our results suggest that *S. fuscum*-derived peat can support large rates of CH₄ production given favourable environmental conditions.

The smallest rates of CH₄ and CO₂ production in Big Run peat, regardless of transplant site, suggest that poor chemical composition constrained microbial activity. The CDA indicated that both organic chemistry and element concentrations were responsible. The positive correlation for both CH₄ production and CO₂ production with holocellulose is consistent with this compound being decomposed more easily than Klason lignin, which accumulates in the residue (Williams *et al.*, 1998). On the other hand, Klason lignin was not entirely inert, and the positive relationship between CH₄ production and ΣP phenols points to the role of *Sphagnum* (Williams & Yavitt, 2003). The *p*-hydroxyl phenols do not have a methoxyl (-OCH₃) group on the 3' and 5' positions of the phenyl propane monomer, suggesting that the presence of the substituted methoxyl group retards methanogenesis. The ΣV phenols are much more prominent in woody plant lignin, and the large acid V to aldehyde V ratio in Big Run peat indicates the presence of extensively decomposed woody tissue (Hedges *et al.*, 1988). The presence of ΣV phenols might not be evident in *Sphagnum*-derived peat, although it plays a very important controlling role in carbon mineralization.

In previous studies, we found a positive relationship between CH₄ production and ΣC phenols (Yavitt *et al.*, 1997, 2000). However, the four peat soils in the present study had very small contents of ΣC phenols. The ΣC phenols are particularly abundant in the leaves of sedge plants (Williams *et al.*, 1998), which dominate in nutrient-rich, peat-forming fens rather than in *Sphagnum*-dominated bogs and nutrient-poor fens (Vitt *et al.*, 1995).

The role of N in decomposition has received considerable attention, but remains controversial. For instance, the negative relationship between CO₂ production and N concentration in our study is completely contrary to findings by Valentine *et al.* (1994), also for *Sphagnum*-derived peat. In our case, peat with a large C:N ratio supported large CO₂ production rates because the C was labile holocellulose. Since many peatlands are N poor (Kuhry & Vitt, 1996), anaerobic bacteria should be adapted to the low N status, and N can retard decomposition (Berg *et al.*, 1996).

The temperature response of carbon mineralization in soil is another important, controversial issue (Giardina & Ryan, 2000). For instance, we predicted that the four soil samples would have their greatest gas production rates after being transplanted into Bleak Lake, because microorganisms adapted to low mean annual temperature (MAT) show more respiratory response to a high incubation temperature than ones adapted to high MAT (Lloyd & Taylor, 1994). However, this prediction was not upheld. Our results were consistent with the hypothesis that CO₂ production is greater at a given temperature in soil from high-latitude sites (low MAT) than low-latitude sites (high MAT) (Enquist *et al.*, 2003), i.e. Bleak Lake peat had greater CO₂ production after transplant in Bleak Lake than Big Run peat after transplant in Big Run. So why did each of the peat soils retain a specific CO₂

production rate after a 3-year exposure to new climatic conditions? The prevailing hypothesis is that 'poor substrate quality' limits temperature response (Giardina & Ryan, 2000). However, this seems unlikely in our case given the wide difference in substrate quality among the four peat soils. It is likely that the popular hypotheses about temperature response of soil carbon mineralization (cf. Giardina & Ryan, 2000) do not apply to the unique situation of *Sphagnum*-derived peat: acid pH; mostly anaerobic, but occasionally aerobic processes; organic rich, but with varying Klason lignin composition; nutrient poor, except where impacted by air pollution.

Whether peat is saturated or drained also influences carbon mineralization rates, although the impact depends on the degree of tissue decomposition (Johnson & Damman, 1991; Belyea, 1996). We did not quantify decomposition *per se*, i.e. tissue mass loss. However, we did not find any pattern in the percentage change of holocellulose (the most easily decomposed organic fraction) among sites even though one site was waterlogged continuously (ELA flooded) and two sites were waterlogged more extensively in the summer (Bleak Lake water track, Big Run) than the other three sites. Our results did suggest increased decomposition of the Klason lignin fraction, as indicated by increase in the acid:aldehyde ratio of V and S phenols (Table 4). Three of the peat soils had a 30% increase in the acid:aldehyde ratio for V phenols, Bleak Lake subsurface peat had a 73% increase, but no pattern emerged as a function of presumed hydrologic regime. Because most decomposition studies use fresh plant biomass that can lose a substantial amount of mass, we hypothesize that the more aged material used in our study undergoes biochemical change largely independent of hydrologic regime.

Conclusions

In summary, *Sphagnum*-derived peat soil supported CH₄ production after transplant in four of six transplant sites and CO₂ production after transplant in all six sites. However, rates varied significantly as a function of peat chemistry. Furthermore, our results uncovered idiosyncratic combinations of peat chemistry and environment that controlled rates of CH₄ and CO₂ production. Idiosyncratic controls will complicate our ability to forecast rates of peat carbon mineralization into the future, given changing climatic, hydrologic, biotic (e.g. plant species) and soil pollution conditions.

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