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Climate change effects on carbon and nitrogen mineralization in peatlands through changes in soil quality

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Abstract

Climate change will directly affect carbon and nitrogen mineralization through changes in temperature and soil moisture, but it may also indirectly affect mineralization rates through changes in soil quality. We used an experimental mesocosm system to examine the effects of 6-year manipulations of infrared loading (warming) and water-table level on the potential anaerobic nitrogen and carbon (as carbon dioxide (CO_2) and methane (CH_4) production) mineralization potentials of bog and fen peat over 11 weeks under uniform anaerobic conditions. To investigate the response of the dominant methanogenic pathways, we also analyzed the stable isotope composition of CH_4 produced in the samples. Bog peat from the highest water-table treatment produced more CO_2 than bog peat from drier mesocosms. Fen peat from the highest water-table treatment produced the most CH_4. Cumulative nitrogen mineralization was lowest in bog peat from the warmest treatment and lowest in the fen peat from the highest water-table treatment. As all samples were incubated under constant conditions, observed differences in mineralization patterns reflect changes in soil quality in response to climate treatments. The largest treatment effects on carbon mineralization as CO_2 occurred early in the incubations and were ameliorated over time, suggesting that the climate treatments changed the size and/or quality of a small labile carbon pool. CH_4 from the fen peat appeared to be predominately from the acetoclastic pathway, while in the bog peat a strong CH_4 oxidation signal was present despite the anaerobic conditions of our incubations. There was no evidence that changes in soil quality have lead to differences in the dominant methanogenic pathways in these systems. Overall, our results suggest that even relatively short-term changes in climate can alter the quality of peat in bogs and fens, which could alter the response of peatland carbon and nitrogen mineralization to future climate change.

Keywords: 13-carbon, carbon dioxide, climate change, methane, peatlands, soil quality

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Introduction

Boreal peatlands are a diverse group of wetlands ranging from precipitation-fed (ombrotrophic) bogs to precipitation and groundwater-fed (minerotrophic) fens. Although peatlands occupy less than 3% of the terrestrial land surface (Bridgham *et al*., 2001), an estimated 455 Pg of carbon ($Pg = 10^{15}$ g), approximately one-third of the terrestrial carbon pool, is currently stored in peatlands (Gorham, 1995). With future climate change, there is the potential for peatlands to release this stored carbon as additional carbon dioxide (CO_2) and/or methane (CH_4) to the atmosphere, forming a positive feedback with anthropogenic increases in greenhouse gas emissions (Bridgham *et al*., 1995; Gorham, 1995; Wieder, 2001).

Numerous studies have demonstrated that temperature and water-table level directly control carbon (Dise *et al*., 1993; Moore & Dalva, 1993, 1997; Funk *et al*., 1994;

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Updegraff *et al*., 1995, 2001; Daulat & Clymo, 1998; Bellisario *et al*., 1999; Kettunen *et al*., 1999; Granberg *et al*., 2001) and nitrogen mineralization rates (Williams & Wheatley, 1988; Updegraff *et al*., 1995; Bridgham *et al*., 1998) in peatlands. It is, therefore, likely that climate change will directly alter peatland mineralization pathways through changes in precipitation regimes (leading to different aerobic status of peat) and changes in temperature.

Climate change, however, could act through an indirect pathway by causing changes in the peat substrate quality (Moore & Dalva, 1993; Chapin *et al*., 1995), either through a change in plant community composition, and hence the quality of incoming litter, or through changes resulting from decomposition processes, e.g., humification. Thus, in addition to direct and immediate effects on mineralization, a changing climate could have indirect and prolonged effects on peatland mineralization dynamics through changes in soil quality.

CH_4 is produced through a limited number of biochemical pathways that rely on a few simple substrates with the fermentation of acetate (acetoclastic pathway) and the reduction of CO_2 (coupled with H_2 oxidation in the autotrophic pathway) being the dominant pathways in freshwater ecosystems (Conrad, 1989). The relative importance of these methanogenic pathways in peatlands is controlled in part by temperature (Svensson *et al*., 1984; Avery *et al*., 1999, 2002), and therefore climate change is likely to have direct effects on CH_4 production pathways. However, studies have suggested that as soil organic matter becomes more recalcitrant, the relative importance of autotrophic methanogenesis increases (Chanton *et al*., 1995; Hornibrook *et al*., 1997, 2000; Miyajima *et al*., 1997). Thus, changes in soil quality resulting from climate change might also indirectly affect the dominant methanogenic pathways in peatlands. This could have large effects on net CH_4 fluxes (Shannon & White, 1996; Hines *et al*., 2001).

We hypothesize that relatively short-term (i.e., several year) perturbations in climate will indirectly affect carbon (as CO_2 and CH_4 production) and nitrogen mineralization in peatlands through changes in soil quality. Additionally, we hypothesize that changes in soil quality will change the relative importance of the acetoclastic and autotrophic CH_4 production pathways. In this paper, we test these hypotheses by measuring anaerobic carbon and nitrogen mineralization potentials under uniform conditions in bog and fen peat from peat monoliths that have been subjected to nine different simulated climates (i.e., manipulations of infrared loading and water-table levels) over 6 years. Because all peat was incubated under uniform temperature and anaerobic conditions, any changes in carbon and nitrogen mineralization dynamics are the result of indirect effects of the climate treatments on soil quality. Additionally, we use stable isotope techniques to look at the importance of CH_4 production pathways in the same samples.

Materials and methods

Sites

Source sites for the mesocosms were in a bog and a fen in the townships of Toivola and Alborn, respectively, in northeastern Minnesota (47°N, 92°W). The bog and fen sites are representative of other northern peatlands and have been described in detail elsewhere (Bridgham *et al*., 1998, 1999; Chapin, 1998; Chapin *et al*., in press; Weltzin *et al*., 2000, 2001, 2003; Updegraff *et al*., 2001).

The peat in the bog site is ~ 3.5 m deep with a basal date of $10\,040 \pm 70$ yr BP. The upper 60 cm is derived largely from *Sphagnum* moss, with increasing herbaceous remains below that point and frequent woody inclusions throughout the profile. The surface 25 cm of peat has a pH of 4.1, 42.2% carbon, 8.4% ash, and 73.7% rubbed fiber content on a dry-mass basis (Bridgham *et al*., 1998). The vegetation at the site is dominated by ericaceous shrubs [*Chamaedaphne calyculata* (L.) Moench., *Andromeda glaucophylla* Link., *Kalmia polifolia* Wang., *Vaccinium oxycoccox* L., *Rhododendron groenlandicum* (Oeder) Kron and Judd], bryophytes [*Sphagnum fuscum* (Schimp.) Klinggr., *S. capillifolium* (Ehrh.) Hedw., *S. magellanicum* Brid., *Polytricum juniperinum Var. affine* (Funck) Brid.], and black spruce [*Picea mariana* (Mill.) BSP]. Bog monoliths were extracted from a central, treeless portion of the bog. Water-table elevation at this site averages ~ -21 cm during the growing season but often drops to -30 cm or lower (Chapin, 1998).

The fen has ~ 4.4 m of sedge peat overlaying about 2 m of unconsolidated aquatic (limnic) peat, with a basal age of 9730 ± 70 yr BP. The surface 25 cm of peat has a pH of 4.9, 38.6% carbon, 22.3% ash, and 29.2% rubbed fiber content on a dry-mass basis (Bridgham *et al*., 1998). To maximize the contrast with the bog, fen monoliths were extracted from low areas (flarks) that were dominated by graminoids [*Rhyncospora alba* (L.), Vahl, *R. fusca* (L.) Ait.f., *Carex limosa* (L.), *C. lasiocarpa* Ehrh., *C. livida* (Wahl,)Wild.] with minimal cover by mosses. The water table at this site is on average $\sim +2$ cm in the flarks during the growing season and rarely drops below -5 cm (Chapin, 1998).

Experimental design

We examined carbon and nitrogen mineralization potentials in bog and fen peat samples that had experienced warming and water-table manipulations in an experimental, mesocosm framework for 6 years. The treatment design was a fully crossed factorial with three infrared-loading (warming) treatments, three water-table treatments, and two ecosystem types (bogs and fens), with three replicates of all treatments. The details of mesocosm construction are provided by Bridgham *et al*. (1999), and a brief summary is provided below.

Twenty-seven intact peat monoliths (2.1 m^2 surface area, 0.5–0.7 m depth) were removed from each peatland source site and placed in insulated plastic tanks that had been sunken into a large field. Beginning in July 1994, infrared loading was augmented with infrared heat lamps (Kalgo Electronics, Bethlehem, PA, USA) mounted $\sim$130 cm above the average surface height of two-thirds of the mesocosm plots. The lamps were left on continuously at either half power (= 'Medium') or full power (= 'High') outputs. The remaining one-third of plots were unheated (= 'Ambient'). The Medium and High warming treatments augmented ambient infrared input at the peat surface by 45^2 and 90 W m^{-2}, respectively (Noormets *et al*., in press). These treatments increased soil temperatures by 1.6–4.1 °C at 15 cm depth during the growing season (May–October), with the soil temperature response being strongly seasonal. Even though both fen and bog plots received the same infrared loading, fen plots were on average 0.8–1.0 °C warmer than bog plots due to ecosystem-dependent control over energy fluxes (Bridgham *et al*., 1999; Noormets *et al*., in press).

Beginning in 1994, water tables were set at approximately -3 cm (= 'Wet'), -16 cm (= 'Intermediate'), and -25 cm (= 'Dry') below the mean peat surface. These hydrology treatments represent a raising of the natural water table in the bog but a lowering of the water table in the fen. Water was replenished by natural rainfall and, during dry periods, by weekly additions of water from a ditch draining a local bog. Water-table levels were maintained only during the growing season (May–October). Because of differential treatment effects on the carbon balance of the plots, the peat surfaces in these mesocosms have been highly dynamic through time, and we have allowed the surface elevation of each plot to change relative to the water table as a treatment response (Weltzin *et al*., 2001).

Sample collection and processing

In January 2000 (6 years after the initiation of treatments), we removed three frozen cores (5.9 cm diameter, $\sim$15 cm depth) from each bog and fen mesocosm. In the bog samples, the upper $\sim$1 cm of green *Sphagnum* capitula was removed with a serrated knife. Cores were kept frozen until processing in the laboratory.

Cores were allowed to thaw overnight at 15 °C, live roots were removed by hand, and the remaining peat was homogenized and returned to -40 °C. Care was taken to minimize the time that peat was thawed for processing (to limit microbial mineralization), and in no case were samples at 15 °C for more than 30 h. The bulk density of root-free peat was calculated for each plot, and subsamples of root-free peat were used to determine the percent moisture of each core by drying at 60 °C for at least 48 h.

Approximately 30 g of field-moist peat was added to 120 mL, crimp-top serum bottles and slurried in a 1 : 1 ratio with deionized water. To make the slurries anaerobic, they were bubbled vigorously with N_2 for at least 10 min before being sealed with gray butyl septa. Once capped, sample bottles were allowed to incubate in the dark at 15 °C for 11 weeks. Thus, all samples were incubated as anaerobic slurries at a constant temperature, and any differences among treatments in mineralization potentials were likely the result of indirect changes in soil quality following warming and water-table manipulation.

Carbon and nitrogen mineralization

At approximately 1, 2, 4, and 11 weeks, headspace samples were removed from the serum bottles and analyzed for CO_2 and CH_4 simultaneously using a Varian 3600 gas chromatograph (Varian, Inc., Palo Alto, CA, USA) equipped with a thermal conductivity detector and a flame ionization detector for CO_2 and CH_4, respectively. On each date, the samples were shaken vigorously prior to injection to release all trapped gas bubbles. After each injection, the pressure in the headspace was measured using an Omega HHP 520 pressure meter (Omega Engineering, Stamford, CT, USA), caps were briefly removed from the serum bottles (allowing accumulated gas to escape), and the samples were bubbled again with N_2 to recreate anaerobic conditions, recapped and returned to the 15 °C incubator. Thus at each sampling date, the rate of gas production was a result of mineralization from the previous sampling date, not from the initiation of the experiment. The cumulative gas production at the end of the experiment was the sum of all gas measured at each sampling date.

Dissolved CH_4 and CO_2 were calculated using Henry's Law, adjusting for solubility, temperature, and pH (Stumm & Morgan, 1995). Headspace CH_4 and CO_2 concentrations were corrected for pressure.

Net nitrogen mineralization was calculated as the difference in available nitrogen (using 2 M KCl extractions) in peat before and after the 11-week incubation. Samples were analyzed for NH_4 and NO_3 on a Lachat autoanalyzer (Hach Company, Loveland, CO, USA). There were 36 cores that did not have initial samples remaining (due largely to our need to use all of the bog peat available to generate enough CH_4 for stable isotope work). Consequently, we filled in these data by using treatment-specific averages of available nitrogen.

Stable isotope analyses

The isotopic signature of CH_4 is dependent in part on the methanogenic pathway, and thus we used stable isotopes to determine the relative contribution of the acetoclastic and autotrophic pathways of CH_4 production (Whiticar, 1999). The acetoclastic pathway results in CH_4 that is enriched in ^{13}C ($\delta^{13}C$ of −65‰ to −50‰) relative to CH_4 from the autotrophic pathway ($\delta^{13}C$ of −110‰ to −60‰, Whiticar *et al*., 1986). Stable isotope analyses were performed on additional subsamples of peat from the 'corner' infrared-loading and water-table treatments (i.e., all combinations of High or Ambient heating and Wet or Dry water-table treatments). Peat was added to serum bottles and anaerobic conditions were created as described above. For bog peat samples, multiple serum bottles (from 1 to 4 depending on the amount of peat) were used for stable isotope analyses due to the low rates of CH_4 production in these samples. As above, all samples were allowed to incubate at 15 °C; however, samples used for stable isotope analyses remained sealed for the entire 11-week incubation.

At the end of the 11-week incubation, trace gases were purged onto a cryogenic distillation vacuum line using a flow of ultra-high-purity helium ($30\,mL\,min^{-1}$). The stable carbon and hydrogen isotopic composition of CH_4 was determined by isotope ratio mass spectrometry. The entire amount of gas in each serum bottle was transferred to the vacuum line so as to avoid any isotope fractionation associated with sample removal. Gases first passed into a liquid nitrogen (LN_2) trap (−192 °C) for removal of H_2O and CO_2. CH_4 moved through this trap and was combusted at 800 °C to CO_2 and H_2O in a CuO furnace. Combustion water was trapped in an acetone slush trap (−112 °C) and CO_2 was collected in an LN_2 trap. Helium carrier gas was removed by vacuum and the CH_4 combustion products, CO_2, and H_2O were transferred into separate Pyrex glass tubes and flame sealed. Numerous blank samples were run during vacuum line preparations and final isotopic values were adjusted accordingly; however, blanks were nearly always below detectable levels. Zinc metal turnings ('Indiana Zinc', Indiana University, Biogeochemical Laboratories, Bloomington, IN, USA) were used to reduce combustion water hydrogen to H_2, *in vitro*, by heating tubes to 500 °C for 40 min (Coleman *et al*., 1982). We included Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP) standards with each set of samples processed for water reduction. The overall CH_4 oxidation and purification efficiency of the procedure was consistently >95%.

Purified gas samples were analyzed for $^{13}C/^{12}C$ ($\delta^{13}C_{CH_4}$) and D/H (δD_{CH_4}) using a Finnigan MAT 252 isotope ratio mass spectrometer (Thermo Electron Corporation, Bremen, Germany). The required minimum sample size for this instrument in manual dual-inlet mode is about 1 mol CO_2 and 4 mol H_2. Analytical precision was generally better than ±0.05‰ and ±1‰ for $^{13}C/^{12}C$ and D/H, respectively. VSMOW and SLAP standards were used to correct δD_{CH_4} values according to the method outlined by Coplen (1988, 1996). Based upon the repeated analysis of CH_4 isotope standards, the accuracy of the entire procedure was about ±0.5‰ and ±10‰ for $^{13}C/^{12}C$ and D/H, respectively.

Statistical analyses

For all statistical analyses, the values from individual cores were averaged within each mesocosm plot. Thus, plots were used as true replicates and there were three replicates of each water-table and warming treatment combination. Cumulative carbon and nitrogen mineralization rates, as well as $\delta^{13}C$ and δD, were analyzed by peat type (bog or fen), heat treatment, and water-table treatment in a three-way ANOVA. In cases where there was a significant difference between peat types, a two-way ANOVA was used to investigate heat and water-table treatment effects. Fisher's least-significant difference tests were used to analyze pairwise comparisons. Rates of CO_2 and CH_4 production were analyzed using a repeated measure ANOVA with type, heat treatment, and water-table treatment as the categorical variables and time as the repeated variable. Again, when the type effect was significant, data from bog and fen samples were analyzed separately. All statistics were done using SYSTAT Version 10 (Systat Software, Inc., Point Richmond, CA, USA).

Results

Cumulative mineralization

Over the 11-week incubation, fen peat produced on average ~six-fold more CO_2, ~800-fold more CH_4, and ~nine-fold more nitrogen than bog peat (Table 1,

$P<0.001$). For CH_4 and nitrogen, the response to water-table treatments depended strongly on peat type ($P<0.01$); therefore, we subsequently analyzed water table and heat effects separately for bog and fen plots.

Within the bog plots, peat from the Wet treatment respired more CO_2 than peat from the Dry water-table treatment ($P=0.041$). Peat from the heat treatments did not differ in CO_2 production except that peat from the Ambient heat treatment produced more CO_2 than peat from the Medium or High heat treatments only within the Wet water-table treatment ($P<0.009$; data not shown). Bog peat from the different heat and water-table treatments did not differ in carbon mineralized as CH_4 (Table 1).

In the fen peat, there were no treatment effects on carbon respired as CO_2. In contrast, peat from the Wet treatment produced more CH_4 than peat from the Intermediate and Dry treatments ($P=0.002$), but there were no heat treatment effects on CH_4 production potentials (Table 1).

Bog peat from the Ambient and Medium heat treatments mineralized more nitrogen than peat from the High heat treatment (Table 1, $P=0.031$), with no effect of the water-table treatments. Negative mineralization in the High heat treatment (Table 1) indicates net immobilization, but this was not significantly different than zero. In the fen peat, nitrogen mineralization was only influenced by the water-table treatments; peat from the Intermediate and Dry treatments mineralized more nitrogen than peat from the Wet treatment (Table 1, $P=0.011$).

Rate of carbon mineralization through time

The rates of CO_2 production decreased through the length of this experiment, while the rates of CH_4 production increased (Figs 1 and 2). Bog peat from the Wet treatment had higher rates of CO_2 mineralization than peat from the Intermediate or Dry treatments (Fig. 1a, $P=0.015$), but this effect of the water-table treatments dissipated through time (water table × time interaction, $P<0.001$). The heat treatments had no significant main effect on CO_2 production in the bog peat ($P=0.51$), but initially peat from the Ambient heat treatment had higher rates of CO_2 production than peat from the High heat treatment (heat × time interaction, $P<0.002$, Fig. 1b). However, within the Wet water-table treatment, peat from the Ambient heat treatment produced more CO_2 than peat from the other heat treatments (water table × heat interaction, $P=0.018$), similar to the cumulative CO_2 mineralization results.

In the fen peat, there were initially higher rates of CO_2 production in peat from the Wet treatment, but this effect dissipated through time (water table × time

Table 1 Mean ($\pm$ 1 SE) cumulative carbon and nitrogen mineralization after 11 weeks of incubation at 15 °C

	Carbon		
Treatment	CO_2–C ($\mu g\,cm^{-3}$ dry peat)	CH_4–C ($\mu g\,cm^{-3}$ dry peat)	Nitrogen ($\mu g\,cm^{-3}$ dry peat)
Bog	62.9 ± 2.0^{1}	0.17 ± 0.06^{1}	4.0 ± 1.3^{1}
Heating			
Ambient	65.5 ± 5.2^{a}	0.10 ± 0.04^{a}	6.0 ± 2.0^{a}
Medium	61.6 ± 2.4^{a}	0.16 ± 0.10^{a}	6.8 ± 1.3^{a}
High	61.5 ± 1.7^{a}	0.24 ± 0.16^{a}	-0.63 ± 2.3^{b}
Water table			
Wet	68.5 ± 4.4^{a}	0.26 ± 0.12^{a}	2.9 ± 2.5^{a}
Intermediate	61.4 ± 2.5^{ab}	0.21 ± 0.15^{a}	2.5 ± 2.5^{a}
Dry	58.8 ± 2.2^{b}	0.04 ± 0.03^{a}	6.6 ± 1.3^{a}
Fen	413.2 ± 19.9^{2}	134.7 ± 9.7^{2}	37.5 ± 6.0^{2}
Heating			
Ambient	382.9 ± 16.8^{a}	132.9 ± 13.4^{a}	29.0 ± 8.5^{a}
Medium	391.1 ± 10.8^{a}	140.7 ± 13.0^{a}	49.8 ± 12.0^{a}
High	465.7 ± 54.4^{a}	130.7 ± 23.6^{a}	33.6 ± 10.1^{a}
Water table			
Wet	457.6 ± 46.4^{a}	177.9 ± 14.2^{a}	15.0 ± 10.1^{a}
Intermediate	408.1 ± 32.7^{a}	128.4 ± 12.9^{b}	45.9 ± 9.7^{b}
Dry	374.1 ± 14.5^{a}	97.9 ± 11.6^{b}	51.5 ± 7.4^{b}

Significant differences ($P<0.05$) between bog and fen peat are indicated by numbers. Means within a column followed by different letters are significantly different ($P<0.05$) within a peat type (bog or fen) and the same main treatment (infrared loading or water table).

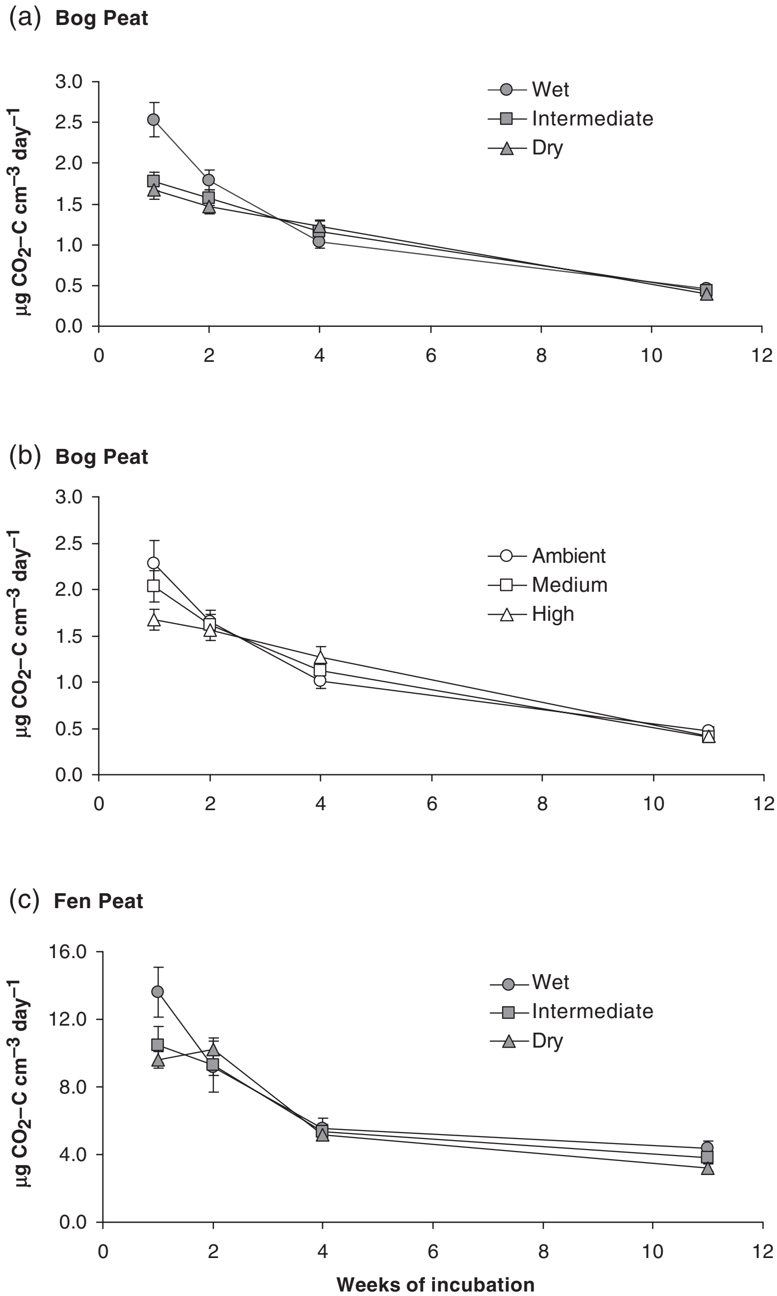

Fig. 1 Rates of respired carbon (as mean CO_2 production $\pm$ 1 SE) through time in an 11-week incubation in (a) bog peat by water-table treatment, (b) bog peat by infrared-loading treatment, and (c) fen peat by water-table treatment.

interaction, $P = 0.005$), similar to the bog peat (Fig. 1c). The heat treatments did not affect CO_2 production potentials in fen peat (data not shown).

Neither the heat or water-table treatments affected CH_4 production potentials in the bog peat ($P = 0.51$ and 0.48, respectively). However, the time course of CH_4 production depended on the water-table treatment (water table $\times$ time interaction, $P = 0.033$), likely driven by a switch in the relative magnitude of CH_4 production in the peat from the Wet treatment (Fig. 2a). Interpreting the meaning of this water table $\times$ time interaction is difficult because of high variability in the final CH_4 concentrations resulting from low rates of CH_4 production in bog peat.

Fen peat from the Wet treatment produced the most CH_4 ($P < 0.001$). Moreover, differences in CH_4 production in peat from the different water-table treatments increased over time (water table $\times$ time interaction,

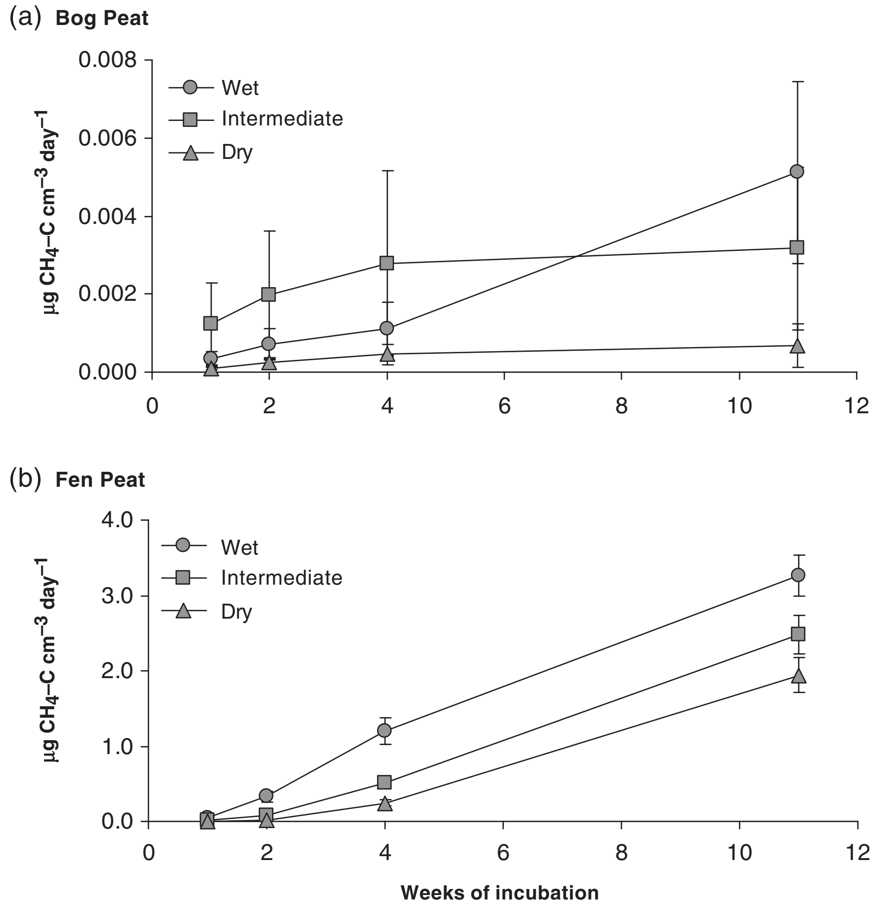

Fig. 2 Rates of respired carbon (as mean CH_4 production $\pm$ 1 SE) through time in an 11-week incubation in (a) bog peat by water-table treatment and (b) fen peat by water-table treatment.

$P<0.001$, Fig. 2b). The heat treatments did not affect CH_4 mineralization potentials in fen peat (data not shown).

The ratio of CO_2–C to CH_4–C in the bog peat remained high (over 10 000) at all sampling dates during the course of this experiment, reflective of the extremely low rates of CH_4 production in bog peat. Neither the heat nor water-table treatments altered this ratio in the bog peat. In fen peat, however, the CO_2–C/CH_4–C ratio decreased through time ($P=0.020$, Fig. 3), likely reflecting both decreased rates of CO_2 production and increased rates of CH_4 production (Figs 1 and 2). Fen peat from the different water-table treatments had marginally different CO_2–C/CH_4–C ratios ($P=0.080$), but this effect weakened through time (water table $\times$ time interaction, $P=0.016$).

Stable isotopes

$\delta^{13}C$ and δD stable isotopes were analyzed to investigate the relative contribution of the acetoclastic and the autotrophic methanogenic pathways. CH_4 from bog peat was enriched in ^{13}C relative to CH_4 from fen peat (-30.5 ± 2.2‰ for bog peat compared to -47.8 ± 2.7‰ for fen peat, Fig. 4). There were no differences in the δD signatures in CH_4 from bog and fen peat (-280.8 ± 22.9‰ for bog peat and -260.2 ± 12.1‰ for fen peat, Fig. 4). Additionally, there were no treatment effects on $\delta^{13}C$ or δD signatures for CH_4 from bog or fen peat.

Discussion

Because all peat was incubated under uniform temperature and anaerobic conditions, any differences in CO_2, CH_4, or nitrogen mineralization potentials were the result of indirect effects on soil quality resulting from manipulations of water table and heating in the mesocosm plots during the previous 6 years. Overall, our results support our initial hypothesis that relatively short-term changes in climate have indirect effects on soil quality which alters cumulative mineralization

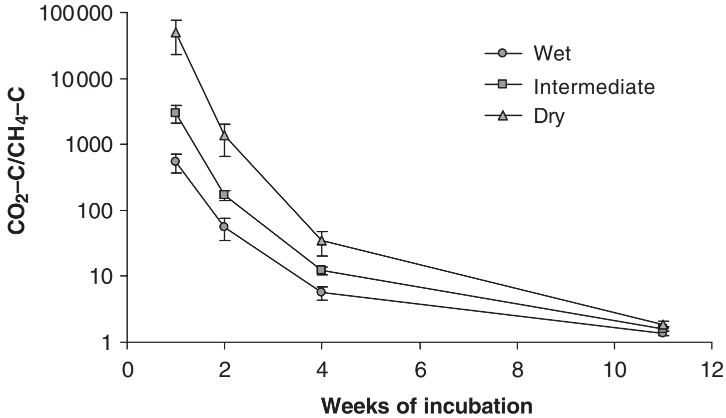

Fig. 3 Ratio of CO_2–C produced to CH_4–C produced through the course of an 11-week incubation in fen peat; note the log scale.

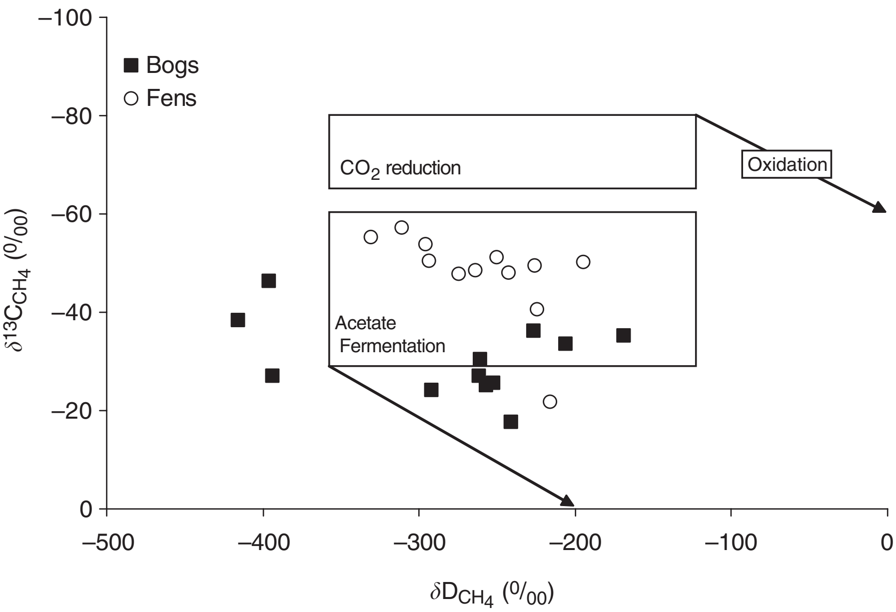

Fig. 4 Stable C and H isotopic ratio cross-plot for methane produced in bog and fen peat following an 11-week incubation. Range boxes for CO_2 reduction and for acetate fermentation represent approximate end member values derived from Whiticar *et al*. (1999) and Avery *et al*. (1999). The oxidation vector represents the isotopic separation associated with methane oxidation reported by Whiticar *et al*. (1999).

(Table 1), as well as the dynamics of carbon mineralization through time (Figs 1 and 2). Thus, climate change may be an important control of carbon (as CO_2 and CH_4 production) and nitrogen mineralization dynamics in peatlands long after the initial climate perturbation. However, the lack of treatment effects on the $\delta^{13}C$ or δD signatures for CH_4 suggests that 6 years of climate manipulations have not changed the dominant methanogenic pathway (Fig. 4).

The mesocosm system used in this experiment allowed for a unique, controlled manipulation of climatic variables in a bog and a fen. While rates of carbon and nutrient cycling as well as plant community composition and productivity in the mesocosms are similar to natural bogs and fens (Chapin, 1998; Weltzin *et al*., 2000, 2001, 2003, unpublished data; Updegraff *et al*., 2001), the specific responses of peatland mineralization dynamics observed in peat from the mesocosms may not be directly applicable to natural ecosystems. We suggest, however, that the general patterns observed in this experiment (i.e., indirect effects of climate change on peatland mineralization dynamics through changes in soil quality) are likely to be similar in natural bogs and fens.

In a separate experiment 1 year after the climate change treatments were initiated, peat from the mesocosm plots was incubated for 2 weeks at 30 °C (unpublished data). The CO_2 mineralization potential of bog and fen peat did not differ, and there was no effect of heating or water-table manipulation on CO_2 mineralization. CH_4 mineralization potential was higher in fen peat than in bog peat, similar to the results in the current study. Fen peat from the Dry water-table treatment produced slightly less CH_4 than peat from the other water-table treatments ($P = 0.061$). The lack of water-table and heat treatment effects on CO_2 and CH_4 production potentials after 1 year of climate manipulation supports the notion that differences in mineralization in the current study must be in response to changes in soil quality resulting from extended climate manipulations in the mesocosm plots.

While the term 'soil quality' has been used extensively in the soil literature (e.g., Doran *et al*., 1994), it is often defined ambiguously and encompasses the properties and sizes of labile carbon pools, turnover rates of those pools, nutrient concentrations, soil physical structure, microbial community structure, etc. It was beyond the scope of this experiment to attempt to unravel the many potential changes in the abiotic and biotic properties of the fen and bog peats from 6 years of climate manipulations that underlie the changes in mineralization that we observed. Also, based upon our previous experience in attempting to relate carbon and nutrient mineralization dynamics with specific physiochemical variables in peat (Updegraff *et al*., 1994, 1995; Bridgham *et al*., 1998), we believe that it is unlikely that we would have found simple cause–effect relationships of individual soil quality parameters and mineralization in the current study.

However, the convergence of CO_2 production with time, in the different climate treatments supports an interpretation that they altered a relatively small labile carbon pool that was rapidly consumed. In the bog peat, both water-table and heating treatments affected the initial rate of CO_2 mineralization, but these differences diminished over time (Fig. 1a, b). Rates of CO_2 production also converged over time in the different water-table treatments in the fen peat (Fig. 1c). Both empirical studies (Wedin & Pastor, 1993; Updegraff *et al*., 1995; Bridgham *et al*., 1998) and ecosystem models (Pastor & Post, 1986; Parton *et al*., 1988) have suggested that carbon and nitrogen mineralization are driven by substrates in both labile and recalcitrant soil pools. In these studies and models, much of the variation in mineralization is accounted for by differences in the size and dynamics of the relatively small labile pool.

The labile carbon and nitrogen pools in peat could be affected by climate change through changes in the vegetation community structure (and hence changes in incoming litter material) and/or changes resulting from decomposition processes, e.g., humification. Although our experimental design does not allow us to separate these effects, there is evidence that both could play a role in the context of the mesocosms experiment. Specifically, Updegraff *et al*. (2001) demonstrated that net CO_2 and CH_4 fluxes from the mesocosm plots were directly related to climate change variables, which have the potential to alter the carbon quality of remaining peat. There have also been large treatment effects on nitrogen concentrations in porewater, nitrogen availability measured with exchange resins, and overall nitrogen retention within a plot (unpublished data).

Additionally, the productivity and foliar cover of bryophytes, graminoids, and shrubs have changed in response to climate manipulations in the mesocosm plots (Weltzin *et al*., 2000, 2001, 2003). This clearly alters the litter inputs into the system with potential effects on the decomposability of the resulting peat (Scheffer *et al*., 2001). Wedin & Pastor (1993) also found that changes in potential nitrogen mineralization, after a comparable number of years in a prairie, could be explained by changes in plant community composition and litter quality. Changes in belowground production may also be important, as root litter and exudates act as a relatively labile source of carbon and nitrogen for microbial mineralization compared to more recalcitrant peat, with this labile carbon source being particularly important for methanogenesis (Whiting & Chanton, 1993; Chanton *et al*., 1995; Updegraff *et al*., 2001). It should be noted that roots were removed from our peat slurries prior to the incubation, as our focus was on changes in mineralization potentials in the peat. Therefore, our results likely underestimate potential changes in mineralization dynamics through changes in carbon availability, as there have been dramatic treatment effects on belowground productivity in the mesocosm plots (Weltzin *et al*., 2000), and CH_4 fluxes are strongly correlated with instantaneous net ecosystem production in the mesocosms (Updegraff *et al*., 2001).

Despite the treatment and temporal effects that we found for CH_4 production in this experiment, we found no treatment effects on the $\delta^{13}C$ or δD signatures of CH_4 in either the bog or fen plots, suggesting that changes in peat quality did not lead to shifts in the dominant pathways of methanogenesis. The $\delta^{13}C$ signal seen in CH_4 from fens suggests that acetoclastic methanogenesis was the dominant pathway of CH_4 production over the course of this incubation (Fig. 4). The average $\delta^{13}C_{CH_4}$ value from the fens was -47.8 ± 2.7‰, which is slightly more enriched than the typical values resulting from acetoclastic methanogenesis reported by Whiticar *et al*. (1986), but consistent with values from acetoclastic methanogenesis in other peatlands (Hornibrook *et al*., 1997; Avery *et al*., 1999). The apparent importance of this pathway in fen peat in this experiment is contrary to the findings of others who have shown autotrophic methanogenesis to be the dominant source of CH_4 in many peatlands (Williams & Crawford, 1984; Hines *et al*., 2001; Horn *et al*., 2003).

The apparent importance of the acetoclastic methanogenic pathway in fen peat in this experiment should be interpreted with caution, as the methanogenic microbial community was likely altered by the removal of roots and the slurring of peat and may not have fully developed during the 11-week incubation. Avery & Martens (1999) demonstrated that a significant amount of variation between the $\delta^{13}C$ values of CH_4 produced in sediment incubation experiments could be attributed to changes in the $\delta^{13}C$ value of the ΣCO_2 pool, which became enriched during times of high CH_4 production resulting in enriched CH_4 even though there was not a dramatic shift in methanogenic pathways. Further, the magnitude of isotopic fractionation for autotrophic methanogens will depend on their microbial growth stage (Botz *et al*., 1996). Thus, autotrophic methanogenesis may have been occurring with little isotopic fractionation of an enriched CO_2 substrate, contributing to the enriched CH_4 produced during this experiment.

The C and H isotopic composition of CH_4 from bog peat, while quite variable, is strongly suggestive of CH_4 oxidation (Whiticar, 1999), despite the anaerobic conditions of our peat slurries. It is possible that despite bubbling vigorously with N_2 there were oxic microsites remaining in our slurries. If methanotrophs were able to take advantage of a remnant oxygen source, the resulting shift in $\delta^{13}C$ and δD values of CH_4 could be large considering the extremely low rates of CH_4 production in the bog peat throughout this experiment. However, we cannot rule out the possibility of anaerobic CH_4 oxidation, which has been suggested to occur in peat (Smemo *et al*., 2002).

In conclusion, while the direct and immediate controls of climate on carbon and nitrogen dynamics are relatively well characterized, our results suggest that even short-term changes in climate will also affect cumulative carbon and nitrogen mineralization, as well as the temporal dynamics of mineralization *indirectly*, through changes in relatively small labile carbon and nitrogen soil pools. As roots were removed from our peat slurries, our results likely underestimate potential changes in mineralization dynamics through changes in carbon availability, and suggest that climate change may be an important control of carbon (as CO_2 and CH_4 production) and nitrogen mineralization after the initial climate perturbation

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