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Reduction of the temperature sensitivity of minerotrophic fen methane emissions by simulated glacial atmospheric carbon dioxide starvation

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[1]   Variations to the global wetland CH_4 source strength in response to changes in orbital insolation patterns and atmospheric CO_2 concentration ($[CO_2]_a$) are hypothesized to play an important role in determining glacial-interglacial variations in atmospheric CH_4 concentration ($[CH_4]_a$). Here the interactive effects of temperature, a major controlling variable determining wetland CH_4 flux, and the low $[CO_2]_a$ of glacial intervals are investigated for the first time. We measured the temperature dependence of CH_4 emissions from replicated mesocosms ($n = 8$ per CO_2 treatment) collected from a minerotrophic fen and an ombrotrophic bog incubated in either ambient (c. 400 ppm) or glacial (c. 200 ppm) $[CO_2]_a$ located in the United Kingdom. CH_4 fluxes were measured at 5°C, 10°C, 15°C, 20°C, and 25°C and then in reverse order over a 20 day period under each $[CO_2]_a$ treatment. Results showed that the Q_{10} temperature response of CH_4 emissions from the *Carex*/*Juncus*-dominated fen declined significantly by approximately 39% under glacial $[CO_2]_a$ (ambient $[CO_2]_a = 2.60$, glacial $[CO_2]_a = 1.60$; $P < 0.01$). By contrast, the response of CH_4 emissions from the *Sphagnum*-dominated bog remained unaltered (ambient $[CO_2]_a = 3.67$, glacial $[CO_2]_a = 3.67$; $P > 0.05$). This contrasting response may be linked to differences in plant species assemblage and the varying impact of CO_2 starvation on plant productivity and carbon availability in the rhizosphere. Furthermore, our results provide empirical evidence to support recent model-based indications that glacial-interglacial variations in $[CH_4]_a$ may be explained by changes in wetland CH_4 source strength in response to orbitally forced changes in climate and $[CO_2]_a$.

1.   Introduction

[2]   Over a 100 year time scale, CH_4 is approximately 25 times more powerful at trapping outgoing long-wave radiation compared to the same mass of CO_2 [*Forster et al.*, 2007], making it a powerful greenhouse gas that requires its sources and sinks to be accurately quantified when seeking to understand both modern and ancient Earth systems. Prior to anthropogenic influence over the CH_4 cycle, the causes of long-term natural variation in atmospheric CH_4 concentration ($[CH_4]_a$) observed in ice cores are uncertain. In particular, the approximately 50% decline in $[CH_4]_a$

between interglacials (c. 800 ppm) and glacials (c. 350 ppm) [*Loulergue et al.*, 2008] remains largely unexplained. Discussions of the causes of this decline have thus far focused on changes to wetland areas with changing sea level and the strength of the tropospheric CH_4 sink (reaction with the OH radical) [e.g., *Chappellaz et al.*, 1993; *Kaplan et al.*, 2006; *Valdes et al.*, 2005]; however, these two potential explanations are not without conflicting evidence [e.g., *Arneth et al.*, 2007; *Weber et al.*, 2010]. Recently, modeling and experimental studies have suggested that the 50% decline may be caused by variations in wetland CH_4 emissions in response to orbitally forced changes in climate and atmospheric CO_2 concentrations ($[CO_2]_a$) [*Boardman et al.*, 2011; *Levine et al.*, 2011; *Singarayer et al.*, 2011].

[3]   Wetlands are the largest natural biogenic source of CH_4 to the atmosphere [*Lelieveld et al.*, 1998; *Whalen*, 2005], with emissions controlled by a number of key biotic and abiotic factors [*Lai*, 2009; *Le Mer and Roger*, 2001; *Segers*, 1998; *Whalen*, 2005]. These include temperature, pH, water table, $[CO_2]_a$, and species assemblage [*Daulat and Clymo*, 1998; *Dunfield et al.*, 1993; *Megonigal and Schlesinger*, 1997; *Strom et al.*, 2005]. When anaerobic conditions are established, $[CO_2]_a$ is one of the most important drivers regulating ecosystem productivity and the supply of

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organic substrate for methanogenesis to occur in the rhizosphere [*Kuzyakov*, 2002; *Megonigal et al.*, 1999; *Vann and Megonigal*, 2003; *Whiting and Chanton*, 1993]. Ice core records indicate low [CO_2]$_a$ existed repeatedly during glacials (c. 180–200 ppm) over the past 800 ka [*Luthi et al.*, 2008]. Such low values impose CO_2 starvation conditions for C_3 plants as they become substrate (CO_2) limited during the carboxylation reaction of photosynthesis [*Tissue et al.*, 1995; *Cowling and Sykes*, 1999; *Sage and Coleman*, 2001], thus causing an approximately 50% decrease in photosynthetic capacity (at optimal temperatures) and subsequent decreases in productivity and root biomass, when compared to C_3 plants grown in modern day [CO_2]$_a$ [*Dippery et al.*, 1995; *Pagani et al.*, 2009; *Polley et al.*, 1993; *Sage*, 1995]. Glacial [CO_2]$_a$ has been shown to reduce CH_4 emissions from certain wetland types [*Boardman et al.*, 2011]; however, the interaction between temperature and CO_2 starvation on wetland emissions during glacials remains to be investigated.

[4] Pleistocene and Holocene variations in [CO_2]$_a$ and [CH_4]$_a$ are strongly correlated with past temperature [*Loulergue et al.*, 2008; *Monnin et al.*, 2001; *Petit et al.*, 1999; *Shakun et al.*, 2012], suggesting a direct link between temperature and the sources and sinks of these gases. The influence of temperature on wetland CH_4 flux is often represented in process-based models [e.g., *Cao et al.*, 1996; *Gedney et al.*, 2004; *Li et al.*, 2010; *Walter et al.*, 1996] as a Q_{10} value, i.e., the proportional change in reaction rate (here CH_4 emission) with an increase of 10°C in temperature. Temperature coefficients (Q_{10}) range from 1 to 35 for methanogenesis in wetland soils [*Segers*, 1998; *Whalen*, 2005]. This wide range of values most likely reflects the temperature sensitivity of microbial processes that precede methanogenesis, because these processes limit the temperature response of methanogens [*Bergman et al.*, 1998], and/or the temporal and spatial differences in substrate availability and quality within wetland soils [*Davidson and Janssens*, 2006]. We therefore investigated the hypothesis that low glacial [CO_2]$_a$ alters the temperature dependence of CH_4 emissions from wetlands compared to modern day [CO_2]$_a$ through species-specific changes in primary productivity and a reduction in below-ground carbon allocation and exudation. Our experimental design included minerotrophic (nutrient-rich) and ombrotrophic (nutrient-poor) wetland mesocosms that were exposed to [CO_2]$_a$ typical of glacial maxima (180–200 ppm) for >400 days (one season) and control mesocosms that were maintained at modern ambient [CO_2]$_a$ for the same duration in controlled environment units (CEUs).

2. Materials and Methods

2.1. Site Description and Field Sampling

[5] We collected a total of 32 peat mesocosms (11 × 40 cm) complete with intact surface vegetation in autumn 2006 from wetlands of contrasting nutrient status in the United Kingdom. The temperature response study we report here was performed during the second growing year of a long-term glacial maxima [CO_2]$_a$ simulation experiment [*Boardman et al.*, 2011]. Mesocosms were collected from a minerotrophic fen in Anglesey, Wales (Cors Goch; 53.31°N, −4.25°W), and an ombrotrophic bog in

Snowdonia, Wales (Migneint; 52.97°N, −3.84°W). Both sites have provided mesocosms for previous wetland biogeochemistry experiments [*Freeman et al.*, 2004; *Hutchin et al.*, 1995; *Kang et al.*, 2001]. Cors Goch is a base-rich alkaline fen that overlies Carboniferous limestone. Mesocosm samples were taken from areas containing *Sphagnum tenellum*, *Sphagnum recurvum*, *Juncus subnodulosus*, and *Carex lepidocarpa*. Migneint is a base-poor ombrotrophic blanket bog that only receives nutrients from rainwater. Cores were collected from sites containing the species *Juncus effusus*, *Eriophorum vaginatum*, *Sphagnum papillosum*, and *Hypnum cupressiforme*. More physiochemical details of site characteristics can be found in the studies of *Boardman et al.* [2011] and *Kang et al.* [2001]. During the experiment, there was no statistical difference ($P > 0.05$) in ambient and simulated glacial vascular plant numbers between the fen and bog mesocosms.

[6] Mesocosms were created by inserting sections of PVC pipe (11 × 40 cm) into representative locations at both sites. Pipe sections were inserted into the ground using a combination of scissors and a custom-made iron chisel (100 × 0.5 cm). Scissors were used to initially cut around the perimeter vegetation and position the pipe approximately 2–3 cm into the ground. The chisel was then used to cut roots deeper in the rhizosphere as the pipes were slowly inserted into the peat. Each mesocosm was removed by creating a small trench at the side of the pipe. Mesocosms were immediately fitted with a base cap and sealed (silicone sealant) to maintain the anaerobic condition of the core. Samples were promptly transported to the controlled environment facility at the Open University where they were placed into CEUs.

2.2. Controlled Environment Parameters

[7] In total, 16 bog and 16 fen mesocosms were split between two Snijders Microclima MC1750E CEUs. One set of mesocosms (8 from the bog and 8 from the fen) was incubated at simulated glacial CO_2 concentrations (180–200 ppm), and the other was maintained at current [CO_2]$_a$ (c. 390 ppm). CO_2 concentrations in both CEUs were created and maintained by mixing CO_2-free air (<1 ppm) from a purge gas generator (CMC Ltd.) with laboratory air to the desired concentrations. During this short (20 day) study, mesocosms were randomized within their CEU after every sampling point at each temperature, but they were not rotated between CEUs as this would have significantly increased the mesocosm temperature and CEU [CO_2]$_a$ equilibration time. However, the study was completed with mesocosm samples that had been rotated along with their allocated CO_2 exposure between two CEUs on a monthly basis over the previous year to limit block effects [*Boardman et al.*, 2011].

[8] During this experiment, the average CO_2 concentrations were 395 ± 21 (standard deviation) and 199 ± 28 ppm in the ambient and glacial CEUs, respectively. Mesocosms within each CEU received 12 h of light at 250 μmol m^{-2} s^{-1} and 12 h of complete darkness on each day of the temperature response study (20 days in total). Relative humidity was set to a constant 70%, and the water table was fixed to the surface with frequent additions of distilled water. For each mesocosm, CH_4 fluxes were measured at 5°C, 10°C, 15°C, 20°C, and 25°C and then in reverse order to account for any possible lag effects. At each monitoring

temperature, mesocosms were allowed to equilibrate for >24 h (a full day and night cycle) before measurements were taken. Infrared thermometer readings (data not shown) indicated the outside of the mesocosms was at temperature set point within 6 h when changed; therefore, we are confident that internal temperatures would have fully adjusted by measurement time. Previous wetland temperature response experiments with peat monoliths larger than those used in this study (30 × 40 cm) showed that soil temperature equilibrated to changing atmospheric temperature within 15 h [e.g., *Macdonald et al.*, 1998].

2.3. CH$_4$ Flux and Temperature Response Calculations

[9] CH$_4$ emissions were measured using static closed chambers constructed from a clear perspex pipe (11 × 50 cm). A mixing fan secured to the inside of the chambers ensured an evenly mixed chamber atmosphere, and pressure changes were prevented by using a small needle hole (0.8 mm) through a resealing membrane. Measurement times were typically less than 2–3 min per mesocosm flux; therefore, no water vapor corrections were necessary. CH$_4$ concentrations were measured using off-axis integrated cavity output spectroscopy (Los Gatos Research RMA-200 Fast Methane Analyser), with fluxes calculated from the linear increase in CH$_4$ concentration within the chamber. Measurement time and [CO$_2$]$_a$ set point readjustment from opening the CEUs to sample accounted for <3 h out of the 48 h at each temperature point. Q_{10} values were calculated using the linear increase between two temperature points in the experiment as follows:

$$Q_{10} = \left(\frac{R_1}{R_2}\right)^{\left(\frac{10}{T_2 - T_1}\right)}, \qquad (1)$$

where R_1 and R_2 are the rates of CH$_4$ production (mg m^{-2} d^{-1}) at two measured temperatures, T_1 and T_2, respectively. Q_{10} values were calculated for individual mesocosm replicates in the measurement categories of 5°C–10°C, 10°C–15°C, 15°C–20°C, and 20°C–25°C. These data were then averaged, and an appropriate measure of variation (standard error) was calculated for each wetland treatment type/group.

The Mann–Whitney U test was used to determine any statistically significant differences between ambient and simulated glacial CO$_2$ treatments when analyzing average CH$_4$ flux and Q_{10} values. Activation energies were calculated using the natural log of the Arrhenius equation,

$$\ln K = \ln A - \frac{E_a}{R}\left(\frac{1}{T_K}\right), \qquad (2)$$

where K is the rate constant for the chemical reaction (mg m^{-2} d^{-1}), A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas content (8.314 J K^{-1} mol^{-1}), and T_K is the temperature (Kelvin). Equation (2) was used to correlate $\ln K$ with $1/T_K$ to produce slope functions ($-E_a/R$) that enabled us to calculate activation energies for CH$_4$ emissions.

3. Results and Discussion

3.1. Temperature Responses of CH$_4$ Emissions

[10] Bog and fen mesocosms maintained under ambient and simulated glacial [CO$_2$]$_a$ both showed CH$_4$ emissions increasing exponentially between 5°C and 25°C (Figure 1 and Table 1). This is consistent with other controlled environment studies [*Daulat and Clymo*, 1998; *Gauci et al.*, 2004; *Macdonald et al.*, 1998] and with field observations [*Christensen et al.*, 2003]. However, in our experimental mesocosms, bog and fen CH$_4$ emissions contrasted in their response to the glacial CO$_2$ treatment (Figure 1), with CH$_4$ fluxes from the fen mesocosms exhibiting an increasing [CO$_2$]$_a$ effect from 10°C and higher, whereas those from the bog mesocosms remaining unaltered. Average CH$_4$ emissions also reflected this contrasting pattern, with no glacial [CO$_2$]$_a$ effect in average bog mesocosm emissions compared to approximately 23% suppression in fen mesocosm emissions ($P < 0.05$; Table 1).

[11] To further characterize our findings, individual mesocosm Q_{10} values for 5°C–10°C, 10°C–15°C, 15°C–20°C, and 20°C–25°C, plus activation energies for each treatment group, were calculated (Figure 2 and Table 1). Results of this analysis produced values that were typical of wetland
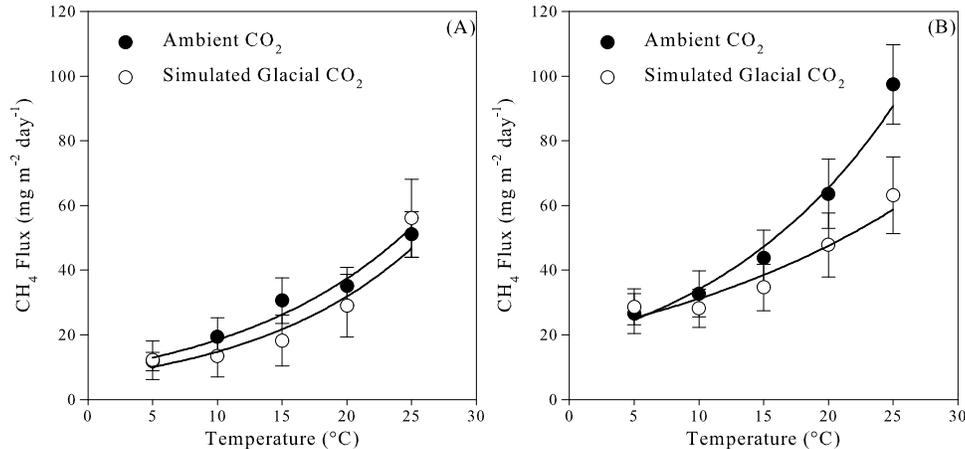
Figure 1. Comparison of CH$_4$ flux responses to changes in temperature in mesocosms collected from (a) an ombrotrophic bog and (b) a minerotrophic fen subjected to glacial [CO$_2$]$_a$. Solid and dashed lines represent regression models for controls and treatments, respectively (equations provided in Table 1). Error bars represent ±1 standard error of the mean.

Table 1. CH$_4$ Flux Versus Temperature Regression Equations, Average CH$_4$ Emissions, and Average Q_{10} Values in the Experiment[a]

Wetland Type	Experimental Group	CH$_4$ Flux Regression Equation	CH$_4$ Flux Regression Coefficient of Determination (R^2)	Average CH$_4$ Emission (mg m^{-2} d^{-1}, ±1 SE)	Average Q_{10} (±1 SE)	Arrhenius Plot Regression Equation	Arrhenius Plot Regression Coefficient of Determination (R^2)	Activation Energy (kJ mol^{-1})
Bog	Ambient CO$_2$	$K = 9.09e_C^{0.07T}$	0.97	29.6 ± 3.00	3.67 ± 0.53	$\ln K = 27.5 - 7088/T_K$	0.99	58.9
	Simulated Glacial CO$_2$	$K = 6.86e_C^{0.08T}$	0.93	25.8 ± 4.21	3.67 ± 0.46	$\ln K = 31.8 - 8475/T_K$	0.94	70.4
Fen	Ambient CO$_2$	$K = 17.7e_C^{0.07T}$	0.98	52.8 ± 4.95*	2.60 ± 0.32**	$\ln K = 26.5 - 6627/T_K$	0.94	55.1
	Simulated Glacial CO$_2$	$K = 20.4e_C^{0.04T}$	0.91	40.5 ± 3.98	1.60 ± 0.10	$\ln K = 16.2 - 3838/T_K$	0.74	31.9

*Significant at $P < 0.05$. **Significant at $P < 0.01$ (between ambient and simulated glacial CO$_2$ figures within the same wetland type).
[a]SE = standard error, T_C = temperature in degrees Celsius, K = rate constant (CH$_4$ flux in mg m^{-2} d^{-1}), T_K = temperature in Kelvin, $\ln K$ = natural log of rate constant.

ecosystems [*Segers*, 1998; *Westermann*, 1993; *Whalen*, 2005]. There was no discernible pattern in CH$_4$ flux Q_{10} response to temperature from the bog mesocosms, with no significant difference ($P > 0.05$) between ambient and simulated glacial [CO$_2$]$_a$ values in three out of the four categories (Figure 2a). A higher activation energy was associated with CH$_4$ emissions from bog mesocosms in the glacial treatment compared to the ambient group (Table 1). Minerotrophic fen mesocosms experiencing the glacial [CO$_2$]$_a$ treatment showed reductions of 62% ($P < 0.05$), 33% ($P < 0.05$), 31% ($P > 0.05$), and 30% ($P > 0.05$) in Q_{10} value in the 5°C–10°C, 10°C–15°C, 15°C–20°C, and 20°C–25°C temperature range categories, respectively (Figure 2b). The average fen Q_{10} value in the simulated glacial [CO$_2$]$_a$ was approximately 39% lower compared to the ambient fluxes ($P < 0.01$; Table 1).

3.2. Heterogeneous CH$_4$ Emission Response to [CO$_2$]$_a$ Starvation

[12] The Q_{10} values and activation energies for CH$_4$ emissions reported in this study are highly dependent on the supply and microbial breakdown of organic carbon in the rhizosphere that precedes methanogenesis [*Bergman et al.*, 1998; *Davidson and Janssens*, 2006]. We therefore suggest that one of the most likely causes of both greater temperature sensitivity in bog CH$_4$ emissions compared to fen CH$_4$ emissions and the heterogeneous temperature response to CO$_2$ starvation is differences in species assemblage and subsequent dominant CH$_4$ production pathways in the rhizosphere. The ombrotrophic bog mesocosms were predominantly covered by Hypnaceae and *Sphagnum* mosses, whereas the minerotrophic fen mesocosms were dominated by *Carex* and *Juncus* species. Bryophyte (e.g., *Sphagnum*) litter decomposes more slowly than tracheophyte (e.g., *Carex*) litter due to the greater presence of decay-resistant phenolic compounds in their cell walls and lower concentrations of nitrogen and phosphorus in their structures [*Aerts et al.*, 1999; *Scheffer et al.*, 2001; *Turetsky*, 2003]. Moreover, *Sphagnum* produces secondary metabolites that inhibit microorganisms involved in the decomposition process [*Verhoeven and Toth*, 1995] and release less labile carbon into the soil through root exudation (e.g., ethanol and acetate) compared to *Carex* plants.

[13] The contrasting structural and physiological characteristics of bryophyte bogs and tracheophyte fens create a difference in dominant CH$_4$ production pathways between these two ecosystem types [*Hornibrook and Bowes*, 2007]. Ombrogenous bogs (where *Sphagnum* species proliferate) create a more stable recalcitrant long-term carbon source where hydrogenotrophic methanogenesis prevails at all depths with little seasonal variation [*Chasar et al.*, 2000; *Hornibrook and Bowes*, 2007; *Kelly et al.*, 1992; *Lansdown et al.*, 1992]. By contrast, minerotrophic *Carex/Juncus* fens exhibit enriched natural abundance ^{14}C (CH$_4$) in their pore waters (i.e., younger), with acetotrophic methanogenesis prevailing over hydrogenotrophic methanogenesis [*Chasar et al.*, 2000; *Galand et al.*, 2005; *Juottonen et al.*, 2005]. Consequently, enzymatic reactions in ecosystems involved in the catabolism of structurally complex (low quality) carbon substrates (i.e., *Sphagnum* bogs) result in both higher activation energies and temperature sensitivities
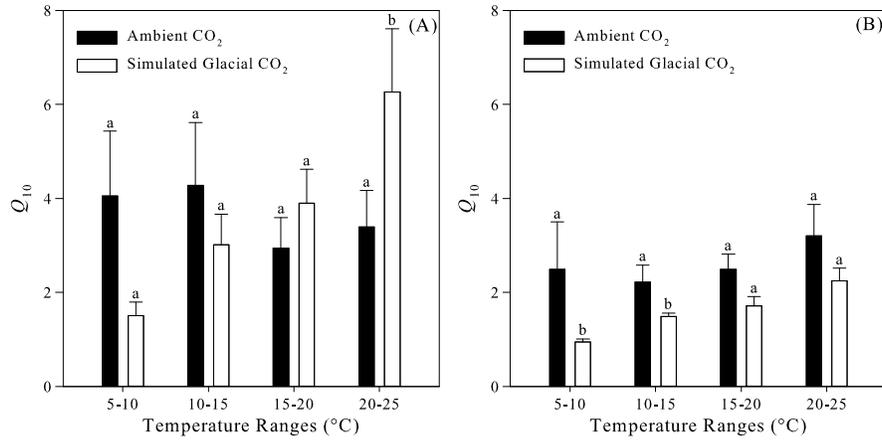
Figure 2. Comparison between ambient and simulated glacial Q_{10} values over four different temperature ranges in (a) an ombrotrophic bog and (b) a minerotrophic fen. Error bars represent ± 1 standard error of the mean. Within each temperature category, bars with different letters are significantly different ($P < 0.05$).

for decomposition [*Craine et al.*, 2010; *Davidson and Janssens*, 2006; *Fierer et al.*, 2005; *von Luetzow and Koegel-Knabner*, 2009]. By contrast, reactions involving simpler, more labile carbon substrates (e.g., acetate) produce lower activation energies [*Davidson and Janssens*, 2006]. Therefore, the quality of organic carbon substrate is inversely correlated with the Q_{10} of organic matter decomposition. Given that methanogenesis is the terminal step of decomposition in anaerobic wetlands, we believe that this relationship is reflected in the Q_{10} values and activation energies measured for CH_4 emission in this study, with higher values associated with the bog mesocosms compared to the fen mesocosms (Table 1).

[14] In complex wetland ecosystems, it is likely that a number of mechanisms combine to produce the heterogeneous temperature response of CH_4 emissions to CO_2 starvation measured in this study and in long-term equivalent experiments [*Boardman et al.*, 2011; *Keller*, 2011]. CH_4 emissions measured at the ecosystem scale are the mixed response of temperature-sensitive and temperature-insensitive subprocesses, similar to CO_2 emissions resulting from respiration [*Mahecha et al.*, 2010]. Given that our results are unlikely to be truly unconfounded (intrinsic) temperature sensitivities, caution should be used when extrapolating these data. However, the nature of our experimental design and the controls we have in place allow us to cautiously hypothesize about the implications of CO_2 starvation and the interaction of temperature on wetland processes.

[15] In our long-term CO_2 starvation experiment (c. 21 months), bog mesocosm CH_4 emissions and dissolved pore water CH_4 concentrations were unaltered by glacial $[CO_2]_a$, whereas fen CH_4 emissions and rhizosphere pore water CH_4 concentrations were reduced by 29% ($P < 0.05$) and approximately 50% ($P < 0.01$), respectively [*Boardman et al.*, 2011]. In that study, we could not verify that this contrasting response was the result of a change in root exudate concentrations in the rhizosphere caused by a reduction in plant productivity. This is because such a signal could have been obliterated by rapid utilization of acetate by acetotrophic methanogens in the fen mesocosms. Differences in plant species assemblage may be one of the many reasons (others include differences in nutrient levels and dissolved

CO_2 in pore waters; see the work of *Boardman et al.* [2011] for more details) for the contrasting CO_2 treatment response of CH_4 emissions between the bog and the fen in both experiments. For example, the bog mesocosms may not have fully altered their physiology in response to CO_2 starvation as the *Sphagnum* species contained in these mesocosms have the ability to recycle CH_4 to create a subsurface CO_2 source that is estimated to account for between 5% and 35% of assimilated carbon [*Kip et al.*, 2010; *Larmola et al.*, 2010; *Parmentier et al.*, 2011; *Raghoebarsing et al.*, 2005]. This may have reduced the effect of a 50% reduction in $[CO_2]_a$ on bog CH_4 emissions. On the other hand, the tracheophyte-dominated fen mesocosms may have fully altered their productivity and released less root exudates into the rhizosphere and limited acetotrophic methanogenesis [*Strom et al.*, 2003].

3.3. The Influence of Substrate Supply on Q_{10}

[16] Our results indicate that the influence of $[CO_2]_a$ starvation on CH_4 emissions in some wetland types is moderated by temperature (Figure 1b). We suggest that, where this is the case, $[CO_2]_a$ starvation only starts to limit CH_4 emission at temperatures $>10°C$. Below $10°C$, biological activity (carbon mineralization) and biomass are constrained in methanogen communities [*Hoj et al.*, 2008; *van Hulzen et al.*, 1999], regardless of $[CO_2]_a$, creating a scenario where the supply of organic substrates to methanogens surpasses the temperature-controlled demand. Increasing the temperature beyond $10°C$ removes the constraint on biological activity, at which point methanogenesis is limited by anaerobic carbon mineralization (i.e., substrate supply). This theory is supported by our Q_{10} results, where there is an indication of increasing Q_{10} values with increasing temperature range, particularly Q_{10} values derived from fen CH_4 emissions (Figure 2b), which is indicative of a system where enzymatic processes are substrate limited at lower temperatures and saturated at higher ones [*Atkin et al.*, 2005]. As species assemblage and primary productivity are among the main determining factors of below-ground carbon allocation and exudation [*Joabsson and Christensen*, 2001; *Kuzyakov*, 2002], we suggest that glacial $[CO_2]_a$ reduces this flow of carbon to the rhizosphere and limits mineralization

rates in tracheophyte-dominated fens. Wetland species composition, which is directly linked to nutrient availability, might therefore be a good indicator of the susceptibility of specific wetland areas during glacials to CO_2 starvation–induced reductions in CH_4 emissions.

3.4. Modeling Glacial Wetland CH_4 Emissions

[17] Our experiment has established that glacial $[CO_2]_a$ values influence the temperature sensitivity of CH_4 emission from tracheophyte-dominated minerotrophic wetland mesocosms. We tested whether this effect could be explained using a wetland CH_4 emission equation adopted in a Last Glacial Maximum CH_4 budget simulation [*Valdes et al.*, 2005]. We used the *Cao et al.* [1996] model equation for representing CH_4 production in wetlands (equation (3)), where the CH_4 production rate (MPR) is a function of soil organic matter decomposition rate (SOMD), temperature (f(TEM)), water table position (f(WTP)), and a fixed factor of 0.47 to represent the percentage of decomposed organic carbon that is transformed to CH_4 under optimal conditions (PO). CH_4 emission to the atmosphere is calculated as the difference between MPR and CH_4 oxidation rate (MOR), where 60% of CH_4 produced in the anoxic zone is oxidized at the soil-water interface. The limitation and subsequent inherent error of using fixed constants to represent values that change with temperature (e.g., PO and CH_4 oxidation) are unavoidable given the complex nature of wetland biogeochemistry and the wide range of values reported for the same processes by researchers. This approach is not uncommon, as wetland CH_4 models vary in complexity and can have substantial parameter and structural uncertainty [*Melton et al.*, 2012]. *Cao et al.* [1996] provided a detailed rationale for the values used in their process-based model and our calculations.

$$MPR = PO\ SOMD\ f(WTP)f(TEM) \qquad (3)$$

[18] In our experiment, f(WTP) was maintained at the surface of the mesocosms, and we therefore assumed fully saturated conditions during calculations. A high water table was actively maintained to reduce any potential differences in CH_4 oxidation in the rhizosphere. SOMD was not measured in our study and thus calculated as an inversion of the CH_4 flux based on 30°C as the optimal temperature for methanogenesis (i.e., f(TEM) equals 1 at 30°C and is insensitive to Q_{10} value; equation (4)). As CH_4 emissions were not defined for 30°C in this study, this information was generated by extending the exponential regressions used to define the raw data up to the temperature optimum (Figure 1b and Table 1).

$$SOMD\ at\ 30°C = \frac{\frac{CH_4\ flux\ at\ 30°C}{PO}}{f(TEM) - MOR} \qquad (4)$$

[19] The inversion calculations suggested that ambient fen SOMD was 669 g C m^{-2} yr^{-1}, whereas simulated glacial SOMD was approximately 43% lower at 383 g C m^{-2} yr^{-1} under optimal conditions. These predicted SOMD values are toward the higher end of those suggested by *Cao et al.* [1996], but minerotrophic wetlands exhibit higher degradation rates [*Aerts et al.*, 1999], higher methanogenic activity [*Juottonen et al.*, 2005], and higher CH_4 emissions [*Nykänen et al.*, 1998] compared to mesotrophic or
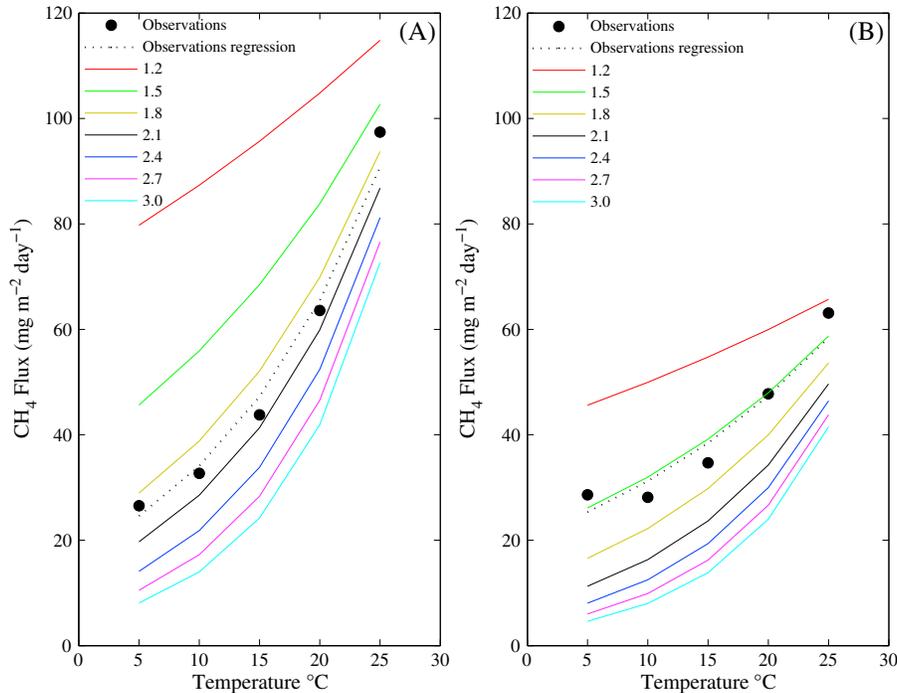
Figure 3. Modeled (a) ambient and (b) simulated glacial fen CH_4 emissions. The dark circles represent the measured raw data, whereas the solid color lines represent the modeled emissions associated with different Q_{10} values. Ambient emissions were modeled based on an SOMD value of 669 g C m^{-2} yr^{-1}, whereas simulated glacial emissions were modeled using an SOMD value of 383 g C m^{-2} yr^{-1}.

ombrotrophic wetlands due to inherent differences in biotic and abiotic factors [*Belyea*, 1996]. We would therefore expect our results to be high within the SOMD range predicted by *Cao et al.* [1996], as their wetland identification and classification approach was not sensitive enough to account for differences based on nutritional status and/or dominant vegetation type. The result of the full modeling investigation showed that incorporating the 43% reduction in SOMD, combined with a 25% decrease in Q_{10} value (2 to 1.5), was sufficient to recreate the difference between ambient and glacial minerotrophic wetland CH_4 emissions measured in the experiment (Figure 3).

[20] The reductions in SOMD and Q_{10} under CO_2 starvation conditions indicated by our investigation are consistent with current CH_4 budget suggestions, where cooler global temperatures and reduced $[CO_2]_a$ are predicted to have caused a reduction in primary production, a decrease in soil respiration/SOMD, and a subsequent decrease in wetland CH_4 emissions during glacial maxima [*Pagani et al.*, 2009; *Singarayer et al.*, 2011], changes that would impact upon wetland carbon mineralization rates and CH_4 emissions [*Whiting and Chanton*, 1993]. Therefore, the empirical evidence presented in this study, plus that provided by recent atmosphere-ocean climate wetland simulations [*Singarayer et al.*, 2011] and atmospheric chemistry transport modeling [*Levine et al.*, 2011], suggests that glacial-interglacial changes could almost entirely be wetland source, rather than atmospheric sink (reaction with the OH radical), driven [*Kaplan et al.*, 2006; *Valdes et al.*, 2005]. Moreover, the results of this experiment and our long-term equivalent experiment [*Boardman et al.*, 2011] suggest that $[CO_2]_a$ fertilization and starvation of wetlands during interglacial and glacial periods, respectively, may play an important part in regulating $[CH_4]_a$. Our calculations point to changes in below-ground carbon allocation (SOMD) in response to varying $[CO_2]_a$, which is dependent on species type, as a potential mechanism that alters wetland CH_4 source strength over such time periods. However, this hypothesis is currently not supported by direct experimental measurements and therefore requires further investigation. Equally, further modeling investigations are required to assess the contribution of different wetland areas to the CH_4 budget during glacial maxima in light of our findings.

4. Conclusions

[21] Our results show that the temperature sensitivity of CH_4 emissions from minerotrophic *Juncus*/*Carex*-dominated mesocosms was reduced by glacial $[CO_2]_a$, whereas that of CH_4 emissions from ombrotrophic *Sphagnum*-dominated mesocosms remained unaltered. This contrasting response may be in part explained by differences in species assemblage and dominant CH_4 production pathways, but the exact mechanisms require further investigation. This study has demonstrated that, where CO_2 starvation reduces CH_4 emissions, this effect is enhanced with increasing temperature. Therefore, our results suggest that minerotrophic (*Carex/Juncus*) wetland ecosystems located in regions where temperatures are consistently above $10°C$ (e.g., middle to low latitudes) could have been especially sensitive to CO_2 starvation during glacial periods. Given that wetlands in the middle to low latitudes were the largest natural biogenic source of CH_4 during glacial

maxima [*Chappellaz et al.*, 1993; *Dallenbach et al.*, 2000; *Weber et al.*, 2010], this in turn suggests reductions in wetland CH_4 emission from such areas may have played an important part in determining glacial-interglacial variations in atmospheric $[CH_4]$ [*Fischer et al.*, 2008; *Singarayer et al.*, 2011]. This study provides empirical evidence to suggest that glacial-interglacial changes in $[CH_4]_a$ could be wetland source, rather than atmospheric sink, driven and further establishes a biological linkage between the CH_4 and CO_2 ice core records.

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