2015

The Relative Importance of Methanogenesis in the Decomposition of Organic Matter in Northern Peatlands

J. Elizabeth Corbett

Malak M. Tfaily

David J. Burdige
Old Dominion University, dburdige@odu.edu

Paul H. Glaser

Jeffrey P. Chanton

Original Publication Citation

Corbett, J.E., Tfaily, M.M., Burdige, D.J., Glaser, P.H., & Chanton, J.P. (2015). The relative importance of methanogenesis in the decomposition of organic matter in northern peatlands. *Journal of Geophysical Research-Biogeosciences, 120*(2), 280-293. doi: 10.1002/2014jg002797

AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Biogeosciences

RESEARCH ARTICLE

10.1002/2014JG002797

Key Points:
- Method allows calculation of relative importance of methanogenic CO_2 production
- Approach assumes equimolar CH_4 and CO_2 production associated with methanogenesis
- After initial permafrost collapse, methanogenesis is less important

Correspondence to:
J. E. Corbett,
jecorbet@gmail.com

Citation:
Corbett, J. E., M. M. Tfaily, D. J. Burdige, P. H. Glaser, and J. P. Chanton (2015), The relative importance of methanogenesis in the decomposition of organic matter in northern peatlands, *J. Geophys. Res. Biogeosci.*, *120*, 280–293, doi:10.1002/2014JG002797.

Received 16 SEP 2014
Accepted 24 JAN 2015
Accepted article online 28 JAN 2015
Published online 24 FEB 2015

The relative importance of methanogenesis in the decomposition of organic matter in northern peatlands

J. Elizabeth Corbett[1,2], Malak M. Tfaily[1,3,4], David J. Burdige[5], Paul H. Glaser[6], and Jeffrey P. Chanton[1]

[1]Earth, Ocean and Atmospheric Science, Florida State University, Tallahassee, Florida, USA, [2]Goddard Institute for Space Studies, New York, New York, USA, [3]Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, USA, [4]Pacific Northwest National Laboratory, Richland, Washington, USA, [5]Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, Virginia, USA, [6]Department of Geology and Geophysics, Pillsbury Hall, University of Minnesota, Minneapolis, Minnesota, USA

Abstract Using an isotope-mass balance approach and assuming the equimolar production of CO_2 and CH_4 from methanogenesis (e.g., anaerobic decomposition of cellulose), we calculate that the proportion of total CO_2 production from methanogenesis varies from 37 to 83% across a variety of northern peatlands. In a relative sense, methanogenesis was a more important pathway for decomposition in bogs (80 ± 13% of CO_2 production) than in fens (64 ± 5.7% of CO_2 production), but because fens contain more labile substrates they may support higher CH_4 production overall. The concentration of CO_2 produced from methanogenesis ($CO_{2\text{-meth}}$) can be considered equivalent to CH_4 concentration before loss due to ebullition, plant-mediated transport, or diffusion. Bogs produced slightly less $CO_{2\text{-meth}}$ than fens (2.9 ± 1.3 and 3.7 ± 1.4 mmol/L, respectively). Comparing the quantity of CH_4 present to $CO_{2\text{-meth}}$, fens lost slightly more CH_4 than bogs (89 ± 2.8% and 82 ± 5.3%, respectively) likely due to the presence of vascular plant roots. In collapsed permafrost wetlands, bog moats produced half the amount of $CO_{2\text{-meth}}$ (0.8 ± 0.2 mmol/L) relative to midbogs (1.6 ± 0.6 mmol/L) and methanogenesis was less important (42 ± 6.6% of total CO_2 production relative to 55 ± 8.1%). We hypothesize that the lower methane production potential in collapsed permafrost wetlands occurs because recently thawed organic substrates are being first exposed to the initial phases of anaerobic decomposition following collapse and flooding. Bog moats lost a comparable amount of CH_4 as midbogs (63 ± 7.0% and 64 ± 9.3%).

1. Introduction

Peatlands worldwide have been found to hold approximately one third of the total carbon in soils [*Gorham*, 1991; *Post et al.*, 1982, 1985]. Wetlands contribute a third of global CH_4 emissions with errors in estimates due to a lack of data and understanding of these complex systems [*Bridgham et al.*, 2013]. In peatlands, anaerobic decomposition of plant material at rates less than carbon accumulation results in net carbon storage [*Moore et al.*, 1998]. Due to anaerobic conditions as well as the general absence of alternate electron acceptors (nitrate, iron, and sulfate), methanogenesis should be the dominant pathway of respiration below the surface [*Chasar et al.*, 2000a, 2000b; *Corbett et al.*, 2013a; *Romanowicz et al.*, 1995]. Methanogenesis (by either acetate fermentation (equation (1)) or CO_2 reduction (equations (2)–(4)) produces equimolar amounts of CO_2 and CH_4 [*Barker*, 1936; *Tarvin and Buswell*, 1934] in environments where cellulose, a glucose polymer, or hemicellulose, a more complex sugar polymer, are the initial organic material substrates [*Conrad*, 1999]. These materials are the main initial substrates driving anaerobic degradation in freshwater aquatic sediments, peatlands, wetlands, ruminants, arthropods feeding on plant material, and in many types of sewage sludge as well as in decomposition in landfills [*Conrad*, 1999; *Barlaz*, 2006]. Even wood is composed of 70% cellulose and hemicellose [*Sjostrom*, 1993].

For example, acetate fermentation produces equimolar quantities of methane and CO_2

$$\text{Acetate fermentation}: CH_3COOH \rightarrow CH_4 + CO_2 \tag{1}$$

while CO_2 reduction is the sum of equations (2) and (3):

$$2CH_2O + 2H_2O \rightarrow 2CO_2 + 4H_2 \tag{2}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3}$$

with a net overall equation for CO_2 reduction of

$$2CH_2O \rightarrow CH_4 + CO_2 \tag{4}$$

For cellulose and hemicellulose the reactions are, respectively [*De La Cruz et al*., 2013],

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow 3nCO_2 + 3nCH_4 \tag{5}$$

$$(C_5H_8O_4)_n + nH_2O \rightarrow 2.5nCO_2 + 2.5nCH_4 \tag{6}$$

Fats and proteins decompose under anaerobic conditions to produce CH_4/CO_2 in a ratio of 6/4, but these are likely less abundant [*De La Cruz et al*., 2013].

In Glacial Lake Agassiz Peatland (GLAP) sites in northern Minnesota and other peatlands, however, dissolved pore water inorganic carbon (DIC, dissolved CO_2) concentrations are considerably greater than dissolved methane concentrations [*Valentine et al*., 1994; *Bridgham et al*., 1995; *Romanowicz et al*., 1995; *Chasar et al*., 2000a, 2000b; *Keller and Bridgham*, 2007; *Wright et al*., 2011; *Corbett et al*., 2013a]. The high DIC/CH_4 that is generally observed indicates that (1) methanogenesis is not the only major pathway of CO_2 production in these systems [*Keller and Bridgham*, 2007] and/or (2) dissolved methane may be escaping the pore water system in much greater quantities than dissolved CO_2 or may be consumed by processes such as anaerobic oxidation of methane (AOM) [*Smemo and Yavitt*, 2011; *Gupta et al*., 2012].

The "excess" CO_2 that is produced by nonmethanogenic pathways must come from other pathways including aerobic oxidation of organic matter, high molecular weight (HMW) organic matter (OM) fermentation, or respiration with alternative electron acceptors (e.g., sulfates, iron, manganese, nitrate, or humics) [*Keller and Bridgham*, 2007; *Lovley et al*., 1996]. Vascular plant roots can deliver oxygen to the belowground pore water system driving aerobic respiration [*Chanton et al*., 2008], respiration via sulfate reduction occurs in some peatland systems [*Vile et al*., 2003a, 2003b; *Keller and Bridgham*, 2007], and evidence of the fermentation of HMW organic molecules has also been observed [*Keller and Bridgham*, 2007; *Tfaily et al*., 2013; *Vile et al*., 2003a]. In addition to the pathways mentioned above, humic acids could also act as additional electron acceptors fueling anaerobic respiration and suppressing net methanogenesis in peats [*Keller and Bridgham*, 2007; *Smemo and Yavitt*, 2011; *Gupta et al*., 2012]. It has been observed that humic acid addition lowers methane production in peats but not CO_2 production [*Blodau and Deppe*, 2012]. Also, CO_2 produced by respiration in vascular plant roots may be directly input into the subsurface. These pathways do not fractionate the carbon substrate during respiration so the produced CO_2 carries the original $\delta^{13}C$ signature of the organic carbon substrate [*Lapham et al*., 1999].

The high CO_2/CH_4 ratios observed in the GLAP and other peatlands may also be a result of CH_4 loss through the root system of vascular *Carex* plants and ebullition. Ebullition has been shown to be the dominant pathway of CH_4 loss from the pore water of some peatlands [*Glaser et al*., 2004]. CH_4 loss in the anaerobic subsurface may also be the result of anaerobic methane oxidation (AOM), which has been shown to occur in some peatland systems [*Smemo and Yavitt*, 2011; *Gupta et al*., 2012]. However, we will consider methane production to be gross methane production—AOM.

In this paper, we will use isotope-mass balance equations to determine the relative importance of the pathways used in organic matter decomposition at several sites and to calculate the net CO_2/CH_4 ratios produced belowground. *Corbett et al*. [2013a] developed an isotope-based approach to determine the relative amounts of CO_2 production from fractionating (methanogenesis) and nonfractionating (i.e., respiration via alternative electron acceptors (most likely oxygen, sulfate, and humic acids) and HMW OM fermentation) pathways. This approach also allows one to estimate the relative importance of methane loss from various depths in the pore water and to quantify the amount of subsurface methane produced before loss [*Corbett et al*., 2013a]. This earlier study compared a single bog and fen site and found that methanogenesis was of greater relative importance in the bog site relative to the fen site, while methane loss was greater in the fen site.

The aim of this study is to apply the approach of *Corbett et al*. [2013a] to two additional bog-fen pairs in the GLAP in northern Minnesota and also across sites in a permafrost thaw wetland gradient in Canada to identify whether the patterns observed by *Corbett et al*. [2013a] are consistent. We include permafrost thaw sites here to better understand organic matter decay and respiration pathways that occur as previously frozen organic material undergoes thawing. An objective is to evaluate whether the low CH_4/CO_2 ratios observed in pore water are due to methane loss [e.g., *Glaser et al*., 2004] or due to low relative importance of methane production relative to other modes of organic matter decomposition. We hypothesize that methanogenesis will be more important in *Sphagnum*-dominated bogs due to different transport processes and in the differences in the nature of the dissolved organic matter between the two types of wetlands [*Tfaily et al*., 2013]. Similarly, a higher percent of methane should be lost from fens, where plant-induced gas ventilation is more developed [*Chanton*, 2005]. Additionally, we hypothesize that at the thawed permafrost sites, there will be more relative CO_2 production from nonmethanogenic pathways at the recent-collapse moat sites relative to midbogs, since stored, frozen organic matter at the thawed permafrost sites has just reinitiated the decomposition process, and newly released organic matter there may contain more organically bound oxygen and more humic acid electron acceptors [*Tfaily et al*., 2013; *Leifeld et al*., 2012]. *Hodgkins et al*. [2014] observed that methane production is less important in the early stages of thaw along a thaw gradient in arctic Sweden.

2. Methods

2.1. Field Sites

The Glacial Lake Agassiz Peatlands (GLAPs) located in northern Minnesota formed about 5000 years ago when a shift to a colder, wetter climate, raised the regional water table and initiated peat formation [*Glaser et al*., 1997]. Raised bogs, characterized by *Sphagnum* moss, and patterned fens, dominated by vascular plants such as *Carex*, comprise the main types of environments found in the GLAP terrain [*Glaser et al*., 1981, 1997]. These vegetation patterns are also observed in permafrost collapse-scar bogs where the midbog is dominated by *Sphagnum* mosses, and the bog moat is dominated by both *Carex* and *Sphagnum* vegetation [*Prater et al*., 2007]. The collapse-scar bog, composed of both the midbog and bog moat, is an area that was once permafrost but has recently undergone several yearly freeze/thaw cycles typical to those the GLAP has been subjected to for thousands of years. The bog moat is an area where rapid thawing of permafrost soils is occurring, and the adjacent, frozen peat plateau is calving off into the collapse-scar wetland [*Prater et al*., 2007]. In the GLAP, the flat landscape and the sparse network of rivers maintain high water tables by reducing drainage and runoff, which accounts for continual peat development [*Glaser*, 1987; *Glaser et al*., 2006]. Continued carbon accumulation in peatlands may directly depend on this moisture availability in order to maintain peat growth [*Charman et al*., 2012]. Drought and higher temperatures may alter the biogeochemistry of these systems sufficiently so that they become carbon sources rather than sinks [*Fenner and Freeman*, 2011; *Freeman et al*., 2001a, 2001b].

Pore water samples were collected from the GLAP in northern Minnesota [*Glaser et al*., 1981] and from discontinuous permafrost sites in Alberta, Canada [*Prater et al*., 2007; *Prater*, 2005]. At GLAP, two additional bog-fen pairs were compared and contrasted with the previously studied RLII bog and fen [*Corbett et al*., 2013a]. These were the Sturgeon River (SR) Bog (48.16°N, 94.22°W) and Fen (48.16°N, 94.24°W) pair and the Red Lake IV (RLIV) Bog (48.33°N, 94.41°W) and Fen (48.32°N, 94.38°W) pair (Figure 1a). Sites were remote and only accessible by helicopter.

At each of the three distinct sites in a zone of discontinuous permafrost in northern Alberta, Canada, we contrasted the collapsing edge of a bog moat, where recently thawed peat was falling into the collapse-scar bog with the middle of the wetland (midbog) where new peat was growing within the collapse feature. These sites were Meander (59. 5°N, 117.2°W), Lutose (59.2°N, 117.2°W), and Zama (59.1°N, 117.2°W) collapse-scar bogs (Figure 1b).

2.2. Field Measurements, Stable Isotopes, and Concentrations

A peristaltic pump with Teflon tubing was used to collect pore water from 1.25 cm diameter PVC piezometers at 0.5 m depth intervals [*Chason and Siegel*, 1986; *Romanowicz et al*., 1993; *Siegel and Glaser*, 1987]. All field samples refer to pore water measurements, which were collected at or below the water table. A depth of 0 m corresponds to the top of the water table, not the top of the peat. DIC samples were first filtered with Whatman Grade GF/D glass microfiber prefilters (2 μm particle retention) and 25 mm diameter Whatman Grade GF/F glass microfiber filters with 0.7 μm particle retention. Following filtration, this pore water was injected into 30 mL evacuated vials sealed with butyl rubber septas. Pore water for methane analysis was collected in 60 mL syringes and injected without filtration into 120 mL evacuated vials containing

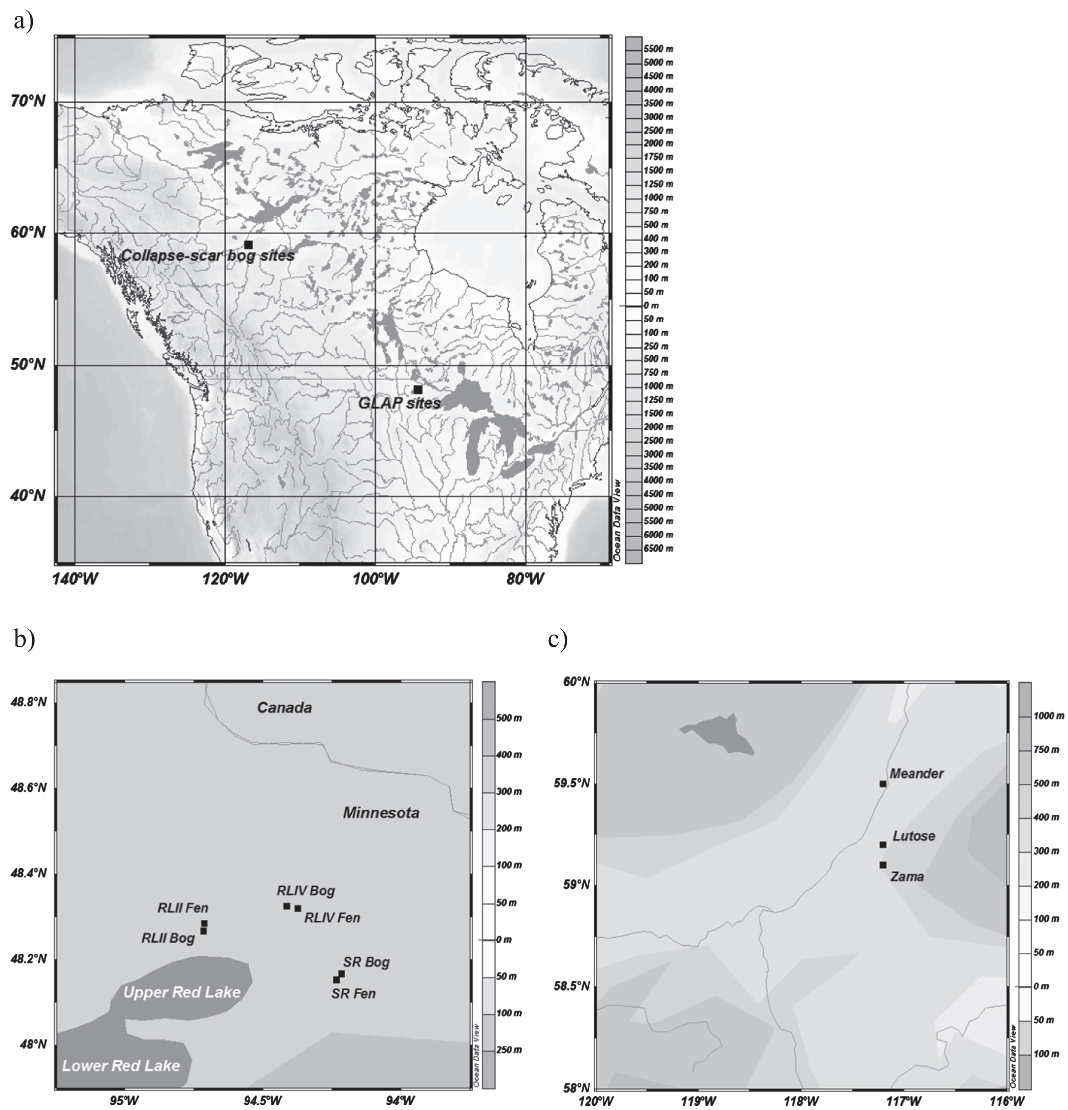

Figure 1. (a) Overview of North America sampling sites. Map of sampling sites in (b) Glacial Lake Agassiz Peatlands (GLAP) in northern Minnesota, USA, and (c) permafrost collapse-scar bog sites in northwest Alberta, Canada. Maps were created with Ocean Data View.

0.5 g KOH. DIC samples were frozen within a few hours at a field station. All samples were shipped to Florida State University for analysis. Evacuated vials containing DIC and methane pore water samples were brought to atmospheric pressure with helium. DIC samples were acidified with 0.3 mL of 40% H_3PO_4. All samples were shaken to extract gas from the water into the headspace. The gas concentration and isotopic ratio in the headspace were determined by direct injection on a gas chromatographic (GC) combustion-interfaced Finnigan MAT Delta V isotope ratio mass spectrometer (GC isotope ratio mass spectrometry). Gas concentrations in pore water were calculated from the headspace volume to water volume ratio and the extraction efficiency of the gas. The extraction efficiency of methane as measured with repeated extractions was 0.95. The extraction efficiency of the DIC in an individual vial was determined in reference to dissolved bicarbonate standards.

Isotope data are described in conventional δ notation with units of per mil (‰), relative to the standard Pee Dee belemnite (PDB). We use National Institute of Standards and Technology and OZTECH (9412 Rocky Branch Drive, Dallas, TX 75243, Phone: 214-348-8330) isotope standards ($\delta^{13}C_{VPDB} = -44.46$ and $\delta^{18}O_{VSMOW} = +9.31$) for calibration and have performed numerous intercalibrations with other isotope labs.

2.3. Isotope-Mass Balance Calculations

Isotope-mass balance equations were developed to partition the relative importance of the fractionating methanogenic pathways versus the nonfractionating "other" pathways for the generation of CO_2 in peatlands [*Corbett et al.*, 2013a]. The proportions of CO_2 from nonfractionating pathways and methanogenesis were calculated with measured pore water δ^{13}C-CO_2 and δ^{13}C-CH_4 values.

We assume that DIC results from two processes: (1) respiration and HMW OM fermentation, which produce DIC with an isotopic composition similar to the organic matter, and (2) methanogenesis (acetate fermentation and CO_2 reduction), which produces δ^{13}C-enriched DIC along with δ^{13}C-depleted CH_4. Assuming that methanogenesis from cellulose produces approximately equimolar amounts of carbon to CO_2 and CH_4, the isotopic signature of the CO_2 produced solely from methanogenesis can be calculated.

$$\left(\delta^{13}\mathrm{C}-\mathrm{OM}\right)\times(1) = (0.5)\times\left(\delta^{13}\mathrm{C}-\mathrm{CH_4}\right) + (0.5)\times\left(\delta^{13}\mathrm{C}-\mathrm{CO_{2\text{-}meth}}\right) \tag{7}$$

For example, if methane is produced at −60‰ from −26‰ organic matter, then the coproduced DIC (CO_2) must have an isotopic value of +8‰. We used a measured average of −26‰ [*Corbett et al.*, 2013a] to represent the δ^{13}C-OM. Using pore water δ^{13}C-CH_4 values, we then solved for δ^{13}C-$CO_{2\text{-meth}}$ (the δ^{13}C of the CO_2 produced from methanogenesis) in these samples. CH_4 isotopes do not fractionate during ebullition as CH_4 undergoes a phase change from the dissolved to gaseous state [*Chanton*, 2005], so the process that most significantly affects the CH_4 isotopic ratio in the pore water is net methanogenesis.

This calculated value of δ^{13}C-$CO_{2\text{-meth}}$ and the measured δ^{13}C of the pore water DIC (δ^{13}C-$CO_{2\text{-pw}}$) can then be used to partition the fraction of total DIC (CO_2) coming from either nonfractionating pathways (i.e., oxic respiration, sulfate reduction, and HMW OM fermentation) or fractionating processes (i.e., methanogenesis) with the following mass balance equations (equations (8)–(10)) where ($fCO_{2\text{-OM decay}}$) represents the fraction of CO_2 production from the nonfractionating pathways discussed above and ($fCO_{2\text{-meth}}$) represents the fraction of CO_2 produced by methanogenesis.

$$\left(\delta^{13}\mathrm{C}-\mathrm{CO_{2\text{-}pw}}\right)\times(1) = (-26‰)\times\left(f\mathrm{CO_{2\text{-}OM\ decay}}\right) + \left(\delta^{13}\mathrm{C}-\mathrm{CO_{2\text{-}meth}}\right)\times\left(f\mathrm{CO_{2\text{-}meth}}\right) \tag{8}$$

$$f\mathrm{CO_{2\text{-}OM\ decay}} + f\mathrm{CO_{2\text{-}meth}} = 1 \tag{9}$$

Combining these equations yields

$$\left(\delta^{13}\mathrm{C}-\mathrm{CO_{2-pw}}\right)\times(1) = (-26‰)\times\left(1-f\mathrm{CO_{2\text{-}meth}}\right) + \left(\delta^{13}\mathrm{C}-\mathrm{CO_{2\text{-}meth}}\right)\times\left(f\mathrm{CO_{2-meth}}\right) \tag{10}$$

which can then be solved for $fCO_{2\text{-meth}}$.

If methanogenesis did not produce an equimolar amount of CH_4 and CO_2, the resulting value of $fCO_{2\text{-meth}}$ would be altered proportionately. If the CH_4:CO_2 production ratio increases, for example, from 50:50 to 60:40, then the $fCO_{2\text{-meth}}$ would decrease proportionately by approximately 10%. Alternatively, if the production ratio decreases to 40:60, the $fCO_{2\text{-meth}}$ increases by 10%.

Fen samples at GLAP have been shown to have some (5–15%) contribution of DIC from the underlying mineral soil [*Chasar et al.*, 2000b]. We therefore examined how this additional source of CO_2 from mineral soil might affect the percent CO_2 from methanogenesis ($CO_{2\text{-meth}}$) and percent methane loss (see below) by modifying equation (10) to account for mineral soil DIC input. It was found that on average CO_2 derived from mineral soil decreased the percent $CO_{2\text{-meth}}$ and percent methane loss by only 3.8 and 1.6% [*Corbett et al.*, 2013a].

An estimate of CH_4 lost from the pore water can also be determined by knowing the value of $fCO_{2\text{-meth}}$ [*Corbett et al.*, 2013a]. First, an estimate of the amount of CO_2 produced by methanogenesis ($CO_{2\text{-meth}}$) can be determined with $fCO_{2\text{-meth}}$ and the pore water CO_2 concentration measured at a certain depth ($CO_{2\text{-conc}}$) by

$$f\mathrm{CO_{2\text{-}meth}}\times\mathrm{CO_{2\text{-}conc}} = \mathrm{CO_{2\text{-}meth}} \tag{11}$$

If the composition of the starting material is cellulose like, then an equal amount of CH_4 and CO_2 would be produced from methanogenesis. However, the pore water methane concentration at any given depth ($CH_{4\text{-conc}}$) is generally less than this amount of $CO_{2\text{-meth}}$ [e.g., *Corbett et al.*, 2013a]. We suggest that this is due

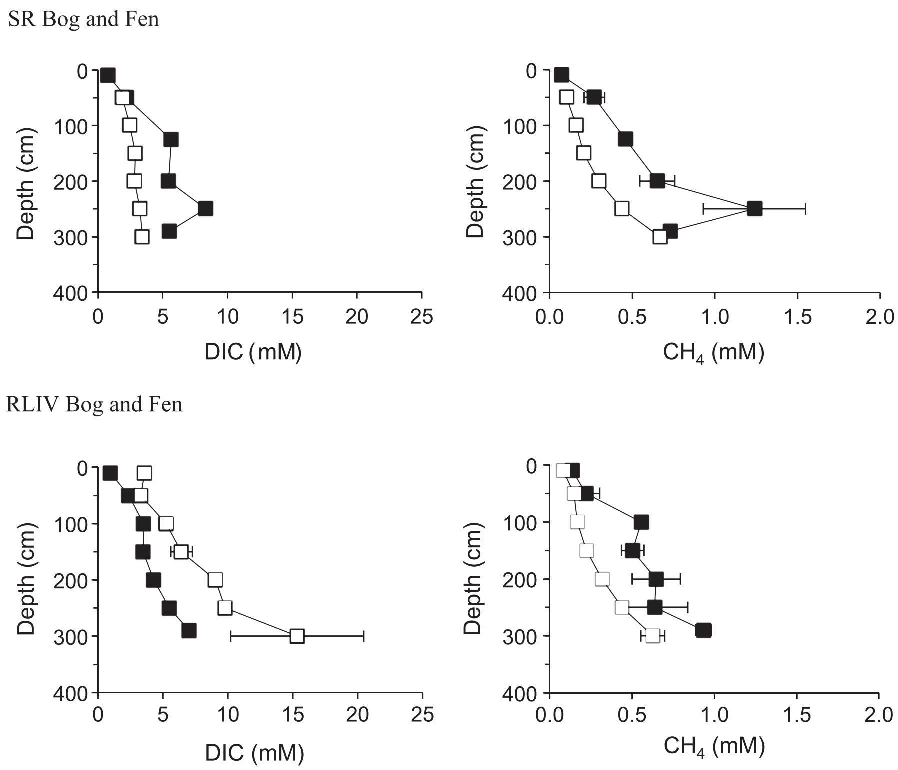

Figure 2. Depth profiles of pore water dissolved inorganic carbon (DIC) and dissolved methane for SR Bog (black squares) and SR Fen (white squares) and RLIV Bog (black squares) and RLIV Fen (white squares) peatland (Minnesota) sites.

to the loss of methane, a gas much less soluble in water than CO_2, from the system. Subtracting the measured amount of methane from the amount of methane that should be present (which is equal to $CO_{2\text{-meth}}$) yields the relative amount of methane that has escaped the pore water system. The fraction of methane that has been lost from the pore water is then given by

$$(CO_{2\text{-meth}} - CH_{4\text{-conc}})/\,CO_{2\text{-meth}} = \text{Fraction methane lost} \tag{12}$$

Finally, if we assume that the total amount of produced CO_2 is equal to $CO_{2\text{-conc}}$, then based on equation (11),

$$1/fCO_{2\text{-meth}} = CO_{2\text{-conc}}/\,CO_{2\text{-meth}} = (\text{produced } CO_2)/\,CO_{2\text{-meth}} \tag{13}$$

Since the total amount of CH_4 produced is also equivalent to $CO_{2\text{-meth}}$ (based on the stoichiometry of methanogenesis), $1/fCO_{2\text{-meth}}$ also equals the ratio of produced CO_2/produced CH_4. When this production ratio is 1, then only methanogenesis is occurring and as this ratio increase from 1, the relative importance of nonmethanogenic processes that produce CO_2 increases. This approach underestimates the amount of methane that has been produced because it assumes that the concentration of CO_2 at the bottom of the profile represents the sum of CO_2 production. CO_2 lost by diffusive and ebullitive fluxes and by pore water advection is not accounted for. Thus, our methane loss numbers are lower limits.

3. Results

Pore water DIC and CH_4 concentrations increased with depth in both SR Bog and Fen and RLIV Bog and Fen sites (Figure 2). The bogs had higher measured CH_4 concentrations than the fens, but in both cases, the CH_4 concentration was considerably less than the DIC concentration. At all sites the $\delta^{13}C\text{-}CO_2$ became more enriched with depth, more so in the bogs than the fens (Figure 3). The $\delta^{13}C\text{-}CH_4$ values at both bog sites became more enriched with depth, while fen sites became more depleted with depth (Figure 3). Enrichment of DIC in $\delta^{13}C$ is indicative of the strength of methane production in generating DIC.

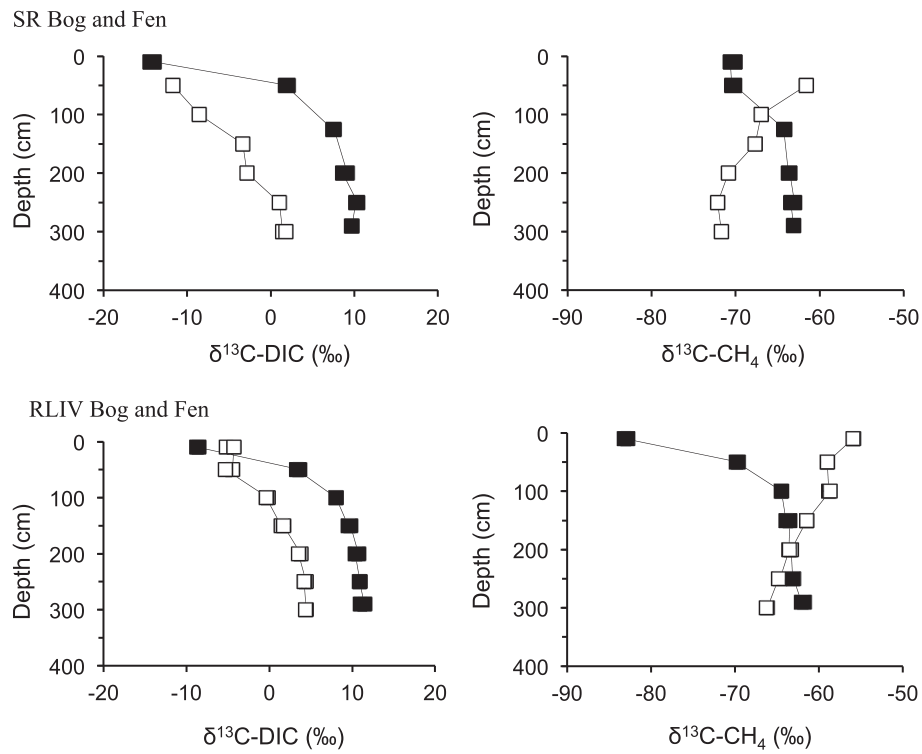

Figure 3. Depth profiles of pore water dissolved δ^{13}C-CO_2 (δ^{13}C-DIC) and δ^{13}C-CH_4 for SR Bog (black squares) and SR Fen (white squares) and RLIV Bog (black squares) and RLIV Fen (white squares).

Isotope-mass balance calculations (equations (7)–(12)) were applied to the pore water data, and averages of the percent $CO_{2\text{-meth}}$ (%$CO_{2\text{-meth}} = 100 \times fCO_{2\text{-meth}}$), and CH_4 loss were calculated for the bogs and fens. The %$CO_{2\text{-meth}}$ and CH_4 loss were determined, and values calculated for each depth were averaged for each site. Averages of these depth averages were used to determine the overall %$CO_{2\text{-meth}}$ and CH_4 loss for the bog and fen sites, and these data from the RLIV and SR sites were combined with data from the RLII sites [*Corbett et al*., 2013a] in subsequent analyses. The averages of the three bogs and three fens were compared; however, due to the low sample size ($n = 3$ for each type of wetland) overall trends as opposed to statistical significance are reported below. Collectively, GLAP fen sites had a lower value of %$CO_{2\text{-meth}}$ (64 ± 5.7%) than the GLAP bog sites (80 ± 13%) (Table 1 and Figures 4 and 5). The produced CO_2/CH_4 values (equation (13)) were slightly higher in the fens (1.6 ± 0.21) than in the bogs (1.4 ± 0.46) (Table 1). Both bog sites showed an increase of %$CO_{2\text{-meth}}$ with depth with the greatest increase between 10 and 50 cm. In contrast, %$CO_{2\text{-meth}}$ was more constant with depth in the fen sites (Figure 4). CH_4 loss was similar in the SR Bog and Fen sites but higher in RLIV Fen than RLIV Bog (Table 1). Overall, the results indicated that only about 10–20% of the produced CH_4 remained in the pore water belowground for all of the sites. The average concentration of $CO_{2\text{-meth}}$ was slightly higher in fens (3.7 ± 1.4 mmol/L) than in bogs (2.9 ± 1.3 mmol/L) and increased with depth in both environments (Table 1).

Pore water DIC concentrations from the permafrost sites ranged from 1 to 6 mmol/L, and no consistent pattern was found across the wetlands (bog moat or collapsing edge to midbog) (Figure 6). Methane concentrations ranged from close to zero to up to 1.5 mmol/L (Figure 6). The midbogs had more enriched δ^{13}C-CO_2 than the bog moats, and δ^{13}C-CH_4 values varied from −55 to −80‰ (Figure 7). $CO_{2\text{-meth}}$ and CH_4 loss were determined as described above, and values calculated for each depth in all midbog and bog moat sites were averaged. Combining these depth averages allowed us to determine the overall %$CO_{2\text{-meth}}$ and CH_4 loss of the midbog ($n = 3$) and bog moat ($n = 3$) sites. Overall, the results showed more $CO_{2\text{-meth}}$ in the midbog (55 ± 8.1%) as compared to the bog moat sites (42 ± 6.6%) (Table 1 and Figures 8 and 9). The produced CO_2/CH_4 ratios (equation (13)) were slightly higher in the bog moats (2.6 ± 0.47) relative to midbog sites (1.9 ± 0.31) (Table 1). CH_4 loss varied little across these wetlands being 64 ± 9.3% in the midbog

Table 1. The Percentage of Total Belowground CO_2 Production Derived From Methanogenesis (%$CO_{2\text{-meth}}$), the Ratio CO_2/CH_4 Produced Belowground, CH_4 Loss (as a Percentage of Total CH_4 Production), and $CO_{2\text{-meth}}$ (Which Also Equals the Amount of CH_4 Produced) for Peatlands in Minnesota, USA, and Permafrost Collapse Wetlands in Alberta, Canada[a]

Type	Site	%$CO_{2\text{-meth}}$	CO_2/CH_4 Produced	CH_4 Loss (%)	$CO_{2\text{-meth}}$ (mmol/L)
Peatland	SR Bog	76 ± 27	1.7 ± 1.1	82 ± 9.2	4.1 ± 2.9
	RLIV Bog	83 ± 25	1.4 ± 0.80	81 ± 12	3.6 ± 2.2
	RLII Bog	81 ± 12	1.3 ± 0.24	82 ± 5.1	3.9 ± 1.6
	All Bogs (*n* = 3)	80 ± 13	1.4 ± 0.46	82 ± 5.3	2.9 ± 1.3
	SR Fen	51 ± 8.2	2.0 ± 0.34	80 ± 7.3	1.5 ± 0.5
	RLIV Fen	75 ± 5.4	1.3 ± 0.11	95 ± 1.4	5.7 ± 3.5
	RLII Fen	65 ± 14	1.6 ± 0.51	90 ± 3.8	4.0 ± 2.0
	All Fens (*n* = 3)	64 ± 5.7	1.6 ± 0.21	89 ± 2.8	3.7 ± 1.4
Permafrost	Meander Midbog	54 ± 13	1.9 ± 0.48	67 ± 18	1.9 ± 1.2
	Lutose Midbog	53 ± 18	2.1 ± 0.75	60 ± 21	0.97 ± 0.35
	Zama Midbog	58 ± 9.8	1.8 ± 0.28	67 ± 3.7	1.8 ± 1.4
	All Midbogs (*n* = 3)	55 ± 8.1	1.9 ± 0.31	64 ± 9.3	1.6 ± 0.63
	Meander Bog Moat	46 ± 18	2.5 ± 1.3	66 ± 19	0.68 ± 0.36
	Lutose Bog Moat	37 ± 7.9	2.8 ± 0.56	72 ± 4.7	0.88 ± 0.17
	Zama Bog Moat	42 ± 1.6	2.4 ± 0.09	51 ± 7.8	0.91 ± 0.44
	All Bog Moats (*n* = 3)	42 ± 6.6	2.6 ± 0.47	63 ± 7.0	0.82 ± .20

[a]Uncertatinty estimates for each site represent the standard deviations of the reported depth averages at each site. Uncertainty estimates for the combined site averages (All Bogs, All Fens, All Mid Bogs, and All Bog Moats) were calculated using the standard deviation from each site average. Uncertainty of site averages = (sqrt ((stdev1)^2 + (stdev2)^2 + (stdev3)^2))/3.

sites and 63 ± 7.0% from the bog moat sites (Table 1). The average concentration of $CO_{2\text{-meth}}$ was higher in midbogs (1.6 ± 0.63 mmol/L) than in bog moats (0.82 ± 0.20 mmol/L) (Table 1), and $CO_{2\text{-meth}}$ increased with depth in both environments.

4. Discussion

4.1. Glacial Lake Agassiz Peatland Sites

In the GLAP peatland sites $\delta^{13}C\text{-}CO_2$ became more enriched with depth as methanogenic pathways drove $\delta^{13}C\text{-}CO_2$ to more positive values (Figure 3). Within the bog-fen pair that was previously investigated, *Corbett et al*. [2013a] found that %$CO_{2\text{-meth}}$ was larger in a bog as compared to a fen. The results here, from two additional bog-fen pairs confirm this observation (Figure 4). It appears that CO_2 production from methanogenesis is of greater relative importance in bogs than fens, although methane production was the dominant mode of organic carbon remineralization in both peatland types (Table 1 and Figures 4 and 5).

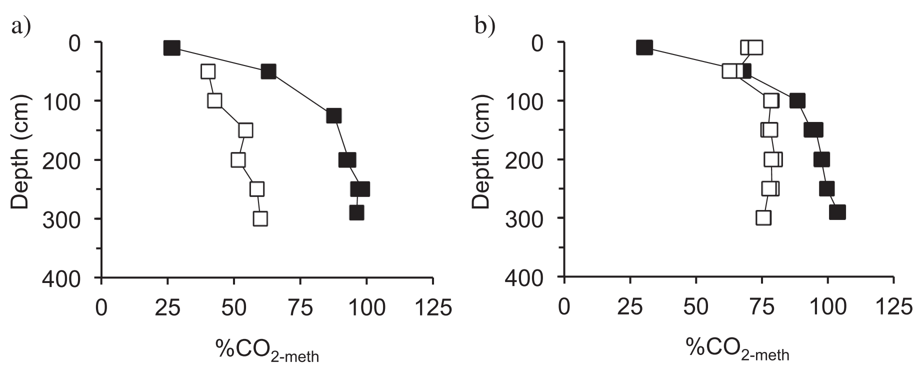

Figure 4. Depth profiles of percent CO_2 production from methanogenesis (%$CO_{2\text{-meth}}$) in (a) SR Bog (black squares) and SR Fen (white squares) and (b) RLIV Bog (black squares) and RLIV Fen (white squares). Note that the importance of methane production increases with depth especially in bogs. Values of %$CO_{2\text{-meth}}$ were determined as discussed in section 2.3.

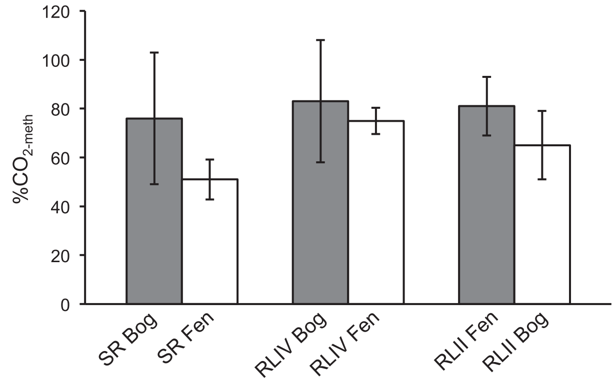

Figure 5. A comparison of %$CO_{2\text{-meth}}$ averages between Minnesota bogs and fens. The %$CO_{2\text{-meth}}$ is consistently higher in bogs than in fens.

Near-surface depths in the bogs and fens had lower values of %$CO_{2\text{-meth}}$ than deeper depths indicating a greater prevalence of nonfractionating pathways at the surface (Figure 4). Surface CO_2 produced from nonfractionating pathways may have been driven by oxic respiration, HMW OM fermentation, or respiration via alternative electron acceptors such as humics. Specifically in the fen, oxygen penetration via *Carex* may fuel aerobic, nonfractionating degradation of organic substances. *Carex* roots may allow for oxygen penetration into the pore waters of peat and thus create mixed redox zones and greater dissolved organic carbon (DOC) reactivity [*Aller*, 1998; *Burdige*, 2006; *Burdige and Komada* [2015]; *Chanton et al*., 2008]. Root exudates also increase the pools of labile DOC in the near-surface fen.

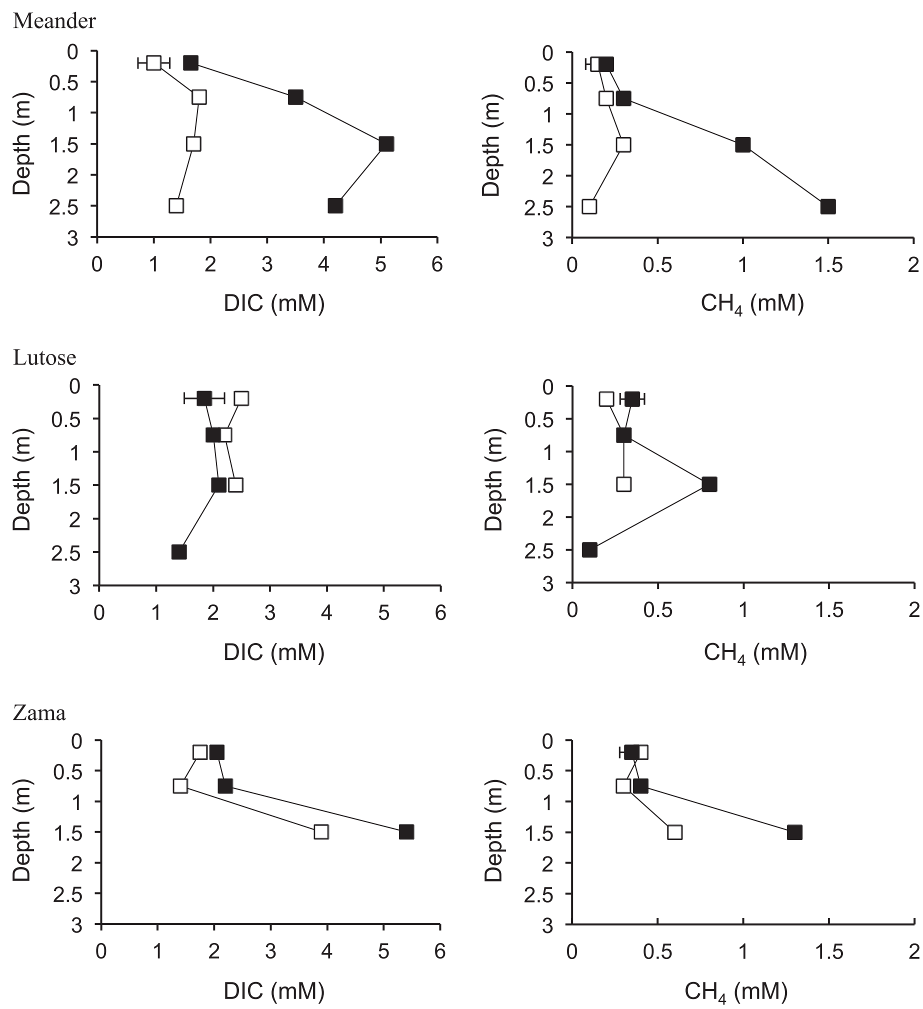

Figure 6. Depth profiles of dissolved inorganic carbon (DIC) and dissolved methane concentrations for Meander bog moat (white squares) and midbog (black squares), Lutose bog moat (white squares) and midbog (black squares), and Zama bog moat (white squares) and midbog (black squares). Sites are permafrost collapse features in Alberta, Canada.

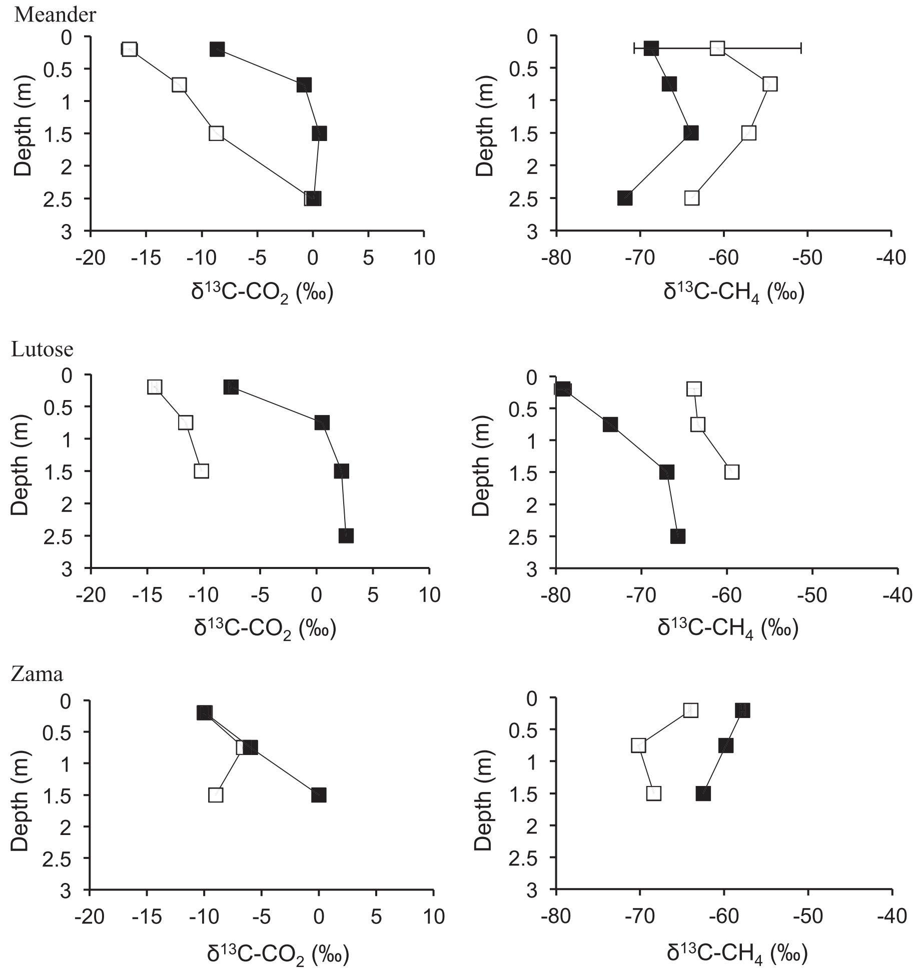

Figure 7. Depth profiles of δ^{13}C-CO_2 (δ^{13}C-DIC) and δ^{13}C-CH_4 for Meander bog moat (white squares) and midbog (black squares), Lutose bog moat (white squares) and midbog (black squares), and Zama bog moat (white squares) and midbog (black squares). Sites are permafrost collapse features in Alberta, Canada.

Sulfate and nitrate/nitrite are at or below the detection limit in the pore waters at these sites [*Corbett et al.*, 2013a], so these modes of respiration do not contribute nonfractionated CO_2 in the GLAP. Microorganisms have been shown to use humic acids to oxidize organic compounds [*Cervantes et al.*, 2000; *Lovley et al.*, 1996]. This additional mode of respiration can (1) inhibit methanogenesis [*Ye et al.*, 2012] and (2) contribute to the

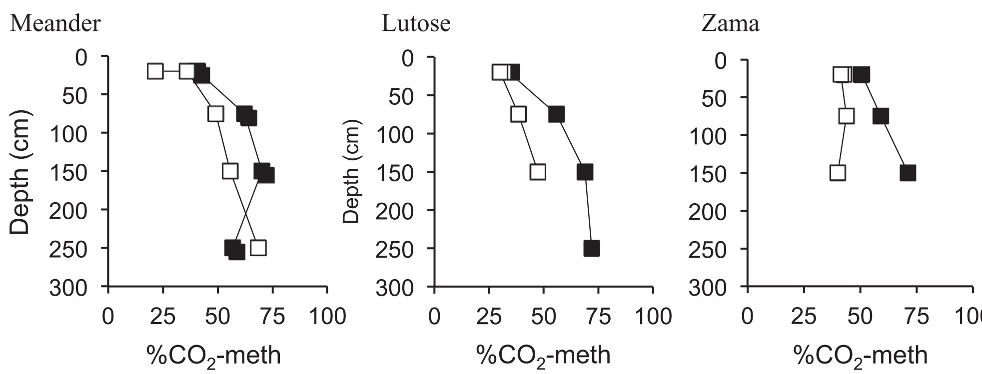

Figure 8. Depth profiles of percent CO_2 production from methanogenesis in Lutose midbog (black squares) and bog moat (white squares), Meander midbog (black squares) and bog moat (white squares), and Zama midbog (black squares) and bog moat (white squares). Sites are permafrost collapse-scar features in Alberta, Canada.

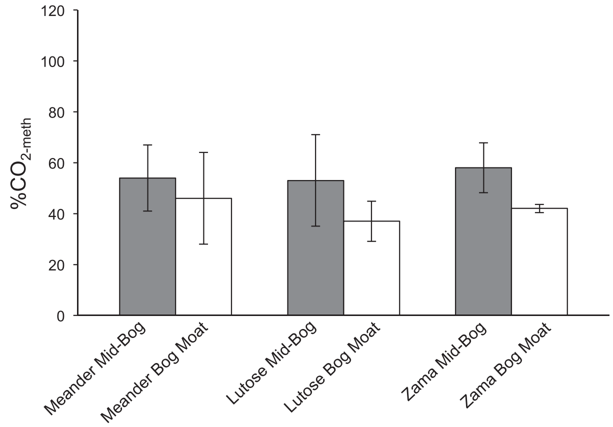

Figure 9. A comparison of %$CO_{2\text{-meth}}$ averages between midbog and bog moat sites, Alberta, Canada. The %$CO_{2\text{-meth}}$ is consistently higher in midbogs than bog moats.

production of CO_2 from nonfractionating pathways [*Blodau and Deppe*, 2012; *Heitmann et al*., 2007; *Keller and Bridgham*, 2007]. Fungal ribosomal RNA has also been reported in both bogs and fens in the GLAP [*Lin et al*., 2012]. Fungi aerobically degrade compounds in the peat surface, which may contribute to $CO_{2\text{-OM decay}}$ and therefore lower values of %$CO_{2\text{-meth}}$.

Below the oxic zone, CO_2 production from organically bound oxygen [*Leifeld et al*., 2012] with subsequent reduction of the remaining organic matter could result in unfractionated CO_2. The microbial breakdown of HMW OM to low molecular weight (LMW) OM with CO_2 as a byproduct [*Burdige*, 2006, Figure 7.10; *Corbett et al*., 2013a, Figure 2] would result in the reduction of the remaining organic matter to provide an electron balance for the oxidized CO_2. *Tfaily et al*. [2013] showed that dissolved organic matter (DOM) in peat pore water undergoes a compositional change, losing organically bound oxygen with depth. The loss of oxygen from DOM molecules is consistent with HMW OM fermentation that would allow for CO_2 production by nonfractionating pathways. Compounds with low O/C increased with depth in both bogs and fens although bogs showed less of an increase of these compounds with depth [*Tfaily et al*., 2013]. Together, all of these observations are consistent with a greater relative percent of methanogenesis in bogs as compared to fens, as observed in this study and in *Corbett et al*. [2013a].

Processes such as HMW OM fermentation will produce more reduced dissolved organic matter end products when CO_2 is lost as a byproduct. An environment utilizing this pathway may produce and export a greater amount of LMW-reduced substrates than environments utilizing other pathways (i.e., respiration) where LMW OM compounds are not stored but are eventually consumed. Fen environments, which utilize more HMW fermentation, contained lower DOC concentrations and stored a greater percent of LMW DOC than bog environments [*Corbett et al*., 2013b]. This observation can be explained by greater oxygen input into the fen pore water, which can stimulate phenol oxidase activity [*Freeman et al*., 2001b] and create mixed redox zones. This may then create more labile OM intermediates through the breakdown of HMW OM [*Chanton et al*., 2008] and as a result more subsequent DOC breakdown. In addition, root exudates themselves contribute a second type of labile, LMW DOC to the fen pore waters. In bogs, the lack of oxygen input reduces the phenol oxidase activity and hydrolysis [*Freeman et al*., 2001b] resulting in the buildup of recalcitrant, HMW DOC. Therefore, identifying the occurrence of specific microbial processes in a given environment may provide information on the types and quality of the stored DOC. In terms of DOC export to downstream ecosystems, however, the DOC concentration may be a more important factor than its quality as most DOC exported to a oxygenated downstream environment is eventually remineralized.

In the GLAP, and other peatlands, labile compounds produced in the surface are transported to depth by downward advection [*Corbett et al*., 2013b]. Downward advection has been identified in the GLAP peatlands with measurements of groundwater levels and pore water chemistry [*Siegel and Glaser*, 1987], groundwater flow models [*Reeve et al*., 2000; *Siegel et al*., 1995], and isotopic studies [*Levy et al*., 2013; *Gorham and Hofstetter*, 1971]. Greater rates of downward advection observed in the fens would bring more labile dissolved organic matter to the deep fens as compared to the deep bogs [*Chasar et al*., 2000a; *Chanton et al*., 2008; *Siegel et al*., 2001]. In addition, more labile dissolved organic matter would be added to fens at depth in the form of root exudates from *Carex*, which is the dominant species in the fen [*Chanton et al*., 2008]. The presence of more recent, reactive DOM in the deep fens, possibly in the form of compounds with more organically bound oxygen, seems to support the production of greater amounts of $CO_{2\text{-OM decay}}$. In a study done to assess the organic matter composition of peat taken from six peatlands in Switzerland over an average depth range of 0–2 m, *Leifeld et al*. [2012] showed that compounds containing organically bound oxygen were lost with depth as degradation occurred. OM material with less organic oxygen found in the bogs results in methanogenesis being a more important pathway in the bog as compared to the fen (Figures 4 and 5). However, the presence of more labile organic material may support higher overall production rates in the fen, so the average concentrations of $CO_{2\text{-meth}}$ in fen environments are comparable to those in bogs.

Although anaerobic oxidation of methane has been reported in peatlands [*Smemo and Yavitt*, 2011; *Gupta et al*., 2012], and anaerobic methane oxidation in the catotelm may cycle some methane, at depths below 50 cm net methane production dominates in peats. In both the SR and RLIV bogs, δ^{13}C-CH_4 values became more enriched with depth, while in both fens δ^{13}C-CH_4 values became more depleted with depth (Figure 3), indicative of different methanogenic pathways in the bogs and fens [*Chasar et al*., 2000b]. Bogs in GLAP are dominated by CO_2 reduction (δ^{13}C-$CH_4 = -60$ to -100‰), while fens are dominated by acetate fermentation (δ^{13}C-$CH_4 = -50$ to -65‰) at the surface and then shift to CO_2 reduction with depth [*Chasar et al*., 2000a, 2000b; *Chanton et al*., 2005; see also *Hornibrook et al*., 1997, 2000]. Methane oxidation did not appear to be a significant pathway at any depth in the peat based on the δD of methane [*Chasar et al*., 2000a, 2000b; *Chanton et al*., 2005] and the values of the isotope separation factor [*Corbett et al*., 2013a; *Whiticar*, 1999]. Therefore, the enrichment of δ^{13}C-CH_4 in the surface of the fens is attributed to acetate fermentation rather than methane oxidation [*Whiticar*, 1999].

Pore water CO_2/CH_4 ratios greater than 1 that have been observed in this and other peatlands can also be attributed to CH_4 escape from the subsurface environment. CH_4 loss varies from 50 to 90% across wetland systems, driven by ebullition [*Glaser et al*., 2004] and plant transport [*Popp et al*., 2000; *Whiting and Chanton*, 1992]. The addition of two more bog/fen pairs in this study indicates slightly greater amounts of methane loss in fens as compared bogs (Table 1). This result may be due to the difference in vegetation between the environments, as fens contain vascular plants, which can enhance gas transport relative to the *Sphagnum* moss, which dominates bogs.

4.2. Alberta Canada Collapse Bog Sites

In this portion of the study, we hypothesized that there would be more relative CO_2 production from nonmethanogenic pathways at the recent-collapse moat sites relative to midbog, since stored, frozen organic matter at the moat site had just begun to undergo anaerobic decomposition and should contain more organically bound oxygen to support greater relative nonmethanogenic pathways [*Hodgkins et al*., 2014]. The midbogs had more enriched δ^{13}C-CO_2 and greater %$CO_{2\text{-meth}}$ values than the bog moats (Figures 7 and 8), indicating that methanogenesis is a more prevalent pathway in the midbogs. Overall, there was less %$CO_{2\text{-meth}}$ in the bog moat than the midbog sites (Table 1 and Figures 8 and 9), consistent with our hypothesis that organic matter more recently exposed to anaerobic conditions produces less CH_4 but that methane production increases over time. Similar findings have been reported by *Hodgkins et al*. [2014], where it was observed that CH_4 production increased with an increase in thaw stage. Based on incubation studies, collapse-scar bogs were found to produce the least amount of CH_4 followed by bogs, and fen environments were found to produce the most CH_4 (collapse-scar bogs $<$ bogs $<$ fens). Organic matter lability also increased with along the thaw gradient. In our study, CH_4 loss varied from 51 to 72% (Table 1) and was similar overall between bog moats and midbog areas even though the amount of $CO_{2\text{-meth}}$ was lower in bog moats. This observation can be explained by the greater density of *Carex* roots in the bog moat, which can act as conduits that enhance gas escape from the pore water [*Knapp and Yavitt*, 1992; *Whiting and Chanton*, 1992].

5. Summary

At various sites within GLAP in northern Minnesota and permafrost sites in Alberta, Canada, isotope-mass balance calculations were used to quantify the concentrations of CO_2 produced from methanogenesis, and therefore, the CH_4 concentrations initially present before loss due to ebullition, diffusion, and plant-mediated transport. Similar findings in *Corbett et al*. [2013a], methanogenesis was of greater relative importance in *Sphagnum*-dominated bogs as compared to *Carex*-dominated fens. *Carex*-dominated fens had less %$CO_{2\text{-meth}}$ (64 ± 5.7%) than *Sphagnum*-dominated bogs (80 ± 13%) but had slightly higher amounts of

$CO_{2\text{-meth}}$ than bogs (3.7 ± 1.4 and 2.9 ± 1.3 mmol/L, respectively) due to the presence of more labile organic substrates in fens, which support higher overall production rates. On average, fens lost a slightly higher amount of subsurface methane loss (89 ± 2.8%) than bogs (82 ± 5.3%) due to the presence of *Carex* roots in the fens, which supports plant-induced gas ventilation. In discontinuous permafrost sites, the midbog sites had slightly more $\%CO_{2\text{-meth}}$ than the bog moat (55 ± 8.1% and 42 ± 6.6%, respectively), which supports our hypothesis that the relative importance of methanogenesis is lower in bog moats than midbogs, possibly due to a higher organic oxygen content of the recently thawed organic matter in the bog moat [*Hodgkins et al*., 2014]. The midbog and bog moat sites showed similar amounts of methane loss (64 ± 9.3% and 63 ± 7.0%, respectively) possibly due to the greater prevalence of vascular plants in the bog moat, although there was less methane produced in bog moats as the organic matter is more recently thawed and exposed to decomposition.

Acknowledgments
This research was supported by the National Science Foundation, EAR-0628349 and DEB 0841158. This research was supported by an appointment to the NASA Postdoctoral Program at the Goddard Institute for Space Studies administered by Oak Ridge Associated Universities through a contract with NASA. The authors thank Claire Langford and Tyler Mauney for their help with the laboratory work. Data presented in this paper can be obtained by sending a written request to the corresponding author.

References

Aller, R. C. (1998), Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors, *Mar. Chem.*, *61*, 143–155, doi:10.1016/S0304-4203(98)00024-3.

Barker, H. A. (1936), On the biochemistry of methane formation, *Arch. Microbiol.*, *7*(1–5), 404–419, doi:10.1007/BF00407413.

Barlaz, M. A. (2006), Forest products decomposition in municipal solid waste landfills, *Waste Manage.*, *26*(4), 321–333.

Blodau, C., and M. Deppe (2012), Humic acid addition lowers methane release in peats of the Mer Bleue bog, Canada, *Soil Biol. Biochem.*, *52*, 96–98.

Bridgham, S. D., C. A. Johnston, J. Pastor, and K. Updegraff (1995), Potential feedbacks of northern wetlands on climate change, *BioScience*, *45*(4), 262–274.

Bridgham, S. D., H. Cadillo-Quiroz, J. K. Keller, and Q. Zhuang (2013), Methane emissions from wetlands: Biogeochemical, microbial, and modeling perspectives from local to global scales, *Global Change Biol.*, *19*, 1325–1346, doi:10.1111/gcb.12131.

Burdige, D. J. (2006), *Geochemistry of Marine Sediments*, pp. 421–424, Princeton Univ. Press, Princeton, N. J.

Burdige, D. J., and T. Komada (2015), Sediment pore waters, in *Biogeochemistry of Marine Dissolved Organic Matter*, 2nd ed., edited by D. A. Hansell and C. D. Carlson, Elsevier, San Diego, Calif.

Cervantes, F. J., S. van der Velde, G. Lettinga, and J. A. Field (2000), Competition between methanogenesis and quinone respiration for ecologically important substrates in anaerobic consortia, *FEMS Microbiol. Ecol.*, *34*, 161–171.

Chanton, J. P. (2005), The effect of gas transport mechanism on the isotope signature of methane in wetlands, *Org. Geochem.*, *36*(5), 753–768.

Chanton, J. P., L. Chasar, P. H. Glaser, and D. I. Siegel (2005), Carbon and hydrogen isotopic effects in microbial methane from terrestrial environments, in *Stable Isotopes and Biosphere-Atmosphere Interactions*, *Physiol. Ecol. Ser.*, edited by L. B. Flanagan, J. R. Ehleringer, and D. E. Pataki, pp. 85–105, Elsevier-Acad. Press, San Diego, Calif.

Chanton, J. P., P. H. Glaser, L. S. Chasar, D. J. Burdige, M. E. Hines, D. I. Siegel, L. B. Tremblay, and W. T. Cooper (2008), Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands, *Global Biogeochem. Cycles*, *22*, GB4022, doi:10.1029/2008GB003274.

Charman, D. J., et al. (2012), Climate-related changes in peatland carbon accumulation during the last millennium, *Biogeosci. Discuss.*, *9*, 14,327–14,364.

Chasar, L. S., J. P. Chanton, P. H. Glaser, and D. I. Siegel (2000a), Methane concentration and stable isotope distribution as evidence of rhizospheric processes: Comparison of a fen and bog in the Glacial Lake Agassiz Peatland Complex, *Ann. Bot.*, *86*, 655–663.

Chasar, L. S., J. P. Chanton, P. H. Glaser, D. I. Siegel, and J. S. Rivers (2000b), Radiocarbon and stable carbon isotopic evidence for transport and transformation of dissolved organic carbon, dissolved inorganic carbon and CH_4 in a northern Minnesota peatland, *Global Biogeochem. Cycles*, *14*(4), 1095–1108.

Chason, D. B., and D. I. Siegel (1986), Hydraulic conductivity and related physical properties of peat, Lost River Peatland, northern Minnesota, *Soil Sci.*, *142*(2), 91–99.

Conrad, R. (1999), Contribution of hydrogen to methane production and control of hydrogen concentrations in methanogenic soils and sediments, *FEMS Microbiol. Ecol.*, *28*, 193–202.

Corbett, J. E., D. J. Burdige, M. M. Tfaily, A. R. Dial, W. T. Cooper, P. H. Glaser, and J. P. Chanton (2013a), Surface production fuels deep heterotrophic respiration in northern peatlands, *Global Biogeochem. Cycles*, *27*, 1–12, doi:10.1002/2013GB004677.

Corbett, J. E., M. M. Tfaily, D. J. Burdige, W. T. Cooper, P. H. Glaser, and J. P. Chanton (2013b), Partitioning pathways of CO_2 production in peatlands with stable carbon isotopes, *Biogeochemistry*, doi:10.1007/s10533-012-9813-1.

De la Cruz, F. B., J. Chanton, and M. A. Barlaz (2013), Measurement of carbon storage in landfills from the biogenic carbon content of excavated waste samples, *Waste Manage.*, *33*, 2001–2005.

Fenner, N., and C. Freeman (2011), Drought-induced carbon loss in peatlands, *Nat. Geosci.*, *4*, 895–900.

Freeman, C., N. Ostle, and H. Kang (2001a), An enzymic “latch” on a global carbon store, *Nature*, *409*, 149.

Freeman, C., C. D. Evans, D. T. Monteith, B. Reynolds, and N. Fenner (2001b), Export of organic carbon from peat soils, *Nature*, *412*, 785.

Glaser, P. H. (1987), The development of streamlined bog islands in the continental interior of north America, *Arctic Alpine Res.*, *19*(4), 402–413.

Glaser, P. H., G. A. Wheeler, E. Gorham, and H. E. Wright Jr. (1981), The patterned mires of the Red Lake Peatland, northern Minnesota: Vegetation, water chemistry and landforms, *J. Ecol.*, *69*(2), 575–599.

Glaser, P. H., D. I. Siegel, E. A. Romanowicz, and Y. P. Shen (1997), Regional linkages between raised bogs and the climate, groundwater, and landscape of north-western Minnesota, *J. Ecol.*, *85*(1), 3–16.

Glaser, P. H., J. P. Chanton, P. Morin, D. O. Rosenberry, D. I. Siegel, O. Ruud, L. I. Chasar, and A. S. Reeve (2004), Surface deformations as indicators of deep ebullition fluxes in a large northern peatland, *Global Biogeochem. Cycles*, *18*, GB1003, doi:10.1029/2003GB002069.

Glaser, P. H., D. I. Siegel, A. S. Reeve, and J. P. Chanton (2006), The hydrology of large peat basins in North America, in *Peatlands: Basin Evolution and Depository of Records on Global Environmental and Climatic Changes*, edited by I. P. Martini, C. A. Martinez, and W. Chesworth, Elsevier, Amsterdam.

Gorham, E. (1991), Northern Peatlands: Role in the carbon cycle and probable responses to climatic warming, *Ecol. Appl.*, *1*(2), 182–195.
Gorham, E., and R. H. Hofstetter (1971), Penetration of bog peats and lake sediments by tritium from atmospheric fallout, *Ecology*, *52*(5), 898–902.
Gupta, V., K. A. Smemo, J. B. Yavitt, and N. Basiliko (2012), Active methanothrophs in two contrasting North American peatland ecosystems revealed using DNA-SIP, *Microbial Ecol.*, *63*(2), 438–445.
Heitmann, T., T. Goldhammer, J. Beer, and C. Blodau (2007), Electron transfer of dissolved organic matter and its potential significance for anaerobic respiration in a northern bog, *Global Change Biol.*, *13*, 1771–1785, doi:10.1111/j.1365-2486.2007.01382.x.
Hodgkins, S. B., M. M. Tfaily, C. K. McCalley, T. A. Logan, P. M. Crill, S. R. Saleska, V. I. Rich, and J. P. Chanton (2014), Changes in peat chemistry associated with permafrost thaw increase greenhouse gas production, *Proc. Natl. Acad. Sci. U.S.A.*, doi:10.1073/pnas.1314641111.
Hornibrook, E. R. C., F. J. Longstaffe, and W. S. Fyfe (1997), Spatial distribution of microbial methane production pathways in temperate zone wetland soils: Stable carbon and hydrogen isotope evidence, *Geochim. Cosmochim. Acta*, *61*(4), 745–753.
Hornibrook, E. R. C., F. J. Longstaffe, and W. S. Fyfe (2000), Evolution of stable carbon isotope compositions for methane and carbon dioxide in freshwater wetlands and other anaerobic environments, *Geochim. Cosmochim. Acta*, *64*(6), 1013–1027.
Keller, J. K., and S. D. Bridgham (2007), Pathways of anaerobic carbon cycling across an ombrotrophic-minerotrophic peatland gradient, *Limnol. Oceanogr.*, *52*(1), 96–107.
Knapp, A. K., and J. B. Yavitt (1992), Evaluation of a closed-chamber method for estimating methane emissions from aquatic plants, *Tellus*, *44B*, 63–71.
Lapham, L., L. Proctor, and J. Chanton (1999), Using respiration rates and stable carbon isotopes to monitor the biodegradation of Orimulsion by marine benthic bacteria, *Environ. Sci. Technol.*, *33*, 2035–2039.
Leifeld, J., M. Steffens, and A. Galego-Sala (2012), Sensitivity of peatland carbon loss to organic matter quality, *Geophys. Res. Lett.*, *39*, L14704, doi:10.1029/2012GL051856.
Levy, Z. F., D. I. Siegel, S. S. Dasgupta, P. H. Glaser, and J. M. Welker (2013), Stable isotopes of water show deep seasonal recharge in northern bogs and fens, *Hydrol. Process.*, *28*(18), 4938–4952, doi:10.1002/hyp.9983.
Lin, X., S. Green, M. M. Tfaily, O. Prakash, K. T. Konstantinidis, J. E. Corbett, J. P. Chanton, W. T. Cooper, and J. E. Kostka (2012), Microbial community structure and activity linked to contrasting biogeochemical gradients in bog and fen environments of the Glacial Lake Agassiz Peatlands, *Appl. Environ. Microbiol.*, *78*(19), 7023–7031.
Lovley, D. R., J. D. Coates, E. L. Blunt-Harris, E. J. P. Phillips, and J. C. Woodward (1996), Humic substances as electron acceptors for microbial respiration, *Nature*, *382*, 445–448.
Moore, T. R., N. T. Roulet, and J. M. Waddington (1998), Uncertainty in predicting the effect of climatic change on the carbon cycling of Canadian peatlands, *Clim. Change*, *40*, 229–245.
Popp, T. J., J. P. Chanton, G. J. Whiting, and N. Grant (2000), Evaluation of methane oxidation in the rhizosphere of a Carex dominated fen in north central Alberta, Canada, *Biogeochemistry*, *51*, 259–281.
Post, W. M., W. R. Emanuel, P. J. Zinke, and A. G. Stangenberger (1982), Soil carbon pools and world life zones, *Nature*, *298*, 156–159.
Post, W. M., J. Pastor, P. J. Zinke, and A. G. Stangenberger (1985), Global patterns of soil nitrogen storage, *Nature*, *317*, 613–616.
Prater, J. L., Jr. (2005), Metabolic pathways in natural systems: A tracer study of carbon isotopes, Doctoral Dissertation. Florida State Univ.
Prater, J. L., J. P. Chanton, and G. J. Whiting (2007), Variation in methane production pathways associated with permafrost decomposition in collapse scar bogs of Alberta, Canada, *Global Biogeochem. Cycles*, *21*, GB4004, doi:10.1029/2006GB002866.
Reeve, A. S., D. I. Siegel, and P. H. Glaser (2000), Simulating vertical flow in large peatlands, *J. Hydrol.*, *227*, 207–217.
Romanowicz, E. A., D. I. Siegel, and P. H. Glaser (1993), Hydraulic reversals and episodic methane emissions during drought cycles in mires, *Geology*, *21*, 231–234.
Romanowicz, E. A., D. I. Siegel, J. P. Chanton, and P. H. Glaser (1995), Temporal variations in dissolved-methane deep in the Lake Agassiz Peatlands, Minnesota, *Global Biogeochem. Cycles*, *9*(2), 197–212.
Siegel, D. I., and P. H. Glaser (1987), Groundwater flow in a bog-fen complex, Lost River Peatland, northern Minnesota, *J. Ecol.*, *75*(3), 743–754.
Siegel, D. I., A. S. Reeve, P. H. Glaser, and E. A. Romanowicz (1995), Climate-driven flushing of pore water in peatlands, *Nature*, *374*, 531–533.
Siegel, D. I., J. P. Chanton, P. H. Glaser, L. S. Chasar, and D. O. Rosenberry (2001), Estimating methane production rates in bogs and landfills by deuterium enrichment of pore water, *Global Biogeochem. Cycles*, *15*(4), 967–975.
Sjostrom, E. (1993), *Wood Chemistry, Fundamentals and Applications*, pp. 276, Acad. Press, San Diego, Calif.
Smemo, K. A., and J. B. Yavitt (2011), Anaerobic oxidation of methane: An underappreciated aspect of methane cycling in peatland ecosystems?, *Biogeosciences*, *8*, 779–793.
Tarvin, D., and A. M. Buswell (1934), The methane fermentation of organic acids and carbohydrates, *J. Am. Chem. Soc.*, *56*(8), 1751–1755.
Tfaily, M. M., R. Hamdan, J. E. Corbett, J. P. Chanton, P. H. Glaser, and W. Cooper (2013), Investigating dissolved organic matter decomposition in northern peatlands using complimentary analytical techiques, *Geochim. Cosmochim. Acta*, doi:10.1016/j.gca.2013.03.002.
Valentine, D. W., E. A. Holland, and D. S. Schimel (1994), Ecosystem and physiological controls over methane production in northern wetlands, *J. Geophys. Res.*, *99*(D1), 1563–1571, doi:10.1029/93JD00391.
Vile, M. A., S. D. Bridgham, and R. K. Wieder (2003a), Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland, *Ecol. Appl.*, *13*(3), 720–734.
Vile, M. A., S. D. Bridgham, R. K. Wieder, and M. Novák (2003b), Atmospheric sulfur deposition alters pathways of gaseous carbon production in peatlands, *Global Biogeochem. Cycles*, *17*(2), 1058, doi:10.1029/2002GB001966.
Whiticar, M. J. (1999), Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chem. Geol.*, *161*, 291–314.
Whiting, G. J., and J. P. Chanton (1992), Plant-dependent CH_4 emissions in a subarctic Canadian fen, *Global Biogeochem. Cycles*, *6*(3), 225–231.
Wright, E. L., C. R. Black, A. W. Cheesman, T. Drages, D. Larges, B. L. Turner, and S. Sjogersten (2011), Contribution of subsurface peat to CO_2 and CH_4 fluxes in a neotropical peatland, *Global Change Biol.*, *17*, 2867–2881.
Ye, R., Q. Jin, B. Bohannan, J. K. Keller, S. A. McAllister, and S. D. Bridgham (2012), pH controls over anaerobic carbon mineralization, the efficiency of methane production, and methanogenic pathways in peatlands across an ombrotrophic—Minerotrophic gradient, *Soil Biol. Biochem.*, *54*, 36–47.

