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Radiocarbon Evidence for the Importance of Surface Vegetation on Fermentation and Methanogenesis in Contrasting Types of Boreal Peatlands

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Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands

J. P. Chanton,¹ P. H. Glaser,² L. S. Chasar,³ D. J. Burdige,⁴ M. E. Hines,⁵ D. I. Siegel,⁶ L. B. Tremblay,⁷ and W. T. Cooper⁷

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[1] We found a consistent distribution pattern for radiocarbon in dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and methane replicated across spatial and temporal scales in northern peatlands from Minnesota to Alaska. The ¹⁴C content of DOC is relatively modern throughout the peat column, to depths of 3 m. In sedge-dominated peatlands, the ¹⁴C contents of the products of respiration, CH₄ and DIC, are essentially the same and are similar to that of DOC. In *Sphagnum*- and woody plant-dominated peatlands with few sedges, however, the respiration products are similar but intermediate between the ¹⁴C contents of the solid phase peat and the DOC. Preliminary data indicates qualitative differences in the pore water DOC, depending on the extent of sedge cover, consistent with the hypothesis that the DOC in sedge-dominated peatlands is more reactive than DOC in peatlands where *Sphagnum* or other vascular plants dominate. These data are supported by molecular level analysis of DOC by ultrahigh-resolution mass spectrometry that suggests more dramatic changes with depth in the composition of DOC in the sedge-dominated peatland pore waters relative to changes observed in DOC where *Sphagnum* dominates. The higher reactivity of DOC from sedge-dominated peatlands may be a function of either different source materials or environmental factors that are related to the abundance of sedges in peatlands.

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1. Introduction

[2] Carbon fixation occurs at a more rapid rate than decomposition under the cold, wet, anaerobic conditions within northern peatlands, so that organic matter accumulates. Peatland soils consist purely of autochthonous organic matter fixed at the land surface. With soil depths up to 3–5 m, peatlands serve as large repositories of stored carbon, an amount representing 25–50% of current levels of atmospheric

CO₂ [Gorham, 1991; Frohling and Roulet, 2007]. The balance between net ecosystem production and decomposition (or heterotrophic respiration) of peat is of considerable interest. *Clymo* [1984] proposed that the peat column would accumulate until the respiration of solid phase peat in the underlying column matched the rate of CO₂ uptake at the surface. Thereafter a peatland would exist in a steady state with respect to its carbon balance in which C fixation balanced decomposition in the soil column.

[3] Peatlands are generally classified as either bogs or fens on the basis of their topography (i.e., 3-D peat landform), water chemistry, vegetation, and hydrology [Sjörs, 1948, 1963]. Raised bogs (1) have raised landforms with interiors higher than their margins, (2) have acidic (pH < 4.2) dilute (Ca < 2 mg L⁻¹) surface waters, (3) have vegetation with no fen indicator species, and (4) receive all their water and salts solely from the atmosphere [Glaser *et al.*, 1981]. Hydrologically, bogs function as recharge mounds with surface waters supplied solely by precipitation that flows downward into the deeper peat strata. Fens, in contrast, are flat or concave peat landforms that receive at least some surface waters that have percolated through mineral soil. As a result fen waters are less

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acidic and less dilute than those of bogs and contain at least some fen indicator species.

[4] Previously, we and others have reported that anaerobic respiration within the peat column to depths of 3 m is fueled by dissolved organic carbon derived in part from surface production rather than from the decomposition of peat at a particular horizon [Aravena *et al.*, 1993; Chanton *et al.*, 1995; Charman *et al.*, 1999; Chasar *et al.*, 2000a; Clymo and Bryant, 2008]. This finding was supported by differences in radiocarbon enrichment of dissolved organic carbon (DOC) and the products of anaerobic respiration, CO₂ and CH₄, relative to peat within a horizon. In most studies, the respiration products were intermediate in their radiocarbon activity between DOC and peat. It also appeared that the respiration products were closer to DOC in radiocarbon content in a sedge-dominated fen but contained somewhat less radiocarbon and were more similar to peat values in a bog dominated by *Sphagnum* and woody plants. A detailed data set was confined to a single bog and a single fen and observations in a single year [Chasar *et al.*, 2000a]. The results of Clymo and Bryant [2008] are somewhat different from other peatlands in that the DOC, while ¹⁴C enriched relative to peat, is depleted relative to the products of respiration, CH₄ and dissolved inorganic carbon (DIC). Clymo and Bryant [2008] attributed this to the more limited hydraulic conductivity of the Ellergower Moss system where they worked. Transport in this system is more controlled by diffusion, rather than pore water advection, so the gases could diffuse down from the surface at a faster rate than the DOC.

[5] These differences observed between sedge-dominated fens and *Sphagnum*- and woody plant-dominated bogs are intriguing in light of other recently reported differences in carbon flow pathways between these two types of peatlands. Shifts with depth in the importance of the two main pathways of methane production, acetate fermentation, and CO₂ reduction have been found in sedge-dominated fens (and marshes) but not in bogs dominated by *Sphagnum* and woody plants, where methanogens carry out CO₂ reduction down the entire depth column [Hornibrook *et al.*, 1997, 2000a, 2000b; Lansdown *et al.*, 1992; Chasar *et al.*, 2000b; Chanton *et al.*, 2005]. Acetate fermentation is associated with the production of methane from more labile organic matter, whereas CO₂ reduction utilizes more recalcitrant organic matter [Sugimoto and Wada, 1993]. The current paradigm is that the near-surface peat strata of sedge-dominated fens produce relatively labile organic matter, while in the surface of bogs dominated by *Sphagnum* and woody plants, the organic matter is more recalcitrant [Kelley *et al.*, 1992; Chanton *et al.*, 2005].

[6] The objective of this study was therefore to determine the spatial and temporal distribution patterns of ¹⁴C in peat profiles from a suite of peatlands, as well as the molecular composition of DOC in peat pore waters, to test the generality of results obtained by Chasar *et al.* [2000a]. Specifically, we asked the following four questions. (1) Are the products of respiration generally ¹⁴C enriched relative to organic matter in peatlands? (2) Are there relative differences in this enrichment in peatlands with surface vegetation dominated by sedges as opposed to those dominated by mosses and woody vascular plants? (3) Are there differ-

ences in radiocarbon content between the respiration products themselves, methane, and DIC? (4) Are any differences observed reflected in the composition of DOC in pore waters? Here we report repeated measurements at the bog and fen sites in Minnesota previously investigated by Chasar *et al.* [2000a] and additional sites in Alberta, Canada, and Minnesota and Alaska, USA. We have also for the first time applied ultrahigh-resolution mass spectrometry (UHR-MS) to develop a molecular fingerprint of DOC from peat pore waters. UHR-MS can distinguish individual elemental compositions of DOC molecules and define the fundamental molecular differences between DOC in different environmental conditions.

2. Study Sites

[7] Three sites were sampled in the central watershed (Red Lake II in work by Glaser *et al.* [1981]) of the Red Lake peatland, a large complex of raised bogs and patterned water tracks within the glacial Lake Agassiz peatlands of northern Minnesota (Table 1). The bog site sampled by Chasar *et al.* [2000a, 2000b] is located at the forested crest of a large bog complex where the water table is usually 5–20 cm below the peat surface and the uppermost pore waters have a pH less than 4. The crest is forested with black spruce (*Picea mariana*) and has an understory of ericaceous shrubs and a nearly continuous carpet of *Sphagnum* species. Water from the bog crest drains downslope across a broad nonforested *Sphagnum* lawn and collects within narrow fen water tracks. The fen site (previously sampled by Chasar *et al.* [2000a, 2000b]) has standing water with a pH of about 5.6 and is dominated by an assemblage of sedges including *Carex lasiocarpa*, *C. limosa*, *Rhychospora alba*, and *R. fusca*. A third site, called the lawn site, is located midslope on the Red Lake II watershed on the broad nonforested *Sphagnum* lawn. The lawn site has a continuous mat of *Sphagnum* and stands of *Carex oligosperma* with small ericaceous shrubs and *Eriophorum spissum*. The pH on the lawn ranges from about 4 just downslope from the forested crest to 4.5 about midslope, at which point a few fen indicator species appear. New samples were collected and analyzed at all three sites in 1998 and have not been reported in the literature.

[8] Samples were collected during 2001 in Turnagain Bog [Duddleston *et al.*, 2002], which is a 200 ha nonforested ombrotrophic peatland located near Anchorage, Alaska, (60°10'N, 149°11'W). The study area is located in the center of the peatland in a *Sphagnum-Myrica gale* stand. Surface waters have a pH of 4.7–5.1, typical of a poor fen. In contrast, Bleak Lake Bog (54°41'N, 113°28'W) is an ombrotrophic peatland located in central Alberta, Canada [Vile *et al.*, 2003; Vitt *et al.*, 1995]. We sampled an open area that has a sparse stand of black spruce (*Picea mariana*) with an understory of ericaceous shrubs (e.g., *Ledum groenlandicum* and *Vaccinium oxycoccos*), *Smilacina trifolia*, and *Rubus chamaemorus* [Szumigalski and Bayley, 1996]. The area contains hummocks mixed with smaller, wetter hollows. Hummocks are dominated by the moss *Sphagnum fuscum*, while hollows are populated by *Sphagnum angustifolium* and *Sphagnum magellanicum* [Vitt *et al.*, 1995, Szumigalski and

Table 1. Characteristics of Peatlands Sampled in this Study

Site	Sampled	Location	Vegetation	pH	Types of Samples
Red Lake II bog crest	1997 and 1998	Northern Minnesota, USA	black spruce, ericaceous shrubs, and <i>Sphagnum</i> carpet	3.8	DIC, DOC, CH ₄ , and peat
Red Lake II fen	1997 and 1998	Northern Minnesota, USA	<i>Carex lasiocarpa</i> , <i>C. limosa</i> , <i>Rhychospora alba</i> , and <i>R. fusca</i>	5.6	DIC, DOC, CH ₄ , and peat
Red Lake II lawn	1998	Northern Minnesota, USA	<i>Carex oligosperma</i> , <i>Eriophorum spissum</i> , small ericaceous shrubs, and <i>Sphagnum</i> carpet	4–4.5	DIC, DOC, CH ₄ , and peat
Turnagain Bog	2001	Anchorage, Alaska, USA	<i>Sphagnum-Myrica gale</i>	4.7–5.1	DIC, DOC, CH ₄ , and peat
Bleak Lake Bog	2003	Northern Alberta, Canada	Sparse black spruce, ericaceous shrubs, and <i>Sphagnum</i> carpet	3.8–4	DIC, DOC, CH ₄ , and peat
Susanne's fen	2003	Northern Alberta, Canada	<i>Carex aquatilis</i> and <i>Carex rostrata</i>	6.4–6.8	DIC, CH ₄ , and peat

Bayley, 1996]. The surface is typically between 0.3 and 0.5 m above the water table, and surface water pH ranged from 3.8 to 4.0.

[9] Susanne's fen is a rich fen in which the surface waters have a pH of 6.4–6.8 approximately 110 km north of Edmonton, Alberta, Canada (54.6°N, 113.4°W) [Popp *et al.*, 1999]. The fen was chosen because of its homogeneity and its proximity to the University of Alberta's Meanook Biological Research Station. The vegetation is dominated by the sedges *Carex aquatilis* and *Carex rostrata*. The water table is typically above the surface of the peat.

3. Methods

[10] Pore water samples were collected at depths ranging from 1 to 3 m using a piezometer and a peristaltic pump [Siegel and Glaser, 1987]. DIC (or $\sum\text{CO}_2$) samples were filtered through glass fiber filters and 10 mL were injected into 25 mL evacuated serum vials fitted with butyl rubber septa. DIC samples were stored frozen and upside down. Prior to analysis they were acidified with 0.3 mL of degassed 30% H₃PO₄ and brought to ambient pressure through an open split tube with nitrogen. Small subsamples (20 μL) of the headspace from the DIC samples were run via direct injection on the gas chromatography–isotope ratio mass spectrometry (GC-IRMS) (HP Finnigan Delta S) to determine $\delta^{13}\text{C}$ DIC. The remainder of the CO₂ in the vial was stripped with a He gas stream, purified cryogenically and transferred to a break seal and submitted to the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS).

[11] Pore water for methane capture was injected into evacuated 500 mL Qorpak brown glass bottles, containing 1.5 g KOH and stored upside down. Storage tests indicate that samples keep for over a year in this manner. The headspaces of the CH₄ samples were pressurized to one atmosphere with an open split and equilibrated with the dissolved phase. Then a small portion of the headspace was analyzed via direct injection into the GC-IRMS (Finnigan Delta S) to determine $\delta^{13}\text{C}$ CH₄. Methane from the rest of the headspace was removed with a helium stream and

combusted over copper oxide at 800°C and the resultant CO₂ was cryogenically trapped, purified, and sealed into a break seal vial.

[12] Pore water for $\delta^{13}\text{C}$ -DOC and radiocarbon analysis was collected in glass syringes and filtered using Whatman 2.7 nm retention glass fiber prefilters (type GF/D) and 0.7 nm retention glass fiber filters (type GF/F). Glass syringes, stainless steel filter holders, foil cap liners, and bottles had been precombusted at 500° for 5 h prior to use. After collecting pore water, samples were flash frozen. Minnesota samples were prepared for $\delta^{13}\text{C}$ -DOC and ¹⁴C analysis by UV oxidation following acidification and DIC removal. The ¹³C split was analyzed using the dual-inlet system on the Finnegan MAT IRMS. CO₂ from the oxidation was preserved in a glass break seal and analyzed at NOSAMS.

[13] For Alaska and Canadian DOC samples, pore water samples were acidified, sparged, freeze-dried, and combusted to CO₂. Combusted samples were cryogenically distilled on a vacuum distillation line, and CO₂ samples were stored in break seals. The CO₂ samples were then analyzed for ¹³C content on a Finnigan Delta S IRMS for the determination of $\delta^{13}\text{C}$ (‰, Vienna Pee Dee belemnite). Break seals with CO₂ splits were sent to NOSAMS.

[14] Selected Minnesota pore water samples were analyzed for concentrations of DOC and dissolved organic nitrogen (DON) using high-temperature oxidation techniques [Burdige and Gardner, 1998]. The DOC molecular weight distribution in these samples was determined using Amicon Centricon microconcentrators with a nominal molecular weight cutoff of 3 kDa [Chin and Gschwend, 1991; Burdige and Gardner, 1998].

[15] Radiocarbon data for Minnesota peat samples were taken from Chanton *et al.* [1995]. For Alaskan and Canadian samples, bulk peat samples were dried in an oven at 60°C, and small (5–10 mg) samples were transferred to break seals along with 1 g CuO and a 0.5 g piece of silver foil. Evacuated sealed tubes were flame sealed and combusted at 580°C overnight. All combusted samples were cryogenically distilled and 30–100 μmol CO₂ aliquots were transferred to break seals and analyzed for $\delta^{13}\text{C}$ and sent to NOSAMS for radiocarbon analysis.

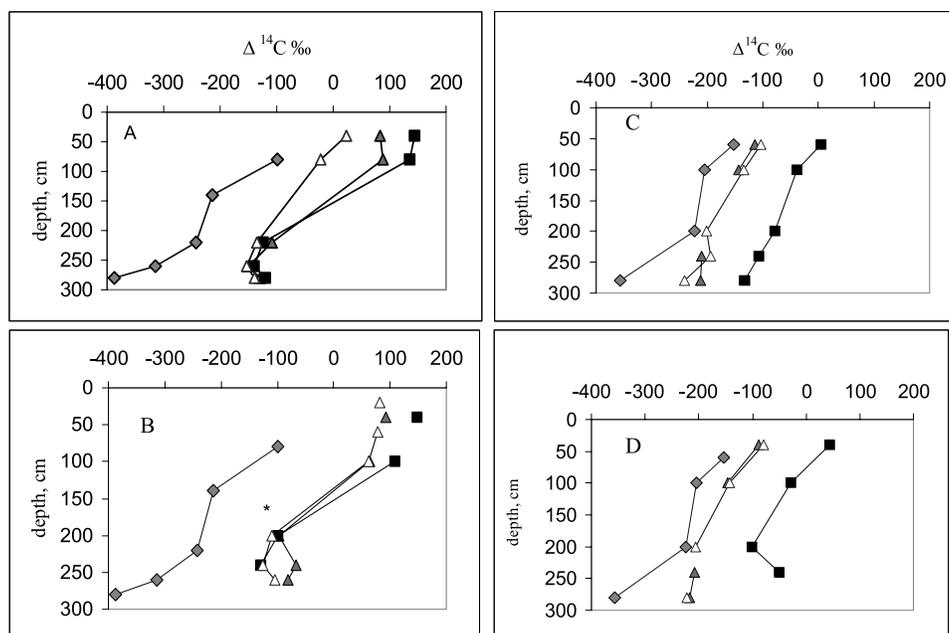


Figure 1. Radiocarbon distribution in glacial Lake Agassiz Red Lake II fen in (a) 1997 and (b) 1998 and Red Lake II bog in (c) 1997 and (d) 1998. Filled diamonds represent peat radiocarbon values, filled triangles represent DIC, open triangles represent CH₄, and filled squares represent DOC. Symbols adjacent to an asterisk are overlapping.

[16] Radiocarbon results are expressed in $\Delta^{14}\text{C}\text{‰}$ as defined by *Stuiver and Polach* [1977]. $\Delta^{14}\text{C}$ is defined as the relative difference between an absolute international standard (base year 1950) and sample activity corrected for age and $\delta^{13}\text{C}$. The $\Delta^{14}\text{C}$ is age corrected to account for decay that took place between collection and the time of measurement so that two measurements of the same sample made years apart will produce the same calculated $\Delta^{14}\text{C}$ result (<http://www.nosams.who.edu/clients/data.html>). To account for differences in ^{14}C caused by isotopic fractionation, these values are also corrected to the values that they would have been if their original $\delta^{13}\text{C}$ were -25‰ . Median reproducibility of the AMS measurement for our samples was $\pm 3\text{‰}$. Sample reproducibility was $\pm 12\text{‰}$.

[17] Frozen pore water samples from the fen and bog crest in Minnesota were used for molecular level UHR-MS analysis of DOC. DOC from a surface (0.2 m) and deep (2.6 m) fen and surface (0.3 m) and deep (2.6 m) bog was characterized in this study. All water samples were filtered through $0.2\ \mu\text{m}$ Whatman Nuclepore QTEC[®] membrane filter cartridges and then acidified with HCl to pH 2 and pumped through polymer solid phase extraction cartridges (Varian Bond Elut PPL[®], $200\ \text{mg}\ 3\ \text{mL}^{-1}$). Extracted DOC was eluted with methanol. Each extract was then diluted in 50:50 methanol:water and stored in the freezer until analysis. Acetonitrile ($10\ \mu\text{L}$) was added as an extra electron donor before introduction into the MS analyzer. Electro-spray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR) mass spectra were acquired with a home-built 9.4 T FT-ICR mass spectrometer at the National High Magnetic Field Laboratory [*Senko et al.*, 1996;

Shi et al., 2000]. Data were collected and processed using a modular ICR data acquisition system. Negative ions were generated from a microelectrospray source equipped with a fused silica needle. Samples and calibrant were infused at a flow rate of $0.5\ \mu\text{L}\ \text{min}^{-1}$. The use of this instrument to obtain UHR mass spectra of DOC has been described in several previous publications [*Kujawinski et al.*, 2002; *Stenson et al.*, 2003; *Tremblay et al.*, 2007].

4. Results and Discussion

4.1. Radiocarbon Profiles of DOC, DIC, CH₄, and Peat

[18] Radiocarbon profiles of DOC, DIC, CH₄, and peat are shown in Figure 1 for the Minnesota Red Lake II fen and Red Lake II bog and in Figure 2 for the Red Lake II lawn transitional site; Bleak Lake Bog in Alberta, Canada; Turnagain peatland in Alaska; and Susanne's fen in Alberta (no DOC data).

[19] The first pattern that is discernable in the data is that in every wetland and at every depth, DOC was substantially enriched in ^{14}C relative to peat. The second discernable pattern is that the products of respiration, CH₄ and DIC, are generally quite similar and are also enriched in radiocarbon relative to the peat. Therefore, the finding of *Chasar et al.* [2000a] that microbial respiration is greater than the sum of peat degradation holds across repeated temporal sampling and in three other wetlands. The data indicate that modern DOC is utilized in anaerobic decomposition in addition to carbon respired from solid phase peat. The elevated CH₄ production and fluxes associated with depressurization events [*Glaser et al.*, 2004; *Rosenberry et al.*, 2003; *Siegel*

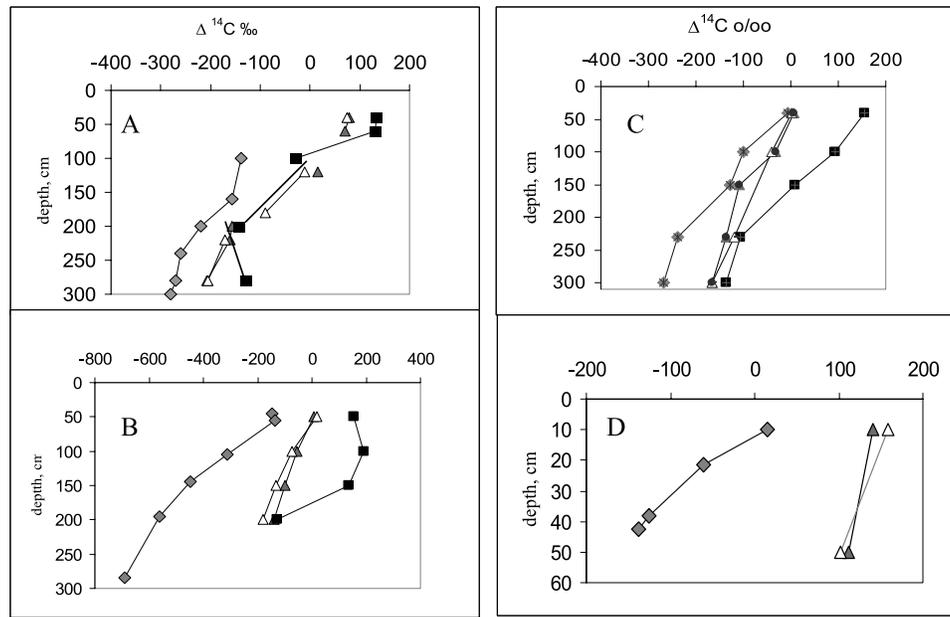


Figure 2. (a) Radiocarbon distribution in Red Lake II lawn, Minnesota, 1998; (b) Turnagain Bog, Alaska, 2001; (c) Bleak Lake Bog, Alberta, 2003; and (d) Susanne's fen, Alberta, 2003. Filled diamonds represent peat radiocarbon values, filled triangles represent DIC, open triangles represent CH₄, and filled squares represent DOC.

et al., 2001] are thus supported in part by the respiration of recently fixed carbon.

[20] A third pattern is that the respiration products are, for the most part, intermediate between DOC and peat radiocarbon value for the peatlands that lack a dominant sedge cover such as the Red Lake II bog site, the Turnagain peatland, and Bleak Lake Bog (Figures 1 and 2). At the Red Lake II fen and lawn sites where sedges were more abundant, the respiration products are more similar to the DOC (Figures 1 and 2). The relative abundance of robust sedges on a peatland, such as *Carex oligosperma* or *C. lasiocarpa*, which are the dominant sedges on bog lawns and fen water tracks, respectively, in Minnesota [Glaser *et al.*, 1981; Glaser, 1992], appear to have an important functional role on the quality of the DOC present in vertical peat profiles. Previous reports on DOC in peat profiles, in contrast, stress either (1) the depth of the water table, which determines the thickness of the aerobic layer and exposure of the peat to aerobic decomposition and diagenesis [e.g., Chanton *et al.*, 1995], or (2) the role of physical transport processes such as molecular diffusion [Clymo, 1984], advection along vertical groundwater flow paths [Siegel *et al.*, 1995; Chanton *et al.*, 1995; Glaser *et al.*, 1997; Waddington and Roulet, 1997], and transverse dispersion along lateral flow paths [Reeve *et al.*, 2001]. Mass transfer rates by means of advection or transverse dispersion are orders of magnitude higher than that possible by molecular diffusion alone. In addition, the relative abundance of sedges on a peatland may also affect the quality of DOC in peat profiles depending on the depth to which their living roots can penetrate and release labile carbon compounds.

4.2. Differences Between Wetland Types Due to Vegetation

[21] Hines *et al.* [2008], for example, observed significant differences in anaerobic metabolism associated with the presence or absence of *Carex* across a spectrum of northern wetlands. Compared to sites with no sedges, peatlands with even a small population of sedges exhibited sharp differences in carbon flow pathways with more CH₄ and less acetate in the anaerobic strata. Rooney-Varga *et al.* [2007] reported a link between vegetation type (as defined by the dominance of *Sphagnum* spp. versus *Carex* spp.) and archaeal community composition at these sites, suggesting that plants (and/or the environmental conditions that control their distribution) influence both archaeal community activity and dynamics.

[22] Evidence for variations in methane production pathways based upon the isotopic fractionation factor involved in methane production, α , defined below,

$$\alpha = \frac{\delta^{13}\text{C}_{\text{DIC}} + 1000}{\delta^{13}\text{C}_{\text{CH}_4} + 1000} \quad (1)$$

further contrasts sedge-dominated sites with *Sphagnum*- and woody plant-dominated sites. Changes in α represent changes in the relative importance of methanogenic pathways, where larger α values are typical of CO₂ reduction and smaller values are typical of increased importance of acetate fermentation [Hines *et al.*, 2008, Chanton *et al.*, 2005; Conrad, 2005; Whiticar, 1999]. At the Red Lake II lawn site, α varied with depth from 1.064 to 1.078. At the Red Lake II fen site α similarly varied with depth, from 1.055 to 1.078, while at the bog site α did not vary with

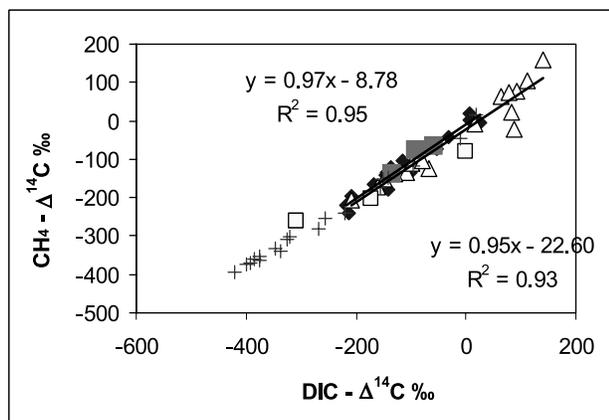


Figure 3. Methane radiocarbon content versus DIC radiocarbon content for sites with *Carex* present (fens and lawns, open triangles) and *Sphagnum*- and woody plant-dominated sites (filled diamonds) from all data in Figures 1 and 2. The former sites have a slope of 0.95, and the latter have a slope of 0.97. Also shown are data by Charman *et al.* [1994, 1999] (open squares), Aravena *et al.* [1993] (filled squares), and Clymo and Bryant [2008] (crosses). The slope of the line though the entire data set is 0.9, the intercept is -21.0 , $r^2 = 0.97$, and $n = 67$. Notice that the Clymo and Bryant data are significantly depleted in radiocarbon relative to the other data sets.

depth and was from 1.076 to 1.080 [Chasar, 2002]. At Bleak Lake Bog and Turnagain peatland α was similarly invariant with depth [Chanton *et al.*, 2005]. Finally, DIC pore water concentrations in the Red Lake II lawn site were as great as 11 mmol in the lawn and fen sites but only reached 7 mmol in the bog. The cation Ca + Mg pore water concentrations in these lawn and fen sites were similar, reaching 1 mmol, while in the bog site, they only reached a maximum of 0.3 mmol [Chasar *et al.*, 2000a]. The low Ca + Mg content indicates that DIC content was dominated by respiration of organic matter not calcite dissolution from groundwater inputs.

[23] Examination of the radiocarbon content of the respiration products, DIC and CH₄, across all sites shows little difference between these two pools (Figure 3). Regression of CH₄ radiocarbon content versus DIC radiocarbon content yields a slope of nearly 1. When methane is produced from the CO₂ reduction pathway, one would expect the ¹⁴C content of the two gases to be similar after correction for isotopic fractionation effects, as discussed in section 3. Similarly, methane and CO₂ produced from acetate decomposition would also be expected to yield similar ¹⁴C values after correction. One implication of this finding is that in wetlands such as these, one may extend a limited budget by analyzing radiocarbon on DIC alone and using its values as a proxy for CH₄.

[24] Charman *et al.* [1999] collected a similar although more limited set of measurements in the peat soil of a small raised mire in the southwest of England. In this data set DIC was enriched somewhat in radiocarbon relative to CH₄, while respiration products were enriched relative to one

DOC sample at one depth and depleted relative to a second. All three pools were ¹⁴C enriched relative to the solid phase peat at each horizon. In contrast, Charman *et al.* [1994] investigated an Ontario bog and found that DIC was slightly ¹⁴C depleted relative to CH₄ at two depths, both of which were enriched relative to peat. Aravena *et al.* [1993] also examined an Ontario bog and found no consistent difference in radiocarbon enrichment between DIC and CH₄, both of which were enriched relative to peat. When the results of all of these studies are plotted along with our data in Figure 3, they appear, overall, to be completely consistent with our results. The results of Clymo and Bryant [2008] for the ¹⁴C content of DIC and CH₄ are also shown in Figure 3, and the two pools have very similar values. The respiration products from Ellergower Moss are ¹⁴C depleted relative to most of our values because of the lower hydraulic conductivity of the site, the greater depth of sampling and the consequently greater age of the peat. Unlike our data, DOC ¹⁴C values at Ellergower Moss are depleted relative to DIC and CH₄ because of the lower hydraulic conductivity at the site and the higher diffusivities of the gases relative to DOC [Clymo and Bryant, 2008].

[25] When DOC radiocarbon values are plotted versus DIC (and by inference, CH₄; Figure 4) it is observed that values from sites populated by sedges correspond closely to a slope of 1, indicating only slight differences between DOC and DIC. We interpret this similarity to indicate that the products of respiration (DIC and CH₄) are for the most part derived from DOC in these sedge-rich peatlands. This suggests that the DOC in these peatlands is relatively labile because these respiration products appear to be derived from this DOC. At sites dominated by *Sphagnum* and woody plants, the DOC spans the same range of ¹⁴C values as the DIC (-225 – 125 ‰) in the sedge-populated wetlands (y axis) but is enriched in radiocarbon relative to DIC (and by inference, CH₄). Such differences indicate that the respiration products in these peatlands are derived from degradation of both the DOC and the peat, suggesting more

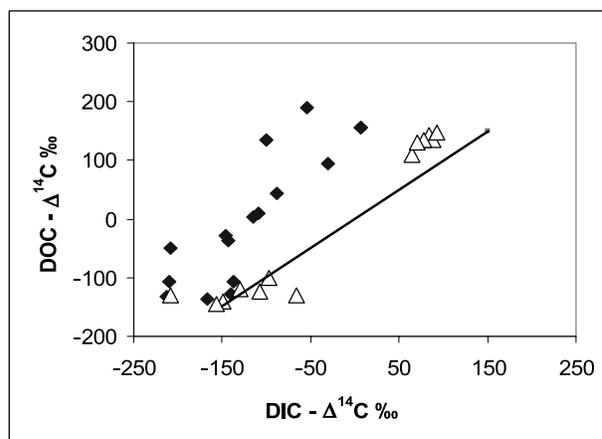


Figure 4. DOC radiocarbon content versus DIC radiocarbon content for sites with *Carex* present, fens and lawns (open triangles), and *Sphagnum*- and woody plant-dominated sites (filled diamonds). The line was drawn with a slope of 1.

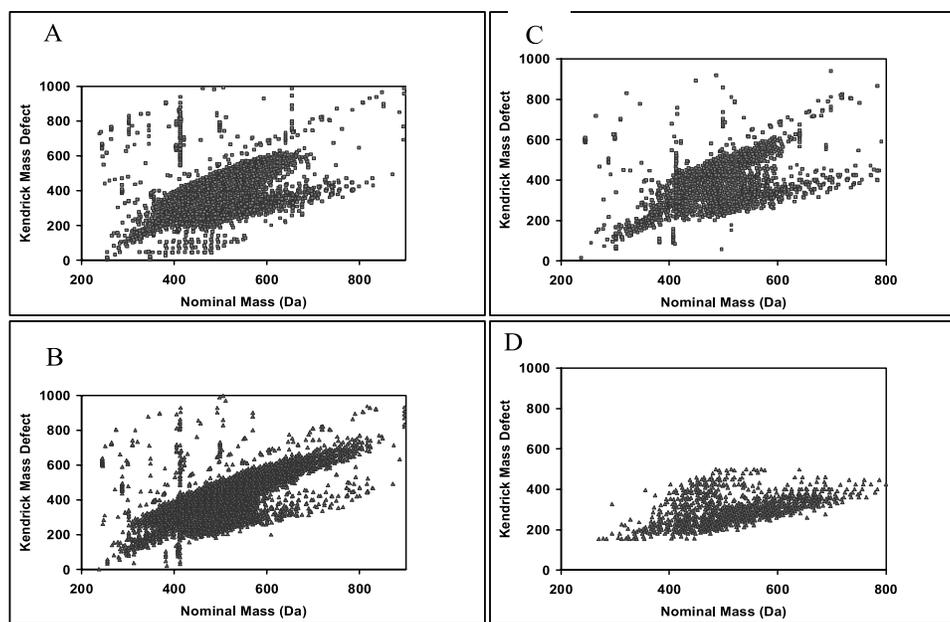


Figure 5. Kendrick plots (nominal mass versus Kendrick mass defect) of DOC: (a) from 0.3 m depth and (b) from 2.6 m depth, Red Lake II bog crest, with *Sphagnum*- and woody plant–dominated peat pore waters, and (c) from 0.2 m depth and (d) from 2.6 m depth in sedge-dominated peat pore waters of Red Lake II fen. See text for definitions of Kendrick masses and defects.

similarity in the reactivity of these two substrates. We suggest that this indicates that at least some of the DOC in *Sphagnum* and woody plant peatlands is less reactive than the DOC from *Carex*-populated peatlands. However, an alternate explanation of our observation is that environmental conditions are such that DOC is rendered more reactive in sedge-dominated fens or conversely that the DOC in the *Sphagnum* and woody plant sites is rendered less reactive [Freeman *et al.*, 2001].

[26] Consistent with our observations is the finding that DOC concentrations are greater at bog sites dominated by *Sphagnum* and woody plants than at fen sites dominated by sedges, further indicating lower reactivity of DOC at the *Sphagnum* and woody plant sites. In comparisons of six bogs and nine fen sites in the glacial Lake Agassiz peatlands the median bog DOC concentration was 6.5 mmol, while the median fen DOC was 2.1 mmol (D. Siegel, unpublished data, 2007). A Mann-Whitney rank sum test indicated a significant difference between the two groups ($P = <0.001$). *Sphagnum*, despite its lack of a root system, excretes a range of recently photosynthesized complex organic compounds that may contribute to significantly higher levels of DOC in bogs [e.g., Rasmussen *et al.*, 1995; Fenner *et al.*, 2004]. This DOC appears to have limited reactivity.

4.3. Evidence From Ultrahigh-Resolution Mass Spectrometry

[27] Further evidence of qualitative differences in DOC from sedge-dominated peatlands and woody *Sphagnum* sites comes from molecular characterization by ultrahigh-resolution mass spectrometry. Visually representing the enormous amount of data that results from the application of UHR-MS can be difficult; for example, each of the DOC

samples analyzed here yielded more than 1500 identifiable molecular formulas. One useful approach for representing and comparing such large molecular data sets is the Kendrick mass analysis [Kendrick, 1963; Hughey *et al.*, 2001; Kujawinski *et al.*, 2002; Stenson *et al.*, 2003], which begins by rescaling each identified formula according to equation (2). This rescaling is equivalent to assigning each mass of CH_2 as 14.0000 amu instead of the International Union of Pure and Applied Chemistry (IUPAC) mass of 14.01565 amu.

$$\text{Kendrick mass} = \text{IUPAC mass}(14.00000/14.01565) \quad (2)$$

[28] The Kendrick mass defect (KMD) is the difference between the nominal Kendrick mass (i.e., the integer portion of the Kendrick mass) and the exact Kendrick mass (equation (2)), multiplied by 1000 (equation (3)).

$$\text{KMD} = (\text{Nominal Kendrick mass} - \text{Kendrick exact mass})1000 \quad (3)$$

The KMD value for any molecule increases as the oxygen content and the degree of unsaturation increase. Thus, high KMD values for any given nominal mass indicate extensive oxygenation and/or unsaturation. Molecular information derived from the Kendrick mass defect can be compactly represented with a Kendrick plot in which Kendrick mass defect (as the ordinate) is plotted against nominal mass (as abscissa) [Hughey *et al.*, 2001]. In such a plot, elemental compositions differing in the number of oxygen atoms and/or the number of double bonds are separated vertically because of their different KMD values.

[29] Figures 5a and 5b contain such Kendrick plots for DOC obtained from the Minnesota bog site at 0.3 and 2.6 m

Table 2. Characterization of Shallow and Deep Pore Water DOC From Minnesota Samples in 1998

	DOC (mmol)	DON (mmol)	C/N	LMW DOC ^a (mmol; <3 kamu)	HMW DOC ^a (mmol; >3 kamu)
<i>Carex</i> -dominated site					
0.6 m	3.3	0.08	40	2.7 (82%)	0.6 (18%)
2.6 m	3.5	0.12	30	3.0 (85%)	0.5 (15%)
<i>Sphagnum</i> - and woody plant- dominated site					
0.6 m	6.3	0.14	46	3.7 (59%)	2.5 (41%)
2.8 m	7.7	0.09	89	5.2 (68%)	2.5 (32%)

^aThe relative concentration of low molecular weight (LMW) and high molecular weight (HMW) DOC by percent of the total is shown in parentheses.

depths, respectively. These plots are quite typical of those observed from DOC in a number of other environments [Stenson *et al.*, 2003; Tremblay *et al.*, 2007]. In particular, KMD values generally increase with nominal mass for all samples. This trend occurs because the potential for unsaturation and/or oxygenation is higher at higher masses. The greater polarity provided by these features is also required for larger organic molecules to have sufficient water solubility to remain in the dissolved phase. Another striking feature of these plots is their similarity. Indeed, over 90% of formulas identified in DOC at 0.3 m are observed in the deeper pore water. The principal difference between the two bog Kendrick plots (Figures 5a and 5b) is the appearance of more highly unsaturated and/or oxygenated compounds at high nominal masses in the DOC at 2.6 m. Increasing unsaturation may well originate as by-products from the utilization of solid phase peats, consistent with the radio-carbon data.

[30] In Figures 5c and 5d are analogous Kendrick plots of DOC from 0.2 and 2.6 m depths, respectively, at the Minnesota fen site. While the surface fen DOC appears to be quite similar to DOC from the surface bog, there is a marked difference in the DOC at depth in the fen peat. In particular, in the deeper sample there is a considerable decrease in the appearance of unsaturated and/or oxygenated compounds across the entire molecular weight spectrum. These data thus reinforce the hypothesis that the sedge-dominated peat produces a more labile DOC, whereas the *Sphagnum* and woody plant DOC is more refractory. Furthermore, preliminary data on their respective C/N ratios and differences in their molecular weight distributions (Table 2) indicate that woody *Sphagnum* peatlands have elevated C/N ratios and higher concentrations of high molecular weight DOC. The elevated C/N ratios in *Sphagnum* and woody plant bog DOC suggest less reactivity, consistent with ¹⁴C results, differences in Kendrick mass plots and DOC molecular weight distributions.

4.4. Differences in Decomposition: Nature or Nurture?

[31] Our first explanation of the difference between DOC and DIC in *Carex*-dominated sites and *Sphagnum*- and woody plant-dominated sites (Figure 4) is that the quality of the DOC differs between these two classes of sites; *Carex* results in the production of more labile DOC than does

Sphagnum. Thus, we suggest that the DOC from these types of sites is qualitatively different in its nature. A second explanation involves occurrences that follow or “nurture” the DOC postproduction. The enzymatic “latch” model [Freeman *et al.*, 2001] suggests that the decomposition of organic matter in peat can be depressed when the absence of oxygen leads to low activity of the enzyme phenol oxidase. Our results would indicate that the activity of the latch increases along the gradient from forested *Sphagnum*-dominated bogs to sedge-dominated fens.

[32] A third explanation involves the periodic introduction of O₂ into what are termed “mixed redox” zones. These zones may enhance the degradation of certain types of organic matter that would otherwise be refractory under more strict anaerobic conditions (e.g., see discussions by Aller [1998], Canfield [1994], and Burdige [2006]). When such mixed redox zones are observed in marine sediments, pore water DOC concentrations also tend to be relatively low as compared to more permanently anoxic sediments [Burdige, 2002]. Differences due to differences in hydraulic conductivity between the sites could also play a role [Clymo and Bryant, 2008], as the DOC may be transported downward more slowly in bog sites relative to fen sites.

[33] We suggest that a mixed redox zone might be simulated by the rhizosphere of *Carex*-populated peatlands. In sedge-dominated fen systems, oxygen is introduced belowground in the aeration of the rhizosphere as shown for many wetland macrophytes [Armstrong *et al.*, 1994; Boon and Sorrell, 1991] or submerged sea grasses [Borum *et al.*, 2006; Burdige *et al.*, 2008]. Aeration of the rhizosphere provides a mechanism whereby more reactive DOC intermediates can be produced near the surface. This DOC can then be either remineralized to CO₂ and methane near the surface or advected downward for remineralization at depth. In contrast, the absence of such oxygen input to peatland systems are dominated by *Sphagnum* and woody plants and with less *Carex* may lead to a situation in which relatively high levels of refractory DOC accumulate in the pore waters, in a fashion that is analogous to that seen in strict anoxic marine sediments [Burdige, 2002].

[34] Thus, we liken the *Carex*-free sites to the more completely anoxic zones. This may seem contradictory at first, as the *Sphagnum* and woody plant sites have a deeper water table and thus an aerobic layer which supports the growth of trees and woody plants. However, this aerobic layer is above the water table. In this model, we suggest that aeration of the water-saturated peat is the important factor, as occurs in the rhizosphere of *Carex*.

4.5. Molecular Weight

[35] The types of organic matter found in peat (e.g., lignin-rich material, such as that derived from woody vascular plants) and the processes by which organic matter in peat is transformed (i.e., humification [Burdige, 2006]) both suggest that peat organic matter is likely to be similarly sensitive to environmental redox condition. Furthermore, the enzymatic latch model described by Freeman *et al.* [2001] suggests that the decomposition of organic matter in peat can be depressed when the absence of oxygen in peat leads to low activity of the enzyme phenol oxidase. This

may explain why concentrations of high molecular weight (HMW) DOC are more elevated in preliminary data from the *Sphagnum* and woody plant sites than in *Carex*-dominated sites (Figure 5 and Table 2). We suggest that the HMW DOC is material that is preserved because of a lack of phenyl oxidase (or some other O₂-requiring enzyme) to initiate its decomposition. The size reactivity model for DOC [Burdige and Gardner, 1998; Burdige, 2002; Amon and Benner, 1994], derived and tested in marine systems, suggests that HWM compounds should be more labile, yet we observe the opposite in the preliminary data from the *Sphagnum* and woody plant sites (Table 2). However, given the broad compositional differences between “marine” and “terrestrial” organic matter [e.g., Burdige, 2006], this opposite behavior in fresh water peatlands is not necessarily surprising and will require further testing.

4.6. Role of Surface Vegetation

[36] Despite the fact that we argue in sections 4.1–4.5 that DOC from woody *Sphagnum*-dominated sites is more refractory than that in sedge dominated sites, DOC from both types of sites are enriched in radiocarbon (particularly near the peat surface), suggesting relatively modern sources. Furthermore, many of these sites have undergone transitions in their history of accumulation from sedge dominated to *Sphagnum* and woody plant dominated. Yet it seems that the surface vegetation is the factor that dominates the underlying reactivity of the DOC. This work has implications for the export of DOC to rivers and coastal waters. DOC exported from northern peatlands should bear values similar to those observed in our study, modern radiocarbon values [Raymond et al., 2007; Benner et al., 2004; Raymond and Bauer, 2001; Mortazavi and Chanton, 2004], especially relative to the solid phase as observed by Guo and Macdonald [2006]. Our results are also consistent with those of Freeman et al. [2004], who argued that increased primary production associated with elevated carbon dioxide levels results in increased export of modern DOC from peatlands.

5. Conclusion

[37] In conclusion, we found a consistent pattern of radiocarbon distribution replicated across spatial and temporal scales in boreal peatlands of North America. The ¹⁴C content of DOC is relatively modern throughout the peat column, to depths of 3 m. The ¹⁴C content of the products of respiration, CH₄ and DIC, are essentially the same and similar to DOC in sedge-dominated peatlands. In *Sphagnum*- and woody plant-dominated peatlands, however, the respiration products are intermediate between the ¹⁴C content of the solid phase peat and the DOC. Molecular level characterization indicated qualitative differences in the DOC in *Sphagnum*- and woody plant-dominated and sedge-dominated peatlands that were consistent with the variations in DOC reactivity. The cause of that reactivity, and whether it is associated with production or environmental effects, is currently under investigation.

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