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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


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1. Introduction

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; Frolking 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.

Peatlands are generally classified as either bogs or fens on the basis of their topography (i.e., 3-D peatlandform), 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...
acids of methane production, acetate fermentation, and CO2
Shifts with depth in the importance of the two main path-
intriguing in light of other recently reported differences in
the spatial and temporal distribution patterns of 14C in peat
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.
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 path-
ways 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 [Hornbrook 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].

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 differ-
ences in this enrichment in peatlands with surface vegeta-
tion 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 prod-
ucts 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 spec-
trometry (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

Three sites were sampled in the central watershed
(Shift 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. fuscus. A third site, called the lawn site, is located
midslope on the Red Lake II watershed on the broad non-
forested 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
lawns 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.

Samples were collected during 2001 in Turnagain Bog
[Chanton 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 ombro-
trophic 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 oxyccos), 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

<table>
<thead>
<tr>
<th>Site</th>
<th>Sampled</th>
<th>Location</th>
<th>Vegetation</th>
<th>pH</th>
<th>Types of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Lake II bog crest</td>
<td>1997 and 1998</td>
<td>Northern Minnesota, USA</td>
<td>black spruce, ericaceous shrubs, and Sphagnum carpet</td>
<td>3.8</td>
<td>DIC, DOC, CH₄, and peat</td>
</tr>
<tr>
<td>Red Lake II fen</td>
<td>1997 and 1998</td>
<td>Northern Minnesota, USA</td>
<td>Carex lasiocarpa, C. limosa, Rhychospora alba, and R. fusca</td>
<td>5.6</td>
<td>DIC, DOC, CH₄, and peat</td>
</tr>
<tr>
<td>Red Lake II lawn</td>
<td>1998</td>
<td>Northern Minnesota, USA</td>
<td>Carex oligosperma, Ericophorum spissum, small ericaceous shrubs, and Sphagnum carpet</td>
<td>4–4.5</td>
<td>DIC, DOC, CH₄, and peat</td>
</tr>
<tr>
<td>Turnagain Bog</td>
<td>2001</td>
<td>Anchorage, Alaska, USA</td>
<td>Carex rostrata, Sphagnum-Myrica gale</td>
<td>4.7–5.1</td>
<td>DIC, DOC, CH₄, and peat</td>
</tr>
<tr>
<td>Bleanne’s Bog</td>
<td>2003</td>
<td>Northern Alberta, Canada</td>
<td>Sparse black spruce, ericaceous shrubs, and Sphagnum carpet</td>
<td>3.8–4</td>
<td>DIC, DOC, CH₄, and peat</td>
</tr>
<tr>
<td>Susanne’s fen</td>
<td>2003</td>
<td>Northern Alberta, Canada</td>
<td>Carex aquatilis and Carex rostrata</td>
<td>6.4–6.8</td>
<td>DIC, CH₄, and peat</td>
</tr>
</tbody>
</table>

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.

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

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 ∑CO₂) 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 δ¹³C 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).

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 δ¹³C 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.

Pore water for δ¹³C-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°C for 5 h prior to use. After collecting pore water, samples were flash frozen. Minnesota samples were prepared for δ¹³C-DOC and ¹⁴C analysis by UV oxidation following acidification and DIC removal. The ¹³C split was analyzed using the dual-inlet system on the Finnigan MAT IRMS. CO₂ from the oxidation was preserved in a glass break seal and analyzed at NOSAMS.

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 δ¹³C (%o, Vienna Peeedee belemnite). Break seals with CO₂ splits were sent to NOSAMS.

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 Centricron microconcentrators with a nominal molecular weight cutoff of 3 kam. Break seals with CO₂ splits were sent to NOSAMS.

Radio carbon 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 δ¹³C and sent to NOSAMS for radiocarbon analysis.
Radiocarbon results are expressed in $\Delta^{14}C\%$ as defined by Stuiver and Polach [1977]. $\Delta^{14}C$ is defined as the relative difference between an absolute international standard (base year 1950) and sample activity corrected for age and $\delta^{13}C$. The $\Delta^{14}C$ 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 $\Delta^{14}C$ result (http://www.nosams.whoi.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 $\delta^{13}C$ were $-25\%$. Median reproducibility of the AMS measurement for our samples was $\pm 3\%$. Sample reproducibility was $\pm 12\%$.

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 $\mu$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 mg 3 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 $\mu$L) was added as an extra electron donor before introduction into the MS analyzer. Electrospray 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 $\mu$L 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, CH$_4$, and Peat

Radiocarbon profiles of DOC, DIC, CH$_4$, 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).

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, CH$_4$ 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 CH$_4$ production and fluxes associated with depressurization events [Glaser et al., 2004; Rosenberry et al., 2003; Siegel et al., 2000].
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**

[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.

Evidence for variations in methane production pathways based upon the isotopic fractionation factor involved in methane production, $\alpha$, defined below,

$$\alpha = \frac{\delta^{13}C_{\text{DIC}} + 1000}{\delta^{13}C_{\text{CH}_4} + 1000}$$

further contrasts sedge-dominated sites with *Sphagnum*- and woody plant-dominated sites. Changes in $\alpha$ represent changes in the relative importance of methanogenic pathways, where larger $\alpha$ 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, $\alpha$ varied with depth from 1.064 to 1.078. At the Red Lake II fen site $\alpha$ similarly varied with depth, from 1.055 to 1.078, while at the bog site $\alpha$ 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 through 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.

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.
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 \( \text{CH}_2 \) as 14.0000 amu instead of the International Union of Pure and Applied Chemistry (IUPAC) mass of 14.01565 amu.

\[
\text{Kendrick mass} = \frac{\text{IUPAC mass}}{14.0000} \quad (2)
\]

[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)).

\[
\text{KMD} = \left( \frac{\text{Nominal Kendrick mass}}{14.0000} - \text{Kendrick exact mass} \right) \times 1000 \quad (3)
\]

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 the 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
4.4. Differences in Decomposition: Nature or Nurture?

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.

4.5. Molecular Weight

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

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

<table>
<thead>
<tr>
<th>DOC</th>
<th>DON</th>
<th>LMW DOC&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HMW DOC&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mmol)</td>
<td>(mmol)</td>
<td>C/N</td>
</tr>
<tr>
<td>Carex-dominated site</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6 m</td>
<td>3.3</td>
<td>0.08</td>
<td>40</td>
</tr>
<tr>
<td>2.6 m</td>
<td>3.5</td>
<td>0.12</td>
<td>30</td>
</tr>
<tr>
<td>Sphagnum- and woody plant–dominated site</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6 m</td>
<td>6.3</td>
<td>0.14</td>
<td>46</td>
</tr>
<tr>
<td>2.8 m</td>
<td>7.7</td>
<td>0.09</td>
<td>89</td>
</tr>
</tbody>
</table>

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

[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 the 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.

[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 is 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.

4.4. Differences in Decomposition: Nature or Nurture?

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.

4.5. Molecular Weight

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 phenol 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 13C 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 13C 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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