

2013

# Surface Production Fuels Deep Heterotrophic Respiration in Northern Peatlands

J. Elizabeth Corbett

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

Malak M. Tfaily

Angela R. Dial

William T. Cooper

*See next page for additional authors*

Follow this and additional works at: [https://digitalcommons.odu.edu/oeas\\_fac\\_pubs](https://digitalcommons.odu.edu/oeas_fac_pubs)

 Part of the [Biogeochemistry Commons](#), [Hydrology Commons](#), and the [Oceanography and Atmospheric Sciences and Meteorology Commons](#)

## Repository Citation

Corbett, J. Elizabeth; Burdige, David J.; Tfaily, Malak M.; Dial, Angela R.; Cooper, William T.; Glaser, Paul H.; and Chanton, Jeffrey P., "Surface Production Fuels Deep Heterotrophic Respiration in Northern Peatlands" (2013). *OEAS Faculty Publications*. 77.  
[https://digitalcommons.odu.edu/oeas\\_fac\\_pubs/77](https://digitalcommons.odu.edu/oeas_fac_pubs/77)

## Original Publication Citation

Corbett, J.E., Burdige, D.J., Tfaily, M.M., Dial, A.R., Cooper, W.T., Glaser, P.H., & Chanton, J.P. (2013). Surface production fuels deep heterotrophic respiration in northern peatlands. *Global Biogeochemical Cycles*, 27(4), 1163-1174. doi: 10.1002/2013gb004677

---

**Authors**

J. Elizabeth Corbett, David J. Burdige, Malak M. Tfaily, Angela R. Dial, William T. Cooper, Paul H. Glaser, and Jeffrey P. Chanton

## Surface production fuels deep heterotrophic respiration in northern peatlands

J. Elizabeth Corbett,<sup>1</sup> David J. Burdige,<sup>2</sup> Malak M. Tfaily,<sup>1</sup> Angela R. Dial,<sup>1</sup> William T. Cooper,<sup>3</sup> Paul H. Glaser,<sup>4</sup> and Jeffrey P. Chanton<sup>1</sup>

Received 20 June 2013; revised 22 October 2013; accepted 26 October 2013; published 3 December 2013.

[1] Multiple analyses of dissolved organic carbon (DOC) from pore waters were conducted to define the processes that govern carbon balance in peatlands: (1) source, reactivity, and transport of DOC with respect to vegetation, peat, and age of carbon substrate, (2) reactivity of DOC with respect to molecular size, and (3) lability to photooxidation of surficial DOC. We found that surface organic production fuels heterotrophic respiration at depth in advection-dominated peatlands, especially in fens. Fen DOC was  $\Delta^{14}\text{C}$  enriched relative to the surrounding fen peat, and fen respiration products were similar to this enriched DOC indicating that DOC was the main microbial substrate. Bog DOC was more variable showing either enrichment in  $\Delta^{14}\text{C}$  at depth or  $\Delta^{14}\text{C}$  values that follow peat values. This variability in bogs is probably controlled by the relative importance of vertical transport of labile carbon substrates within the peat profile versus DOC production from bog peat. These results extended our set of observations to 10 years at one bog-fen pair and add two additional bog-fen pairs to our series of observations. Anaerobic incubations of peat, rinsed free of residual DOC, produced DOC and respiration products that were strikingly similar to the peat values in a bog and two fens. This result demonstrated conclusively that downward advection is the process responsible for the presence of modern DOC found at depth in the peat column. Fen DOC has lower C/N values and up to twice as much LMW (<1 kDa) DOC as bogs due to differences in organic inputs and greater microbial processing. Fluorescence irradiation experiments showed that fen DOC is more photolabile than bog DOC.

**Citation:** Corbett, J. E., D. J. Burdige, M. M. Tfaily, A. R. Dial, W. T. Cooper, P. H. Glaser, and J. P. Chanton (2013), Surface production fuels deep heterotrophic respiration in northern peatlands, *Global Biogeochem. Cycles*, 27, 1163–1174, doi:10.1002/2013GB004677.

### 1. Introduction

[2] Global peatlands hold approximately one third of total soil carbon [Gorham, 1991; Post *et al.*, 1982, 1985] with 450–547 GtC stored in northern peatlands [Gorham, 1991; Yu *et al.*, 2010]. These carbon sinks exist because anaerobic conditions cause organic matter decomposition to be slower than production [Moore *et al.*, 1998]. Since the anaerobic conditions rely on water saturation, climatic changes such as precipitation patterns may affect the carbon storage potential

of these systems. Drought-like conditions may increase aerobic respiration and decrease dissolved organic carbon (DOC) export to adjacent ecosystems [Fenner and Freeman, 2011; Fenner *et al.*, 2001; Freeman *et al.*, 2001; Moore *et al.*, 1998], while higher rates of soil respiration could be caused by rising temperatures. Changing climate apparently will favor vascular plants such as sedges and deciduous shrubs, with a concomitant decline in bryophytes (*Sphagnum* spp.) and lichens [Bragazza *et al.*, 2012; Post *et al.*, 2009; Walker *et al.*, 2006], which may affect DOC quality and greenhouse gas emissions [Corbett *et al.*, 2012]. The capability to predict the future response of these complex carbon sinks to a changing climate is challenging but essential [Gorham, 1991; Limpens *et al.*, 2008; Moore *et al.*, 1998]. In this paper, we compare DOC characteristics and quality in the two principal peatland types, fens and bogs. This analysis will allow for a better understanding of how climate change will affect the remineralization of carbon in these different environments.

[3] Raised bogs and patterned fens comprise the main cover types of the Glacial Lake Agassiz Peatland (GLAP) in terms of aerial abundance [Glaser *et al.*, 1997]. The nearly flat landscape, which inhibits drainage, accounts for continual peat development [Glaser, 1987]. Also, the sparse network of rivers amplifies ground water recharge and helps maintain high water tables by reducing drainage and runoff

Additional supporting information may be found in the online version of this article.

<sup>1</sup>Earth, Ocean, and Atmospheric Science, Florida State University, Tallahassee, Florida, USA.

<sup>2</sup>Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University, Norfolk, Virginia, USA.

<sup>3</sup>Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, USA.

<sup>4</sup>Department of Geology and Geophysics, Pillsbury Hall University of Minnesota Minneapolis, Minneapolis, Minnesota, USA.

Corresponding author: J. Elizabeth Corbett, Earth, Ocean, and Atmospheric Science, Florida State University, 117 N Woodward Ave Tallahassee, FL 32306, USA. (jcorbet@gmail.com)

©2013. American Geophysical Union. All Rights Reserved.  
0886-6236/13/10.1002/2013GB004677

**Table 1.** Sampling Sites With Location, Type of Sample Taken, and Analysis Done

Site	Longitude	Latitude	Type of Sample	Analysis
RLII Bog	48° 15' 17" N	94° 41' 51.34" W	peat, pore water	incubations, radiocarbon, size fractionation, C/N, fluorescence
RLII Fen	48° 17' 23" N	94° 42' 30" W	peat, pore water	incubations, radiocarbon, size fractionation, C/N, fluorescence
RLIV Bog	48° 19' 44.39" N	94° 24' 24.08" W	pore water	radiocarbon
RLIV Fen	48° 19' 22.63" N	94° 22' 39.37" W	peat, pore water	incubations, radiocarbon
SR Bog	48° 09' 38.02" N	94° 13' 00.50" W	pore water	radiocarbon
SR Fen	48° 09' 23.10" N	94° 14' 08.71" W	pore water	radiocarbon
Ridge Bog	48° 03' 45.49" N	94° 08' 38.78" W	peat	radiocarbon
Crest Bog (Fairland Bog)	48° 24' 09.47" N	94° 03' 04.45" W	peat	radiocarbon

[Glaser *et al.*, 2006]. Bog pore water typically has pH values between 3.8 and 4.1,  $\text{Ca}^{2+}$  concentrations between 0.5 and 2.1  $\text{mg L}^{-1}$ , and conductivity between 12 and 50  $\text{uS cm}^{-1}$ . These conditions are mainly due to the raised topography and isolation from groundwater that causes bogs to be ombrotrophic environments. Fen pore water, in contrast, has pH values between 5.2 and 7.0,  $\text{Ca}^{2+}$  concentrations between 3.0 and 19.6  $\text{mg L}^{-1}$ , and conductivity values 23–128  $\text{uS cm}^{-1}$ , which characterize fens as minerotrophic environments. At the GLAP, bog vegetation consists of *Sphagnum* moss for the most part while fen vegetation consists mostly of vascular *Carex* plants in addition to site-specific fen indicator species [Glaser *et al.*, 1981].

[4] The GLAP is underlain by glacial till with high permeability and contains groundwater mounds located under raised bogs [Siegel, 1983; Glaser *et al.*, 1997; Reeve *et al.*, 2000]. Fens, located in areas of low topography, have been generally been viewed as zones of groundwater flow, whereas bogs form local recharge cells that may develop over regional discharge zones in the dry climate of the GLAP [Siegel and Glaser, 1987; Siegel *et al.*, 1995; Glaser *et al.*, 1997]. Evidence for downward groundwater flow has been observed in tritium profiles where bomb-era tritium has been found deep in the bog peat profile [Gorham and Hofstetter, 1971; Siegel *et al.*, 2001]. Modern DOC has been found at depth in the peat pore water as well, and it has been hypothesized that this modern DOC is derived from downward advection of surficial substrates from the surface, which are more labile than substrates in the deeper peat [Chasar *et al.*, 2000; Chanton *et al.*, 2008].

[5] DOC is produced as organic matter decays but may also be released from plant roots. In fens, these roots may be some 0.5 to 1 m deep [e.g., Popp *et al.*, 2000]. The difference in vegetation patterns and pore water chemistry found in bogs and fens suggests that the DOC pools in these ecosystems may be distinct, in part because of these different sources. D'Andrilli *et al.* [2010] and Tfaily *et al.* [2013] observed molecular composition changes of fen DOC with depth, but few changes of bog DOC with depth. These trends are broadly consistent with the hypothesis that fen DOC is more reactive and labile than bog DOC, although these differences in reactivity may either be due to the nature of the organic matter itself or to the differing conditions in the two environments [nature versus nurture, see Chanton *et al.*, 2008; D'Andrilli *et al.*, 2010].

[6] Differences in the organic matter lability between bogs and fens may be indicated from C/N ratios of dissolved organic matter (DOC/DON). Lower C/N ratios are indicative of more labile organic matter [Finzi *et al.*, 1998; Melillo *et al.*, 1982]. The size of the DOC compound may also be

related to its reactivity. Low molecular weight (LMW) DOC is a product of the processing of high molecular weight (HMW) DOC [Burdige and Gardner, 1998; McArthur and Richardson, 2002], and is generally thought to be of lower reactivity [also see Amon and Benner, 1996].

[7] The goals of this work are to: (1) examine the consistency of radiocarbon profiles in a bog and fen over a decadal time period, (2) extend previous observations of differences in the radiocarbon distributions between DOC, DIC, and solid-phase peat between bogs and fens to two additional bog-fen pairs, (3) evaluate the relative proportions of LMW- and HMW-DOC in the bogs and fens and examine how these characteristics may be indicative of DOC reactivity and processing, (4) analyze differences in radiocarbon and DOC/DON values between LMW-DOC and HMW-DOC, (5) examine the relative lability of bog/fen DOC by assessing its sensitivity to sunlight, and (6) test the hypothesis [Chasar *et al.*, 2000; Chanton *et al.*, 2008] that modern DOC is advected downward from surface peat, and thus respiration in deep peat is also influenced by organic matter production at the surface.

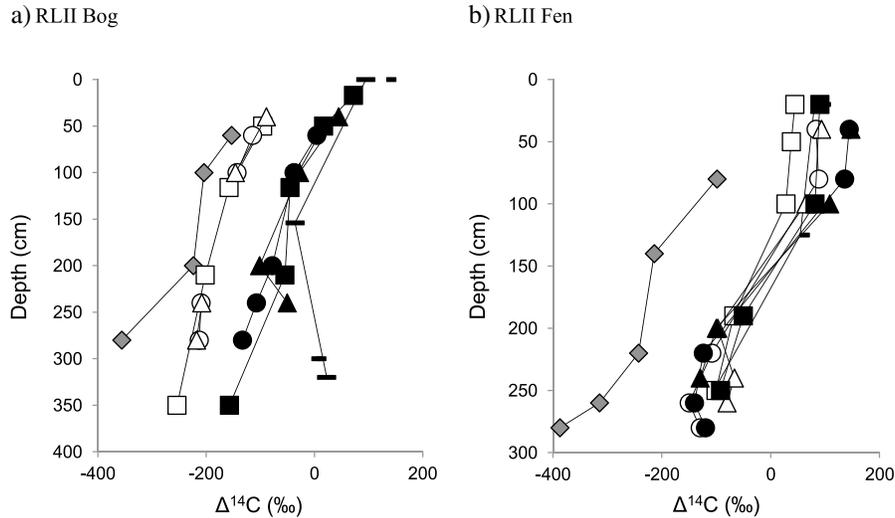
## 2. Methods

### 2.1. Sites and Field Measurements

[8] Pore water and peat samples were collected from various sites in the Glacial Lake Agassiz Peatlands (GLAP) in northern Minnesota [Glaser *et al.*, 1981] (Table 1). 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. These samples 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 profile.

### 2.2. Radiocarbon

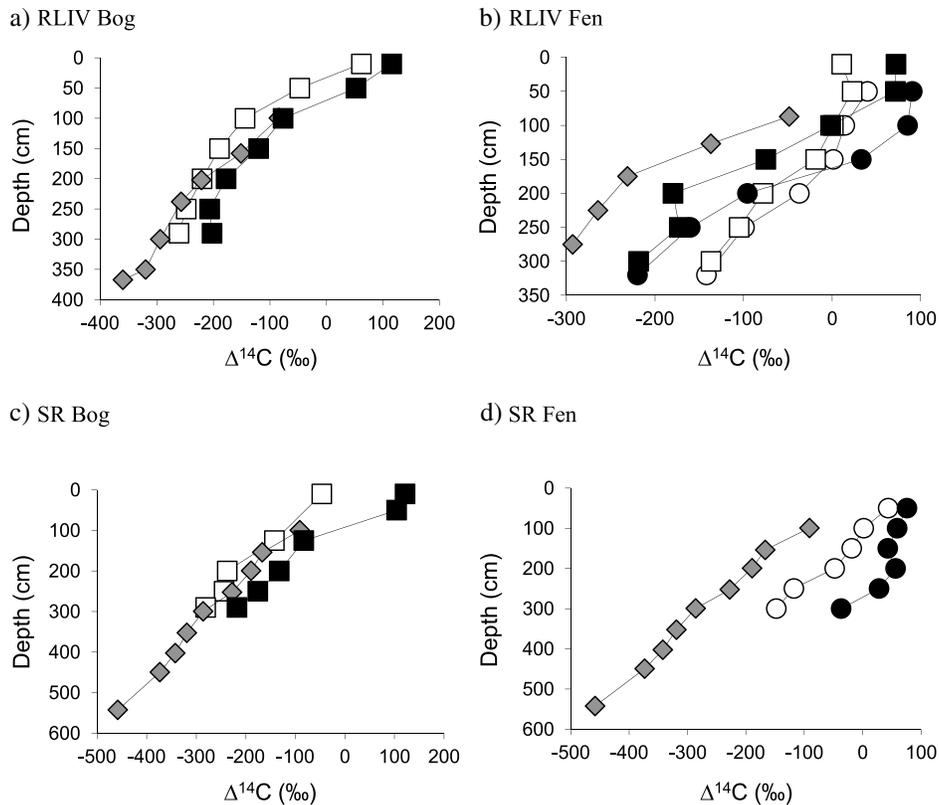
[9] The preparation of  $\Delta^{14}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -peat samples was done at the National High Magnetic Laboratory at Florida State University. DOC was freeze dried in combusted Pyrex glass tubes. Oxidizing agents, cupric oxide, copper shots, and silver, were added to the tubes. These tubes were evacuated and flame sealed on a vacuum line. The sealed tubes were then combusted at 580°C for 18 h to convert the organic carbon to  $\text{CO}_2$  gas [Peterson *et al.*, 1994]. Following combustion, the produced  $\text{CO}_2$  was then taken back to the vacuum line, and the  $\text{CO}_2$  was cryogenically purified. The purified  $\text{CO}_2$  gas was split to produce samples for  $\delta^{13}\text{C}$ -DOC and  $\Delta^{14}\text{C}$ -DOC analysis. The preparation of  $\Delta^{14}\text{C}$ -DIC and  $\Delta^{14}\text{C}$ - $\text{CH}_4$  was done at Florida State University.



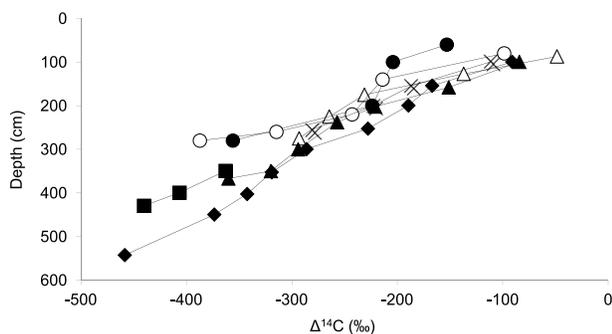
**Figure 1.** RLII (a) Bog and (b) Fen  $\Delta^{14}\text{C}$  distribution pattern of DOC, respiration products (DIC), and solid phase peat has remained relatively constant over a 10 year period. In both graphs, black symbols represent DOC, open symbols DIC, and grey symbols peat. In both panels, peat from 1997/1998 (grey diamonds), DOC from 1997 (black circles), DOC from 1998 (black triangles), DOC from 2007 (black squares), DOC from 2008 (small black dashes), DOC from 2009 (large black circles), DIC from 1997 (white circles), DIC from 1998 (white triangles), DIC from 2007 (white squares).

The samples were cryogenically purified on a vacuum line. The break seal tubes for  $\Delta^{14}\text{C}$  analysis were sent to National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) for analysis. The tubes for  $\delta^{13}\text{C}$ -DOC and

$\delta^{13}\text{C}$ -peat were analyzed with a dual inlet system isotope ratio mass spectrometer (Thermo-Finnegan MAT Delta XP GC-IRMS) at the National High Magnetic Laboratory at FSU. Samples for  $\delta^{13}\text{C}$ -DIC and  $\delta^{13}\text{C}$ - $\text{CH}_4$  were analyzed by direct



**Figure 2.** Radiocarbon data from two additional bog fen pairs, RLIV and SR. In both graphs, black symbols represent DOC, open symbols represents DIC, and grey symbols represent peat. In all panels, boxes represent samples taken in 2009 and circles represent samples taken in 2008.



**Figure 3.**  $\Delta^{14}\text{C}$  values of solid phase peat samples indicate similar rates of accumulation within bog fen pairs and across the peatland. Bog peats are closed symbols: SR Bog (black diamond), Ridge Bog (black squares), RLIV Bog (black triangles), Crest Bog (black crosses), RLII Bog (black circles). Fen peats are represented by open symbols: RLII Fen (white circles) and RLIV Fen (white triangles).

injection on a GC combustion-interfaced Finnegan MAT Delta V isotope ratio mass spectrometer (GC IRMS) [Corbett *et al.*, 2012]. All concentration, radiocarbon, and stable isotope data have been included as supporting information.

### 2.3. Incubations

[10] Duplicate incubations were set up in 125 mL serum vials with Bellco (blue) butyl rubber septa. The samples were from Red Lake (RL) II Bog, RLII Fen, and RLIV Fen. Approximately, 20–30 mL of wet peat from selected 10 cm depth intervals spanning each peat column [Corbett, 2012] was placed in combusted 60 mL glass vials. The peat within each vial was rinsed three times with 20 mL of degassed milli Q water to provide a clean, clear rinse and to remove any residual DOC in the peat. Thus, any DOC and DIC produced in these vials were derived solely from the respiration of the peat itself. The vials were sealed and flushed with  $\text{N}_2$ . To ensure anaerobic conditions, the vials were stored for two weeks, then flushed a second time with  $\text{N}_2$ , and finally incubated at 25°C for 250–300 days. We corrected for any dissolved  $\text{CO}_2$  using the extraction efficiency determined by measuring known concentrations of dissolved sodium bicarbonate in vials of different size and water content. Methane extraction efficiency was 95% as determined from repeated extractions.

### 2.4. Size Fractionation

[11] DOC pore water was filtered using Amicon Stirred Ultrafiltration Cells with 1.0, 3.0, 10, and 100 kDa 62 mm Omega ultrafiltration membrane disc filters.  $\text{N}_2$  gas was used to pressurize the cells. Filters were stored in milli Q water (ultra pure water of resistivity of 18.2  $\text{M}\Omega \cdot \text{cm}$  at 25°C). Milli Q water was first passed through the filters to rinse them before samples were run. The flow rate through the cells was controlled by holding the pressure in the cells to between 1.0 and 10 psi, which also prevented membrane rupture. Standards made with polystyrene sulfonate sodium (PSS) salt with molecular weights of 1.8, 5.18, 18, and 200 kDa with an average concentration of 2300  $\mu\text{M}$  were run through the filters to make sure the filtration system retained the appropriate DOC sizes. The average milli Q water filtrate contained  $55 \pm 17$   $\mu\text{M}$  DOC and the average PSS filtrate contained  $280 \pm 240$   $\mu\text{M}$  DOC. Filtered water was collected

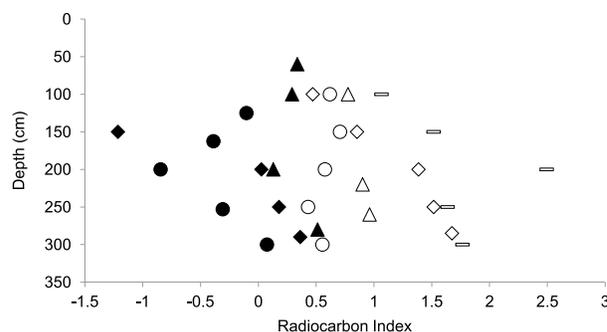
in acidified and combusted DOC vials for DOC and radiocarbon analysis. The percents of DOC in each size fraction ( $\geq 100$  kDa, 10–100 kDa, 3–10 kDa, 1–3 kDa, and  $\leq 1$  kDa) were determined by subtracting the filtrate concentration of the smaller filter size from the larger filter size and dividing the result by the total DOC concentration (mM) and multiplying by 100. For example, 10–100 kDa% =  $(5691 - 3484) / 6372 * 100$ . DOC%  $\leq 1$  kDa was determined by dividing the 1 kDa filtrate concentration by the total concentration and multiplying the result by 100.

### 2.5. DOC/DON Ratios

[12] Pore water was filtered with 47 mm diameter Whatman Grade GF/F Glass Microfiber Filters with 0.70  $\mu\text{m}$  particle retention, and Whatman Grade GF/D glass microfiber filters with 2.0  $\mu\text{m}$  particle retention. Dissolved organic carbon and total nitrogen concentrations were quantified using a Shimadzu TOC 5000 (total organic carbon) analyzer equipped with a TNM-1 (total nitrogen measuring) unit at FSU. The coefficient of variation for multiple analyses of DOC and TN was less than 5.0%. DON was calculated by subtracting  $\text{NO}_x$  and ammonium concentrations from TN concentrations. Ammonium concentrations in pore water samples were determined by colorimetric analysis (Bower and Holm-Hansen, 1980; NERR SWMP protocols; TMG Sept06).  $\text{NO}_x$  (nitrates and nitrites) were determined with a Thermo Model 42  $\text{NO}_x$  chemiluminescence analyzer. Peak areas were quantified with a Hewlett-Packard chromatographic integrator.  $\text{NO}_x$  concentrations were found to be negligible with respect to total nitrogen and ammonium concentrations with average nitrate and nitrite concentrations of  $0.46 \pm 0.43$   $\mu\text{M}$  [Corbett, 2012].

### 2.6. DOC Photodegradation

[13] To examine the lability of surface pore waters, 100 mL samples of pore water from RLII Bog from 0.15 m and RLII Fen from 0.2 m were irradiated over a 4 day period in Teflon bottles by exposure to natural sunlight. These vessels transmit 46% of UVB and 56% of UVA [Molot and Dillon, 1997]. A 4 day period was used because similar irradiation experiments had been done that showed a significant decrease in fluorescence intensity after 4 days. Aliquots (1 mL) were



**Figure 4.** Radiocarbon index as a measure of DOC reactivity across the GLAP peatland ( $(\Delta^{14}\text{C-DIC} - \Delta^{14}\text{C-peat}) / (\Delta^{14}\text{C-DOC} - \Delta^{14}\text{C-peat})$ ). Bogs are represented by closed symbols: RLII Bog 2007 (black triangles), RLIV Bog 2009 (black diamonds), and SR Bog 2009 (black circles). Fens are represented by open symbols: RLII Fen 2007 (white triangles), SR Fen 2008 (white circles), RLIV Fen 2008 (white diamonds), and RLIV Fen 2009 (white dashes).

**Table 2.** Concentration Data (uM) of Filtrate From Bulk Sample That Had Been Passed Through Filters With Various Pore Sizes

Site	Bulk Sample	100 kDa	10 kDa	3 kDa	1 kDa
RLII Bog 0 cm	6372 ± 28	5691 ± 14	3484 ± 652	2626 ± 574	1978 ± 17
RLII Bog 300 cm	5652 ± 35	5282 ± 7.4	3314 ± 318	2911 ± 894	2100 ± 15
RLII Fen 20 cm	3038 ± 27	2994 ± 91	2468 ± 275	2136 ± 635	1839 ± 104
RLII Fen 250 cm	3997 ± 14	3981 ± 167	3414 ± 370	3081 ± 1119	2402 ± 118

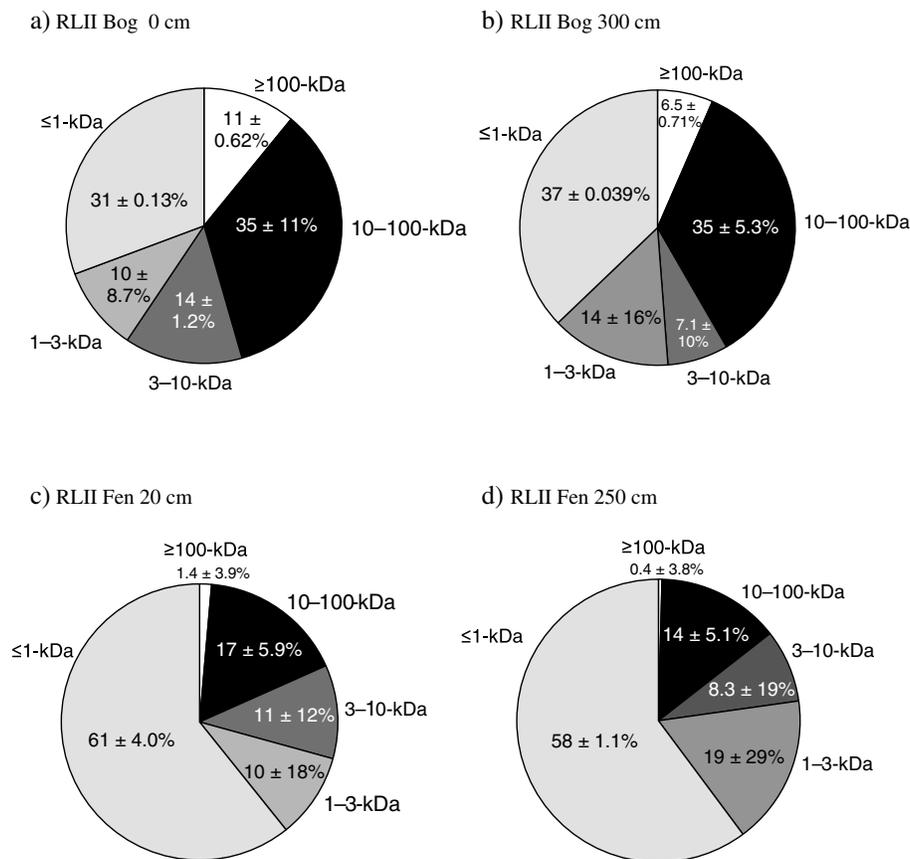
taken out daily to measure changes in DOC fluorescence. To minimize concentration effects on fluorescence degradation in this experiment, the bog sample was diluted to the same DOC concentration as the fen sample at the start of the experiment since a positive relationship has been established between DOC concentration and fluorescence [Hudson *et al.*, 2007]. Samples were analyzed for fluorescence using a Jobin Yvon SPEX Fluoromax-4 spectrophotometer with a Xenon Lamp light source [Tfaily *et al.*, 2013]. The areas were used to compare fluorescence so that units are reported in QSE · nm<sup>2</sup>.

### 3. Results

#### 3.1. Radiocarbon Depth Profiles

[14] Radiocarbon values of peat, DIC, and DOC in RLII Bog and Fen were compared over a 10 year period (Figure 1). We do not report additional  $\Delta^{14}\text{C}$ -CH<sub>4</sub> samples

as Chanton *et al.* [2008] found that the radiocarbon values of the respiration products CH<sub>4</sub> and CO<sub>2</sub> were similar at all depths. A plot of  $\Delta^{14}\text{C}$ -CH<sub>4</sub> vs.  $\Delta^{14}\text{C}$ -CO<sub>2</sub> had a slope of 0.95 and 0.97 for fens and bogs, respectively. A plot of  $\Delta^{14}\text{C}$ -CH<sub>4</sub> vs.  $\Delta^{14}\text{C}$ -CO<sub>2</sub> that includes data from other peatlands [Charman *et al.*, 1994, 1999; Aravena *et al.*, 1993; Clymo and Bryant, 2008] had a slope of 0.9 with an intercept of -21.0. These results suggest that only one of these gases needs to be analyzed for radiocarbon in GLAP peats to use radiocarbon to examine carbon cycling. Thus, the  $\Delta^{14}\text{C}$  values of DIC also represent  $\Delta^{14}\text{C}$  values of methane. A selected subset of samples was run and this trend was verified [Corbett, 2012]. At the RLII sites, DIC and DOC samples had similar radiocarbon values over the 10 year time span, and consistent yearly differences were not observed. In both the bog and fen, peat samples were more  $\Delta^{14}\text{C}$  depleted than the DIC and DOC samples. DIC radiocarbon values in RLII Bog were



**Figure 5.** Size distributions of DOC in the RLII Bog and Fen indicate smaller size in the fen pore water. DOC concentrations of (a) RLII Bog pore water collected at 0 cm, (b) RLII Bog pore water collected at 300 cm, (c) RLII Fen pore water collected at 20 cm, and (d) RLII Fen pore water collected at 250 cm that is either >100 kDa (white), or has been filtered through a 100 kDa filter (black), a 10 kDa filter (dark grey), a 3 kDa filter (medium grey), or a 1 kDa filter (light grey).

**Table 3.** Organic Matter Characterization of Bog and Fen Samples

Site	Peat OC:ON	Bulk Sample DOC:DON	DOC:DON of <1 kDa
Bog	53 ± 17	---	---
0 cm	---	127 ± 0.99	382
300 cm	---	143 ± 3.8	---
Fen	19 ± 2.0	---	---
20 cm	---	87 ± 13	110
250 cm	---	75 ± 13	456

in between the peat and DOC radiocarbon values (Figure 1a). The bog DOC was consistently enriched in radiocarbon as compared to the peat or DIC. This same pattern persisted at this site over the past decade and was also characteristic of two other bogs in Alberta, Canada and in Alaska [Chanton *et al.*, 2008]. The radiocarbon analysis of RLII Fen peat, DIC, and DOC samples showed that peat radiocarbon was the most depleted while DIC radiocarbon values were similar to those of the DOC (Figure 1b). Correcting the DIC values for ground water derived DIC did not affect these distributions [Corbett, 2012; Corbett *et al.*, 2012; Chasar *et al.*, 2000].

[15] The DOC radiocarbon values for RLIV Bog were similar to but slightly  $\Delta^{14}\text{C}$  enriched relative to the peat. DIC radiocarbon values were similar to both of these sources (Figure 2a). In the RLIV Fen, DOC was more enriched in radiocarbon than the corresponding peat and more enriched than bog DOC (Figure 2b). Radiocarbon values of DIC were

more depleted than those of DOC at more shallow depths in the RLIV Fen and then were more enriched than DOC values at depths at below 200 cm for 2008 and 100 cm for 2009.

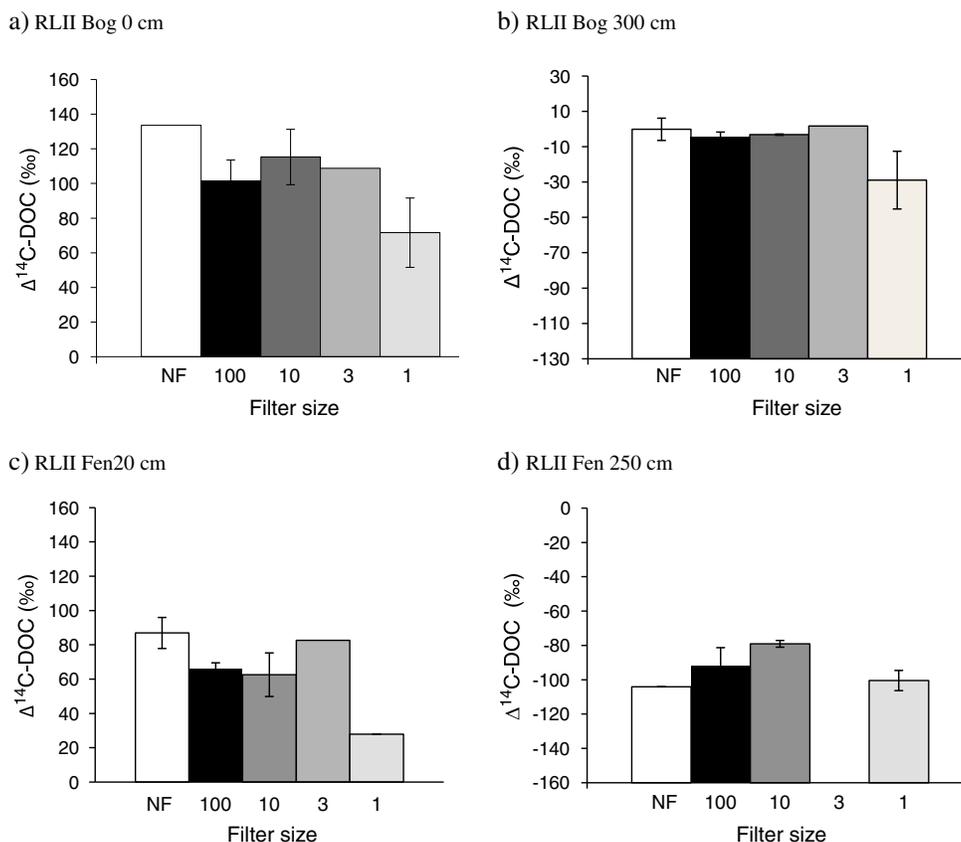
[16] At the Sturgeon River (SR) bog, DIC radiocarbon values overlapped with peat values (Figure 2c). SR Bog DOC radiocarbon was slightly more enriched than DIC or peat values. Nearby SR Bog peat radiocarbon values were used in Figure 2d to compare with DOC and DIC SR Fen radiocarbon profiles since radiocarbon data for the SR Fen peat were not available. There was little difference between bog and fen peat  $\Delta^{14}\text{C}$  depth profiles across the GLAP especially between bog/fen pairs (Figure 3), suggesting that this substitution was valid. These data also indicate that peat is accumulating at about the same rate in bogs and fens at the GLAP. Both DIC and DOC  $\Delta^{14}\text{C}$  in SR fen peats were enriched relative to the SR bog peat. SR Bog DIC radiocarbon was closer to peat than SR Fen DIC, whereas DOC from the SR Fen was more enriched than SR Bog DOC.

### 3.2. Radiocarbon Index

[17] A radiocarbon index (RI) was calculated with the equation:

$$\text{RI} = (\Delta^{14}\text{C} - \text{DIC} - \Delta^{14}\text{C} - \text{peat}) / (\Delta^{14}\text{C} - \text{DOC} - \Delta^{14}\text{C} - \text{peat}) \quad (1)$$

to quantitatively express the difference in radiocarbon values between DIC ( $\Delta^{14}\text{C}$ -DIC) and peat ( $\Delta^{14}\text{C}$ -peat) and DOC



**Figure 6.**  $\Delta^{14}\text{C}$ -DOC values of (a) RLII Bog pore water collected at 0 cm, (b) RLII Bog pore water collected at 300 cm, (c) RLII Fen pore water collected at 20 cm, and (d) RLII Fen pore water collected at 250 cm that is either bulk sample (white), or has been filtered through a 100 kDa filter (black), a 10 kDa filter (dark grey), a 3 kDa filter (medium grey) (lost while processing), or a 1 kDa filter (light grey).

**Table 4.** Results of a 4 Day Irradiation Experiment That Shows the Degradation ( $\text{QSE} \cdot \text{nm}^2 \cdot \text{day}^{-1}$ ) of DOC Fluorescence Due to Exposure to Natural Sunlight for Bog and Fen DOC Surface Samples at 3 mM

Site	Peak A	Peak C
RLII Bog 15 cm	$-1.2 \times 10^4$	$-1.2 \times 10^4$
RLII Fen 20 cm	$-1.3 \times 10^5$	$-3.6 \times 10^4$

( $\Delta^{14}\text{C}$ -DOC) and peat in each depth profile (Figure 4). In fens, the difference between the DIC radiocarbon content relative to the peat ( $\Delta^{14}\text{C}$ -DIC- $\Delta^{14}\text{C}$ -peat;  $150.9 \pm 45.8\%$ ) and the DOC radiocarbon content relative to the peat ( $\Delta^{14}\text{C}$ -DOC- $\Delta^{14}\text{C}$ -peat;  $173.6 \pm 76.4\%$ ) was lower than in bogs ( $4.7 \pm 51\%$  and  $86.9 \pm 72\%$ , respectively), which resulted in RI values closer to 1 while bogs had RI values below 1 and in some cases below zero (in cases when the DIC was slightly more depleted than the peat). Fen RI values ranged from 0.43 to 1.8 with a mean of  $1.1 \pm 0.57$ , and bog RI values ranged from  $-1.2$  to 0.51 with a mean of essentially 0 ( $-0.070 \pm 0.50$ ). Values close to 1 or higher indicate instances where DIC and DOC values are similar and/or much more enriched as compared to peat, as in a majority of the fen results. Low and negative values indicated instances where DIC values lie in between peat and DOC or where DIC and DOC radiocarbon values are similar to peat values, as in a majority of the bog results. The differences between fen and bog radiocarbon index values were found to be statistically significant ( $p < 0.05$ ). These results qualitatively express the observed differences in peat, DIC, and DOC radiocarbon values observed in Figures 1 and 2, where DIC radiocarbon values are closer to DOC values in the fen while DIC radiocarbon values in the corresponding bog are closer to peat values.

### 3.3. Size Fractionation

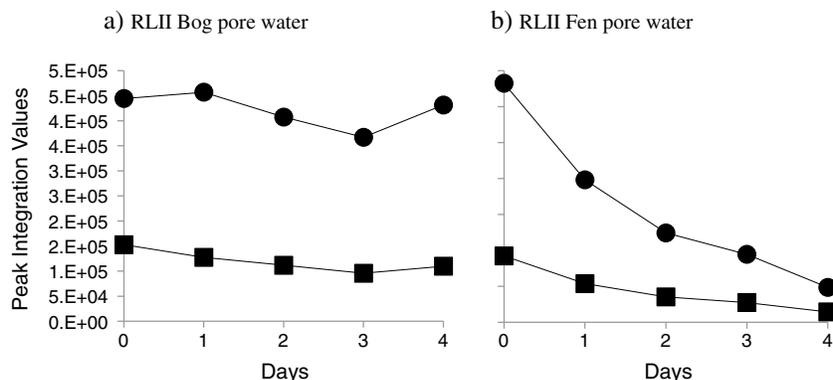
[18] Bog DOC concentrations and size distributions were similar for 0 and 300 cm, overall. Pore water from 0 cm had a slightly higher DOC concentration for NF (nonfiltered) and 100 kDa but was similar in DOC concentration to 300 cm for 10, 3, and 1 kDa size ranges. Fen DOC concentrations were slightly lower in the 20 cm sample than the

250 cm sample, but size distributions were similar between the two depths (Table 2 and Figure 5). The fen samples had a higher fraction of LMW-DOC (DOC  $< 1$  kDa) as compared to the bog samples. For RLII Bog samples, 31% and 37% of the total DOC were LMW-DOC at 0 cm and 300 cm, respectively (Figures 5a and 5b). For RLII Fen samples, 61% and 58% of the total DOC were LMW-DOC at 20 cm and 250 cm, respectively (Figures 5c and 5d). In a similar fashion, the relative concentration of HMW-DOC (defined here as the  $> 10$  kDa fraction) is more than a factor of two larger in the bog (46% and 42% at 0 cm and 300 cm) than in the fen (18% and 14% at 20 cm and 250 cm, respectively).

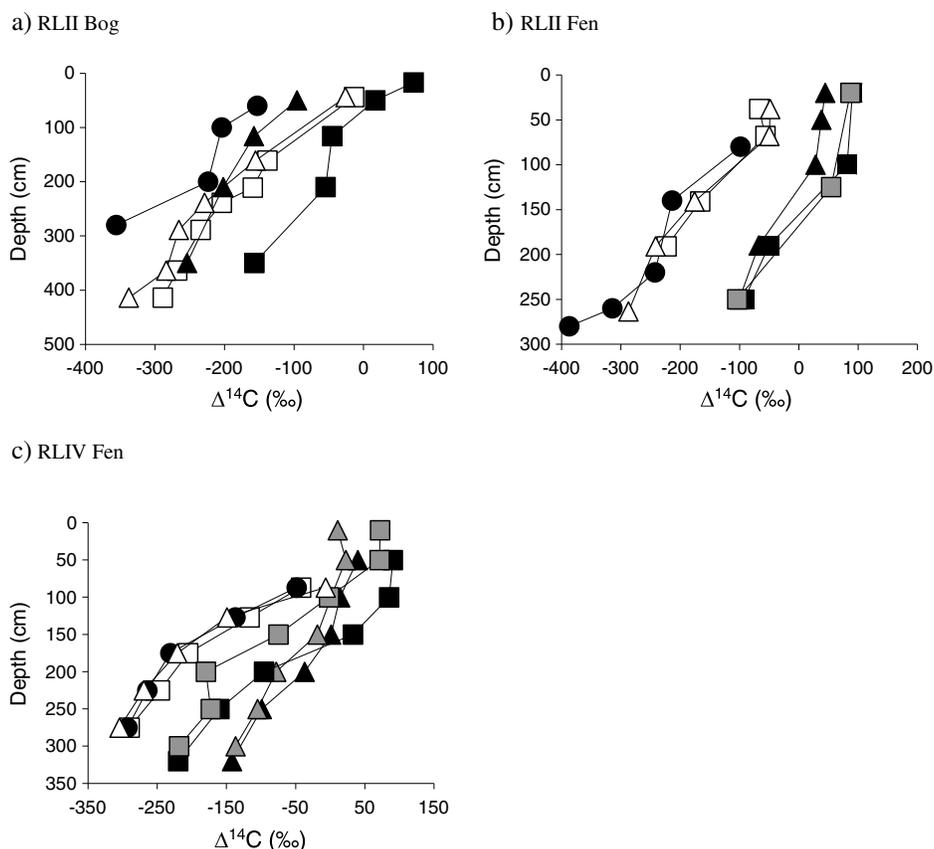
[19] The DOC/DON ratio of bog and fen samples that had been passed through the 1 kDa filters were compared with those of the bulk samples as shown in Table 3. The RLII Bog sample from 0 cm had a higher DOC/DON ratio for the  $\leq 1$  kDa sample as compared to the bulk, nonfiltered sample. The DOC/DON ratio was slightly higher for the bulk RLII Bog sample from 300 cm than the ratio of the bulk surficial sample. The RLII Fen sample from 20 cm and 250 cm had higher ratios for the  $\leq 1$  kDa samples as compared to the bulk samples. Surficial DOC samples were radiocarbon enriched relative to deep samples in both fen and bog (Figures 6a–6d). The fen sample from 20 cm showed a depletion in  $\Delta^{14}\text{C}$  between the bulk sample and the  $\leq 1$  kDa, but in the  $\Delta^{14}\text{C}$  was similar in the bulk sample and the  $\leq 1$  kDa was similar in the fen sample from 250 cm. The bog showed a depletion of  $\Delta^{14}\text{C}$  between the bulk sample and the  $\leq 1$  kDa size fractions at 0 and 300 cm depths.

### 3.4. Irradiation

[20] Fluorescence intensities are reported for spectral features (peaks) previously defined by Coble [1996] and were quantified by integrating over the specific excitation and emission wavelengths characteristic of these peaks. Specifically, peaks A and C represent humic-like terrestrial material with the fluorophores responsible for peak A stimulated by UV light and those responsible for peak C stimulated by visible light. DOC degradation was 3.1 and 12 times greater for fen DOC than bog DOC based on the decrease with time in the fluorescence of peaks C and A, respectively (Table 4, Figures 7a and 7b).



**Figure 7.** Fen DOC was more photo-labile than bog DOC. Peak integration values ( $\text{QSE} \cdot \text{nm}^2$ ) after a period of irradiation under natural sunlight of (a) RLII Bog samples from 0.15 m at 3 mM for peak A (black circles) and peak C (black squares) and (b) RLII Fen samples from 0.2 m at 3 mM for peak A (black circles) and peak C (black squares).



**Figure 8.** Radiocarbon  $\Delta^{14}\text{C}$  values of peat incubations compared to pore water data. Results indicate that in situ modern DOC values observed at depth are due to pore water advection. Solid phase peat is represented by black circles, pore water samples are represented with closed symbols, and incubation samples are represented with open symbols. Squares represent DOC and triangles represent DIC. (a) RLII Bog in situ DOC (black squares) and DIC (black triangles), and incubation DOC (white squares) and DIC (white triangles). (b) RLII Fen in situ DOC from 2007 (black squares) and 2008 (grey squares), in situ DIC from 2007 (black triangles), and incubation DOC (white squares) and DIC (white triangles). (c) RLIV Fen in situ DOC from 2008 (black squares) and 2009 (grey squares), in situ DIC from 2008 (black triangles) and 2009 (grey triangles), and incubation DOC (white squares) and DIC (white triangles).

### 3.5. Incubations

[21] The radiocarbon values of DIC and DOC collected in the field were compared with DIC and DOC values obtained from peat incubations in Figures 8a–8c. All peats were rinsed prior to incubation so the only source of DOC in each vial was the peat. Below the near-surface sampling point, RLII Bog DIC radiocarbon values were similar for both field and incubation samples (Figure 8a), and were slightly more enriched than the incubated peat. DOC radiocarbon values from incubations were more depleted than DOC samples collected in the field and matched both sets of DIC  $\Delta^{14}\text{C}$  values. DOC radiocarbon values from the peat incubations were also slightly more enriched than the incubated peat.

[22] RLII and RLIV Fen radiocarbon values for DOC and DIC from incubations were strikingly similar and were much more depleted in  $\Delta^{14}\text{C}$  than field values (Figures 8b and 8c). In the fen incubations, the DIC and DOC that were produced had radiocarbon values that almost exactly matched the incubated peat radiocarbon values.

### 4. Discussion

[23] The results of this study have shown that (1) radiocarbon profiles in a bog and fen did not vary over a 10 year period (Figure 1), (2) field radiocarbon values of DOC and respiration products were  $\Delta^{14}\text{C}$  enriched over the length of the peat column relative to the solid phase peat in the two new fens that were characterized, whereas in the two new bogs, DIC and peat had relatively similar  $\Delta^{14}\text{C}$  values with the DOC being only slightly enriched (Figures 2 and 4), (3) a higher portion of LMW-DOC was present in fens as compared to bogs (Figure 5), (4) in the bog the LMW size fraction was older than the HMW size fraction as in surface fen, but in the deep fen the LMW and HMW size fractions had similar radiocarbon values (Figure 6), (5) DOC/DON ratios were higher, overall, in the LMW size fraction from both the bog and fen samples (Table 3), and (6) modern DOC found at depth in peat columns must be derived from downward advection as it was not derived from the adjacent peat itself (Figure 8).

#### 4.1. Radiocarbon Depth Profiles

[24] By analyzing the  $\Delta^{14}\text{C}$  of microbial respiration and fermentation products, we can determine the source of substrates supporting microbial populations. Radiocarbon is useful for investigating the sources of respiration and fermentation because the stable carbon isotopes of both DOC and peat in the fens and bogs we studied have  $\delta^{13}\text{C}$  signatures of about  $-26\text{‰}$  (see supporting information). However, DOC has often been found to be significantly enriched in radiocarbon as compared to the peat due to the relative contributions of differing DOC sources.

[25] In the GLAP system, and in other peatlands, microbial respiration at a particular horizon may be supported by two carbon sources. The first is DOC derived from surface vegetation (e.g., root exudates) that is advected downward and is also enriched in radiocarbon. Advection rates in bogs may be higher than previously reported in *Siegel and Glaser* [1987] based on a recently developed inverse pore water model [Corbett, 2012]. Work is being done to develop these results. The second is the peat itself [Chanton *et al.*, 2008], and DOC produced by peat decomposition will have the same radiocarbon signature as the peat (Figure 8). Because DOC in peatlands has these two possible sources, the relative contributions (and relative reactivities) of these two sources play a major role in controlling the radiocarbon signatures of pore water DOC and DIC.

[26] If both types of DOC are input to pore water and are equally reactive at depth then DIC should have a radiocarbon signature similar to that of the DOC. The RLII Fen shows this type of behavior. Here DOC is enriched in radiocarbon relative to the peat as a function of depth due to the input (downward advection) of surface (e.g., root exudates) DOC, while the decrease with depth in the DOC radiocarbon content occurs because of the input of peat-derived DOC whose radiocarbon content decreases with depth.

[27] If both types of DOC are input to peat below the surface but peat-derived DOC now has a lower reactivity at depth (i.e., there is selective remineralization of the more modern component of the bulk DOC derived from surface vegetation), then the DIC at depth will be slightly enriched in radiocarbon relative to the bulk DOC at depth, which again should have a radiocarbon content intermediate of that in the peat and the surface pore water DOC. The RLIV Fen appears to show this type of behavior for both years 2008 and 2009 (Figure 2b). Similar observations of gases ( $\text{CH}_4$  and  $\text{CO}_2$ ) with more enriched radiocarbon values than either DOC or peat have also been made by *Charman et al.* [1999] and *Clymo and Bryant* [2008].

[28] In contrast, if DOC production from peat exceeds downward advection of DOC from surface plants and/or this surface DOC has a lower reactivity than peat-derived DOC, then the DIC radiocarbon content will be intermediate between that of the peat and the bulk DOC. The RLII Bog (Figure 1a) and the SR Fen (Figure 2d) show this type of behavior. As noted earlier, data from the RLII Bog in the 1990s showed a similar arrangement of DIC radiocarbon values relative to peat and DOC radiocarbon values (Figure 1a), as do data from two other bogs, Turnagain Bog in Alaska and Bleak Lake Bog in Alberta, Canada [Chanton *et al.*, 2008]. In fact, due to changes in pore water-groundwater mixing such as drought-like conditions, changes in the pore water chemistry profiles within a site have been observed [Siegel *et al.*, 1995].

Therefore, the amount of modern DOC advected downward may be altered with less surficial, modern DOC advected downward during a drought. Evidence of this change and an exception to the relatively constant temporal pattern of the radiocarbon data can be observed in the radiocarbon data of RLII Bog DOC from 3 m collected in 2007 as compared to 2008 and 2009 (Figure 1a).

[29] At the same time, the results of the incubation of rinsed RLII Bog peat (Figure 8A) also suggest that the enriched pore water DIC values seen in this bog could be related to the selective degradation of modern organic matter found at depth in this bog (see section 4.4 for details). However, the results of this experiment also indicate that the in situ DOC radiocarbon profile in the RLII Bog cannot be explained solely by the selective degradation modern organic matter at depth, and that an explanation of this DOC radiocarbon profile in Figure 1a also requires the input of modern DOC derived from surface vegetation. Therefore, as discussed above for the fen profiles, the decrease with depth in the radiocarbon content of bulk DOC in the RLII Bog similarly appears to show evidence of these two DOC sources.

[30] Finally, if there is little input of root exudates into the deeper peat then the radiocarbon content of DOC and DIC should be similar, and should also essentially be the same as the peat. The RLIV Bog (Figure 2a) and SR Bog (Figure 2c) show this type of behavior, with DOC being only very slightly enriched relative to DIC and peat (except at the surface of the SR Bog). The fact that downward advection of surface, modern labile DOC is less important in these bogs may possibly be due to lower vertical hydraulic conductivity in these bogs relative to RLII or the Alaska and Canadian bogs [Chanton *et al.*, 2008].

[31] The difference between bog and fen DIC and DOC radiocarbon values is also illustrated quantitatively with a radiocarbon index as shown in Figure 4. These findings indicate that across all bog and fen sites, fen DOC is preferentially respired by microbes over the solid-phase peat. However, the apparent increased lability of fen DOC over bog DOC may be better thought of in terms of differences in the relative importance of surface (root exudate-derived) DOC versus peat decomposition-derived DOC.

[32] The discussion above provides a reasonable set of explanations for the radiocarbon profiles in Figures 1 and 2, based on these two proposed sources of DOC to peats and possible vertical (downward) advection of pore water from surface to deep. However, other factors may also be important in explaining these profiles, including lateral (downslope) water transport between closely located bogs and fens [e.g., *D'Andrilli et al.*, 2010].

[33] In addition, to further understand controls on the composition and reactivity of bog versus fen DOC, it is important to have knowledge of differences in the source peat material. The peat C/N ratio reflects the surface vegetation. Following the C/N (by mass) patterns of midsummer living surface vegetation *Carex* has a value of  $25 \pm 3$  and *Sphagnum* has a value of  $45 \pm 18$  (Chanton, unpublished data). These values are similar to those in northern Ontario (Canada) peatlands [Glaser *et al.*, 2004] where fen peat has C/N values close to 25 and bog peat has values of 40–115. At GLAP, fen solid phase peat was also found to have a lower C/N ratio than bog solid phase peat [Table 3 and Chanton

*et al.*, 2008]. We interpret these differences in C/N ratios to indicate that fen peat is more labile than bog peat due to inherent differences in the organic matter found in the surface vegetation. In addition, *Clymo and Hayward* [1982] point out that the inherently slow rate of decay that is characteristic of *Sphagnum* is due in part to its very low nitrogen content, which inhibits microbial attack.

#### 4.2. Reactivity of Bog Versus Fen DOC

[34] Detailed organic geochemical analyses of DOC at fen and bog sites in the GLAP complex [*Tfaily et al.*, 2013] are consistent with the hypothesis that fen DOC is more reactive and labile than bog DOC. These analyses have indicated few changes with depth in bog DOC, but distinct changes in the DOC character in fens. Bog DOC (at all depths), and surface fen DOC have high levels of aromaticity. Fen DOC aromaticity decreases with depth [*Tfaily et al.*, 2013]. Molecular weight estimates based on DOC fluorescence, absorbance ratios and mass spectrometry [*Tfaily et al.*, 2013], suggest that fen DOC is of lower molecular weight than bog DOC, consistent with the DOC size fractionation results presented here (Figure 5 and Table 2). The lack of change in the character of DOC in the bogs is consistent with their lower hydraulic conductivity and the formation and utilization of the DOC at a particular horizon rather than its advection and subsequent reaction down the peat column.

[35] The C/N ratios of bulk DOC (Table 3) further support these broad-scale differences in the reactivity of bog versus fen DOC. In the LMW-DOC fraction, there are also significant differences in the DOC/DON ratio between surface and deep fen pore waters, with the deep LMW-DOC in the fen being significantly depleted in nitrogen (and presumably less reactive) than LMW-DOC in the surface fen.

[36] As a proxy for DOC reactivity, the results of our photodegradation studies indicate that surface fen DOC was 3–12 times more photo-reactive than surface bog DOC (Figure 7). Previous fluorescence studies that look at the degradation of DOC with depth have also found the fen DOC to be more reactive than the bog [*Tfaily et al.*, 2013]. The presence of more photolabile fluorophores in the surface fen DOC as compared to the bog in the surface pore water may be due to the additional input of photolabile DOC from root exudates.

#### 4.3. Molecular Weight and Reactivity

[37] The size-reactivity model for the degradation of organic matter in aqueous systems suggests that CO<sub>2</sub>, ammonia, and LMW-DOC are products of the decomposition of HMW-DOC and ultimately POC [*Amon and Benner*, 1996; *Burdige and Gardner*, 1998]. Briefly, particulate organic carbon (POC) is broken down (by either hydrolysis or oxidative cleavage) to HMW-DOC, which is then either: (1) degraded by further hydrolysis and/or fermentation to mLMW-DOC (monomeric LMW-DOC) such as organic acids like acetate, which in turn can be degraded to CO<sub>2</sub> via respiration (a fast process), or (2) degraded to pLMW-DOC (polymeric LMW-DOC), which is degraded by further hydrolysis and/or respiration to mLMW-DOC (a slow process, which can lead to the buildup of the pLMW-DOC) and then to CO<sub>2</sub> via respiration [*Alperin et al.*, 1994; *Burdige and Gardner*, 1998].

[38] 1. POC → HMW-DOC → mLMW-DOC → CO<sub>2</sub>

[39] 2. POC → HMW-DOC → LMW-DOC → LMW-DOC → CO<sub>2</sub>

[40] This model suggests that different forms of LMW-DOC can be intermediates in organic matter breakdown as well as a product of degradation processes. Although still technically an intermediate, more refractory components of the LMW-DOC pool (e.g., pLMW-DOC) may actually end up being stored due to their refractory and/or nonreactive nature. The decomposition of HMW-DOC to LMW-DOC is accompanied by loss of organic N and the release of ammonia [*Corbett*, 2012].

[41] A study done of a temperate estuary found that a significant amount of the total DOC had a molecular weight less than 3 kDa and that the concentration of the low molecular weight fraction increased with depth in the sediment [*Burdige and Gardner*, 1998]. A recent study of the DOC in prairie pothole lake sediments similarly showed that much of the DOC accumulating in these sediment pore waters is also of low molecular weight [*Ziegelgruber et al.*, 2013]. *Burdige and Gardner* [1998] attributed refractory characteristics to this LMW-DOC, and *McArthur and Richardson* [2002] found lower bacterial growth from the LMW fraction (<10 kDa) of the leachate of forest litterfall collected from several rivers in British Columbia.

[42] Our results demonstrate that the size-reactivity model, which was developed for marine systems, may be applied, with some modification, to bogs and to fens. Specifically, fen DOC contained about twice as much LMW-DOC (≤1 kDa) as did bog DOC (Figure 5). This could be the results of rapid processing of HMW-DOC to generate LMW-DOC consistent with the greater reactivity of fen DOC. Of course, it is also likely that fen pore water has an additional source of LMW-DOC from the direct input of LMW-DOC from root exudates. Root exudates have been found to be comprised of labile, LMW-DOC especially organic acids [*Dakora and Phillips*, 2002; *Jones*, 1998; *van Hees et al.*, 2005]. The input of LMW-DOC from root exudates would bypass the HMW-DOC component of the size reactivity model described above. In the fen, decomposition may quickly lead to the production of LMW-DOC near the surface, and LMW-DOC is also added to fen pore waters from root exudates. This LMW-DOC can then be transported downward by advection.

[43] A further examination of our size fractionation data indicates that in terms of relative concentrations bog DOC also has more than twice as much HMW-DOC (> 10 kDa) than does fen DOC (~42–46% in bogs to <20% in fens). This appears to conflict with the size-reactivity model, since HMW-DOC is presumed to generally be a more reactive subfraction of the DOC pool [*Amon and Benner*, 1996; *Burdige and Gardner*, 1998]. DOC reactivity in peat systems is determined by both the composition of the DOC and environmental conditions (nature versus nurture) [*Chanton et al.*, 2008]. *Sphagnum* (in bogs) produces poly-phenolic aromatic compounds and other tannin-like compounds known to inhibit microbial activity [*Tfaily et al.*, 2013]. For these types of compounds, oxidative processes are important in the initiation of their decomposition. These processes are, however, dependent upon both pH (acidic in bogs) and oxygen availability (low in bog pore water), which results in lower rates of decomposition and the buildup of HMW-DOC in bogs [*Freeman et al.*, 2001; *Tfaily et al.*, 2013]. Marine systems differ in that proteins and carbohydrates generally predominate, and hydrolysis is more important in the initial decomposition of particulate organic matter [*Burdige*, 2006].

[44] Therefore, without the presence of plant roots that may actively pump O<sub>2</sub> into bogs, there should be less oxygen penetration in bogs than in fen, inhibiting the function of oxidative enzymes such as phenol oxidase [Freeman *et al.*, 2001]. This inhibition will then slow down the further breakdown of HMW-DOC in bogs versus fens, and explain the buildup of HMW-DOC in bogs. The fact that the HMW-DOC in bogs is younger than the LMW-DOC (Figure 6) is also consistent with this explanation, assuming that the LMW-DOC is largely comprised largely of refractory pLMW-DOC, and that this oxygen effect represents a “choke point” that slows down the degradation of more reactive HMW-DOC intermediates.

#### 4.4. Incubations

[45] Generally, DOC and DIC that were produced in the incubation of rinsed peat had radiocarbon values that were more depleted than in situ pore water values for these same materials (Figure 8). In previous discussions, we hypothesized that the modern radiocarbon in DOC at depth from field samples resulted from either: (1) downward advection of surficial pore water containing labile (and more modern) DOC (e.g., root exudates) or (2) selective mineralization of more modern material within a peat horizon. Figure 3 shows that peat ages at bog and fen sites can vary widely at certain depths, suggesting the burial of mixtures of modern and old peats fractions [Glaser *et al.*, 2012]. Modern peat components may be available at depth due to the reach of previously living plant roots (i.e., roots from *Picea mariana* present in the bogs and *Carex* present in the fen). Due to the water saturation of these peatlands, it is unlikely that live roots could penetrate deep enough to allow for the modern radiocarbon DOC signatures seen at depth. However, we could not completely rule out this possibility without the incubation study described here, which examined the production (and radiocarbon content) of DOC directly produced from the peat itself. In our studies, evidence of some modern peat component at depth is only seen in the incubations with RLII Bog peat.

[46] DOC and DIC produced during these incubations had radiocarbon values that matched more closely with the peat values at each respective depth than they did with the in situ pore water DOC and DIC values. This occurred because peat was the only carbon source for DOC production in the incubations, and ultimately, for the DIC that was produced from this DOC. Therefore, the radiocarbon values of the DOC and DIC produced in the incubations were significantly more depleted than the DOC and DIC radiocarbon values from samples taken in the field.

[47] It was previously unknown whether the modern DOC signatures in deep peat pore waters came from surficial vegetation or from selective remineralization of modern peats relative to older peat at each depth. These incubation results definitively demonstrate that these modern DOC signatures do not come from the decomposition of peat at depth and must be advected down from the surface. These incubations also provide evidence in support of the explanations in section 4.1 of the radiocarbon depth distributions in Figures 1 and 2. Therefore, surficial organic matter production contributes to microbial respiration at depth within the peat column, especially in fens. Many peatlands will be a continuum and not be clearly distinguished as bogs or fens; however, it is useful to recognize the characteristics of these end-member environments.

## 5. Conclusions

[48] In the GLAP system and in other peatlands in general, microbial respiration below the water table is supported by two carbon sources. The first is DOC derived from surface vegetation (e.g., root exudates) that has been advected downward, and which is also enriched in radiocarbon. The second is the peat itself, and DOC produced by peat decomposition will have the same radiocarbon signature as the peat. Because DOC in peatlands has these two possible sources, the relative contributions (and relative reactivities) of these two sources play a major role in controlling the radiocarbon signatures of pore water DOC and DIC as compared to that of the peat itself.

[49] The presence of modern DOC at depth in both some bog and all fen environments strongly indicates that surficial DOC is brought to deeper portions of the peat column by downward advection of pore water. Incubation studies with rinsed peat conclusively demonstrate the importance of this downward advection as the source of  $\Delta^{14}\text{C}$  enriched pore water DOC. Differences in pore water DOC molecular weight distributions between bogs and fens appear to be related to the differential contributions of these two DOC sources, and differences in oxygenation of bogs and fens and its impact on the dynamics of DOC cycling.

[50] The results of this study also support the observations from past work that fen DOC is (in general) more labile than bog DOC. The differences in DOC lability between bogs and fens suggest these systems may behave differently in response to climate change. Although exceedingly difficult to predict, some scenarios suggest that ongoing and expected climate change may favor vascular plants expansion and a reduction in bryophytes (*Sphagnum* spp.) [Bragazza *et al.*, 2012; Post *et al.*, 2009; Walker *et al.*, 2006]. This change would apparently favor the production of more labile organic material that could then be more easily remineralized to greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>) creating a positive feedback on a warming climate.

[51] **Acknowledgment.** This research was supported by the National Science Foundation, EAR-0628349.

## References

- Alperin, M. J., D. B. Albert, and C. S. Martens (1994), Seasonal variations in production and consumption rates of dissolved organic carbon in an organic-rich coastal sediment, *Geochim. Cosmochim. Acta*, 58(22), 4909–4930.
- Amon, R. M. W., and R. Benner (1996), Bacterial utilization of different size classes of dissolved organic matter, *Limnol. Oceanogr.*, 41(1), 41–51.
- Aravena, R., B. G. Warner, D. J. Charman, L. R. Belyea, S. P. Mathur, and H. Diné (1993), Carbon isotopic composition of deep carbon gases in an ombrogenous mire, northwestern Ontario, Canada, *Radiocarbon*, 35, 271–276.
- Bower, C. E., and T. Holm-Hansen (1980), A salicylate-hypochlorite method for determining ammonia in seawater, *Can. J. Fish. Aquat. Sci.*, 37, 794–798.
- Bragazza, L., J. Parisod, A. Buttler, and R. D. Bardgett (2012), Biogeochemical plant-soil microbe feedback in response to climate warming in peatlands, *Nat. Clim. Change*, doi:10.1038/nclimate1781.
- Burdige, D. J. (2006), *Geochemistry of Marine Sediments*, pp. 421–424, Princeton Univ. Press, Princeton, N. J.
- Burdige, D. J., and K. G. Gardner (1998), Molecular weight distribution of dissolved organic carbon in marine sediment pore waters, *Mar. Chem.*, 62, 45–64.
- 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., R. Aravena, and B. G. Warner (1994), Carbon dynamics in a forested peatland in northeastern Ontario, Canada, *J. Ecol.*, *82*, 55–62.
- Charman, D. J., R. Aravena, C. L. Bryant, and D. D. Harkness (1999), Carbon isotopes in peat, DOC, CO<sub>2</sub> and CH<sub>4</sub> in a Holocene peatland on Dartmoor, SW England, UK, *Geology*, *27*, 539–542.
- Chasar, L. S., J. P. Chanton, P. H. Glaser, D. I. Siegel, and J. S. Rivers (2000), Radiocarbon and stable carbon isotopic evidence for transport and transformation of dissolved organic carbon, dissolved inorganic carbon and CH<sub>4</sub> 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.
- Clymo, R. S., and C. L. Bryant (2008), Diffusion and mass flow of dissolved carbon dioxide, methane, and dissolved organic carbon in a 7-m deep raised peat bog, *Geochim. Cosmochim. Acta*, *72*, 2048–2066.
- Clymo, R. S., and P. M. Hayward (1982), The ecology of Sphagnum, in *Bryophyte Ecology*, edited by A. J. E. Smith, pp. 229–289, Chapman and Hall, London.
- Coble, P. G. (1996), Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, *Mar. Chem.*, *51*, 325–346.
- Corbett, J. E. (2012), DOC reactivity in a northern Minnesota peatland, PhD dissertation, Florida State Univ., Tallahassee, Fla.
- Corbett, J. E., M. M. Tfaily, D. J. Burdige, W. T. Cooper, P. H. Glaser, and J. P. Chanton (2012), Partitioning pathways of CO<sub>2</sub> production in peatlands with stable carbon isotopes, *Biogeochemistry*, doi:10.1007/s10533-012-9813-1.
- D'Andrilli, J., J. P. Chanton, P. H. Glaser, and W. T. Cooper (2010), Characterization of dissolved organic matter in northern peatland soil porewaters by ultra high resolution mass spectrometry, *Org. Geochem.*, *41*, 791–799.
- Dakora, F. D., and D. A. Phillips (2002), Root exudates as mediators of mineral acquisition in low-nutrient environments, *Plant Soil*, *245*, 35–47.
- Fenner, N., and C. Freeman (2011), Drought-induced carbon loss in peatlands, *Nat. Geosci.*, *4*, 895–900.
- Fenner, N., C. Freeman, S. Hughes, and B. Reynolds (2001), Molecular weight spectra of dissolved organic carbon in a rewetted Welsh peatland and possible implications for water quality, *Soil Use Manage.*, *17*, 106–112.
- Finzi, A. C., N. Van Breeman, and C. D. Canham (1998), Canopy tree-soil interactions within temperate forests: Species effects on soil and carbon nitrogen, *Ecol. Appl.*, *8*, 440–446.
- Freeman, C., N. Ostle, and H. Kang (2001), An enzymatic 'latch' on a global carbon store, *Nature*, *409*, 149.
- Glaser, P. H. (1987), The development of streamlined bog islands in the continental interior of north America, *Arct. Alp. 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*, 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*, 3–16.
- Glaser, P. H., B. C. S. Hansen, D. I. Siegel, A. S. Reeve, and P. J. Morin (2004), Rates, pathways, and drivers for peatland development in the Hudson Bay lowlands, northern Ontario, *J. Ecol.*, *92*, 1036–1053.
- 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, 347–377, Elsevier, Amsterdam.
- Glaser, P. H., J. C. Volin, T. J. Givnish, B. C. S. Hansen, and C. A. Stricker (2012), Carbon and sediment accumulation in the Everglades (USA) during the past 4000 years: Rates, drivers, and sources of error, *J. Geophys. Res.*, *117*, G03026, doi:10.1029/2011JG001821.
- 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.
- Hudson, N., A. Baker, and D. Reynolds (2007), Fluorescence analysis of dissolved organic matter in natural, waste, and polluted waters—A review, *River Res. Appl.*, *23*, 631–649, doi:10.1002/rra.1005.
- Jones, D. L. (1998), Organic acids in the rhizosphere—A critical review, *Plant Soil*, *205*, 25–44.
- Limpens, J., F. Berendse, C. Blodau, J. G. Canadell, C. Freeman, J. Holden, N. Roulet, H. Rydin, and G. Schaepman-Strub (2008), Peatlands and the carbon cycle: from local processes to global implications – A synthesis, *Biogeosci. Discuss.*, *5*, 1379–1419.
- McArthur, M. D., and J. S. Richardson (2002), Microbial utilization of dissolved organic carbon leached from riparian litterfall, *Can. J. Fish. Aquat. Sci.*, *59*, 1668–167.
- Melillo, J. M., J. D. Aber, and J. F. Muratore (1982), Nitrogen and lignin control of hardwood leaf litter decomposition dynamics, *Ecology*, *63*, 621–626.
- Molot, L. A., and P. J. Dillon (1997), Photolytic regulation of dissolved organic carbon in northern lakes, *Global Biogeochem. Cycles*, *11*(3), 357–365.
- 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.
- Peterson, B., B. Fry, M. Hullar, S. Saupe, and R. Wright (1994), This distribution and stable carbon isotopic composition of dissolved organic carbon in estuaries, *Estuaries*, *17*, 111–121.
- 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.
- Post, E., et al. (2009), Ecological dynamics across the arctic associated with recent climate change, *Science*, *325*, 1355–1358.
- 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.
- Siegel, D. I. (1983), Ground water and the evolution of patterned mires, Glacial Lake Agassiz peatlands, northern Minnesota, *J. Ecol.*, *71*(3), 913–921.
- 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.
- Tfaily, M. M., R. Hamdan, J. E. Corbett, J. P. Chanton, P. H. Glaser, and W. T. Cooper (2013), Investigating dissolved organic matter decomposition in northern peatlands using complimentary analytical techniques, *Geochim. Cosmochim. Acta*, doi:10.1016/j.gca.2013.03.002.
- van Hees, P. A. W., D. L. Jones, R. Finlay, D. L. Godbold, and U. S. Lundström (2005), The carbon we do not see—the impact of low molecular weight on carbon dynamics and respiration in forest soils: A review, *Soil Biol. Biochem.*, *37*, 1–13.
- Walker, M. D., et al. (2006), Plant community responses to experimental warming across the tundra biome, *Proc. Natl. Acad. Sci. U.S.A.*, *103*, 1342–1346.
- Yu, Z., J. Loisel, D. P. Brousseau, D. W. Beilman, and S. J. Hunt (2010), Global peatland dynamics since the Last Glacial Maximum, *Geophys. Res. Lett.*, *37*, L13402, doi:10.1029/2010GL043584.
- Ziegelgruber, K. L., T. Zeng, W. A. Arnold, and Y. P. Chin (2013), Sources and composition of sediments pore-water dissolved organic matter in prairie pothole lakes, *Limnol. Oceanogr.*, *58*, 1136–1146.