



# Investigating dissolved organic matter decomposition in northern peatlands using complimentary analytical techniques

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## Abstract

The chemical transformations that govern storage, degradation, and loss of organic matter in northern peatlands are poorly characterized, despite the significance of these peat deposits as pivotal reservoirs in the global carbon cycle. One of the most challenging problems concerns the character of dissolved organic matter (DOM) in peat porewaters, particularly higher-molecular weight compounds that may function either as non-reactive sinks or reactive intermediates for organic byproducts of microbial decay. The complexity of these large molecules has defied attempts to characterize their molecular structure in bulk samples with a high degree of precision. We therefore determined the composition and reactivity of DOM from representative bog and fen sites in the Glacial Lake Agassiz Peatlands (GLAP) in northern Minnesota, USA. We applied four complementary techniques: electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR MS), proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR), specific UV absorbance (SUVA) and excitation–emission matrix (EEM) fluorescence spectroscopy. We observed that the vast majority (>80%) of molecular formulas that appear in the surface bog DOM are also present at 2.9 m depth, indicating that much of DOM in the bog is resistant to microbial degradation. In contrast to bog samples, a considerable number of new compounds with low O/C and high H/C elemental ratios were observed in the 3 m fen horizon relative to surface samples. These results indicate a more pronounced difference in the composition of surface and deep DOM in the fen.

SUVA, determined at 254 nm, indicated significantly lower aromaticity in deep fen samples relative to deep bog samples. This trend was verified by <sup>1</sup>H NMR. Aromatic and carbohydrate components represented up to 70% of deep bog DOM but comprised a much smaller proportion of deep fen DOM, which was dominated by functionalized and non-functionalized aliphatics. Molecular formula data determined by FT-ICR mass spectrometry were consistent with results from optical and NMR spectroscopy measurements and showed that compounds with low O/C and high H/C were generated with depth in the fen. Such compounds were absent in both surface fen and in surface and deep bog samples respectively, providing further evidence of qualitative and quantitative differences in the evolution of DOM in fens and bogs. These differences, attributed to either variations in source vegetation or environmental factors that render DOM more reactive in fen sites or less reactive in bog sites, have important implications for the response of peatlands to climate change, since climatic change leading to moister conditions may enhance the abundance of sedge-dominated fens and increase the pool of more labile soil carbon.

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## 1. INTRODUCTION

Peatlands are among the most important carbon sinks. They cover over 4 million km<sup>2</sup> worldwide, occur in over 180 countries and account for about 1/3 of the global wet-

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land resource (Gorham, 1991; Chanton et al., 2008). Peatland classification is generally based upon water chemistry, hydrology, topography and vegetation (Glaser et al., 1981). Generally, bogs are fed only by precipitation, are characterized by raised landforms with interiors higher than their margins, have acidic ( $\text{pH} \sim 4$ ) dilute cationic ( $\text{Ca} < 2 \text{ mg L}^{-1}$ ) surface waters and Sphagnum-dominated vegetation. Fens, which are flat or concave landforms fed by ground water or water that has percolated laterally, have less acidic surface waters compared to bogs ( $\text{pH} > 4$ ). They are usually dominated by sedges, and typically have brown mosses in addition to relatively site-specific fen indicator species (Glaser et al., 1981).

Over the last 10,000 years, an estimated 455 Pg of carbon has been transferred from the atmosphere to organic soils in northern peatlands (Gorham, 1991; Yu et al., 2010). Peatlands are also important sources of methane through anaerobic microbial decomposition of peat and dissolved organic matter (DOM). Despite intensive research in the last three decades, our knowledge of the decomposition pathways of peat and in particular peat porewater DOM is not complete (Keller and Bridgman, 2007). Predictions at the field scale are still very uncertain, and much of the available information is the result of laboratory peat incubations. These laboratory studies suggest that methanogenesis is one of the most common decomposition pathways in Northern peatlands. However, while methanogenesis produces  $\text{CO}_2$  and  $\text{CH}_4$  in equimolar amounts from a cellulose-type substrate (Conrad, 1999), the ratio of  $\text{CO}_2$ : $\text{CH}_4$  produced during anaerobic incubations of wetland soils is often reported to be  $>1$  (van Hulzen et al., 1999; Keller and Bridgman, 2007; Hines et al., 2008; Keller et al., 2009). According to Keller and Bridgman (2007) and Keller et al. (2009), the additional  $\text{CO}_2$  produced during anaerobic decomposition in some wetland soils could result from fermentation or the use of humic acids as alternative electron acceptors. Alternatively, loss of  $\text{CH}_4$  from the belowground system may cause underestimates of methanogenesis. Recent studies using stable isotope partitioning (Corbett et al., 2012) demonstrated that in a *Carex*-dominated fen and Sphagnum-dominated bog, methanogenesis produced 40–60% of  $\text{CO}_2$  in surface horizons and 90–100% of  $\text{CO}_2$  at depth.

DOM in peatland soil plays an important role in the cycling of C, N and P and provides an important substrate for microbial metabolism. It has been reported that anaerobic respiration at depths up to 3 m in the peat column is fueled primarily by DOM derived in part from surface production rather than decomposition of peat at a particular horizon (Chanton et al., 1995; Chasar et al., 2000a; Siegel et al., 2001). The supply of DOM, however, is controlled by the water table, hydraulic gradients, temperature and vegetation type. Changing climatic conditions may thus affect gas exchange between peatlands and the atmosphere by altering these master variables (Clymo, 1984; Gorham, 1991). Predicting the response of peatlands to climate change is in part dependent on elucidation of the molecular composition and reactivity of porewater DOM and how these parameters presently vary across wetlands. Moreover, quantification of the variation in the chemical and molecu-

lar composition of DOM across peatlands will aid in elucidating the biogeochemical role of DOM within these ecosystems.

Chanton et al. (2008) and D'Andrilli et al. (2010) studied organic matter reactivity across northern peatlands using different techniques. Chanton et al. (2008) examined the radiocarbon distribution patterns in DOM, dissolved inorganic carbon (DIC), solid peat and  $\text{CH}_4$  replicated across temporal and spatial scales in peatlands from Alaska to the Glacial Lake Agassiz Peatlands (GLAP) of northern Minnesota. Fen and bog DOM were enriched in  $^{14}\text{C}$  relative to that of the adjacent peat. The products of microbial respiration, DIC and  $\text{CH}_4$ , were also similar and enriched in radiocarbon relative to that of the peat. These data were interpreted to indicate that anaerobic respiration within the peat column is fueled by DOM rather than directly from the decomposition of solid-phase peat at a particular horizon. Moreover, the respiration products were intermediate between peat and DOM radiocarbon values for bogs, where vegetation is dominated by Sphagnum. In sedge-dominated peatlands, the radiocarbon signatures of the respiration products were similar to DOM rather than peat. These results suggest that a fraction of bog DOM is less reactive, whereas most of the DOM in fens supports microbial respiration.

D'Andrilli et al. (2010) investigated the reactivity and composition of fen and bog porewater DOM from the Red Lake II site in the GLAP using ultrahigh resolution (UHR) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). High field (9.4 Tesla) FT-ICR MS was used to describe DOM as a complex mixture of individual organic molecules differing in the numbers of C, H and O atoms. Ultrahigh resolution MS, while powerful, is not suited for extensive characterization of DOM at frequent intervals down a peat profile because of its time- and instrument-intensive nature. Optical spectroscopy, however, is ideal for this type of profiling, and a number of optical techniques have emerged recently as surrogate approaches for evaluating the composition of DOM in various environments.

Optical spectroscopy of DOM characterizes the optically active components commonly referred to as chromophoric DOM, or CDOM. CDOM absorbs visible and UV light and has intrinsic fluorescence properties that differ as a function of source material and light exposure (Coble, 1996). One of the most popular techniques for characterizing CDOM is Excitation Emission Matrix Fluorescence Spectroscopy (EEMS), which involves the collection of multiple emission spectra scanned over a wide range of excitation wavelengths and projection of that data onto a single 3D map of optical space. EEMS spectra can be interpreted to identify the types of fluorescent components of CDOM based on the positions of excitation/emission maxima (Coble, 1996). There is great interest in understanding the molecular basis of optical UV–visible absorption and fluorescence emission of DOM so that they can be used to estimate molecular composition for samples in a variety of environments. For example, Tremblay et al. (2007) and Gonsior et al. (2009) have demonstrated that FT-ICR mass spectra can provide insights into specific compounds responsible for the optical properties of riverine and

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