



## DOM in Northern Peatlands: Correlating Bulk Spectroscopic Properties with Molecular Composition

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Peatlands are some of the most important carbon stores in the world. While covering only 3% worldwide, they account for about 1/3 of the carbon stored in global soils [1]. During the last 10,000 years, an estimated 455 Pg of carbon was transferred from the atmosphere to the organic soils in northern peatlands at an average rate of 0.096 Pg/yr (1 Pg = 1015 g) [2]. Although the formation of this large carbon sink would tend to damp climatic warming, peatlands are an important source for the greenhouse gases CO<sub>2</sub> and CH<sub>4</sub> [3, 4]. Emissions of CH<sub>4</sub> are estimated to release ~ 0.046 Pg of carbon annually. Long-term drainage of peatlands is estimated to be causing their oxidation to CO<sub>2</sub> at a rate of 0.0085 Pg/yr [2]. Changing climatic conditions is therefore expected to affect the carbon flux of peatlands from and to the atmosphere.

Little is known about the chemical processes that link solid phase peat and dissolved organic matter (DOM) within its porewaters, and thus the response of these large carbon reservoirs to climate change remains uncertain. Better elucidation of the molecular composition and reactivity of its porewater DOM is therefore a prerequisite for predicting their response to this potential change in climatic conditions

In this work we have applied UV-Vis absorption spectroscopy, Excitation/Emission Matrix (EEM) fluorescence spectroscopy and ultrahigh resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) to characterize the molecular composition of dissolved organic matter (DOM) in soil porewaters at varying depths from different sites (sedge- dominated fens and sphagnum-dominated bogs) within the Glacial Lake Agassiz Peatlands (GLAP) of northern Minnesota.

Results from previous studies that utilized stable and radiocarbon isotope data suggested that DOM formation and evolution was different in fens and bogs [5]. Here we describe absorption and fluorescence spectroscopy data that confirm qualitative and quantitative differences in porewater DOM. These data are supported by molecular level analyses of DOM from ultrahigh-resolution mass spectrometry, and were consistent with the hypothesis that DOM in Sphagnum-dominated peatlands preserves aromatic compounds at depth, in contrast to DOM in sedge-dominated peatlands. FT-ICR mass spectrometry suggested that a larger fraction of bog DOM appeared to be unreactive relative to fen DOM. FT-ICR MS spectra also showed high abundances of compounds with low O/C and high H/C in deep fen samples. Those compounds were absent in both surface fen and in surface and deep bog samples respectively, providing further evidence of qualitative differences between fen and bog DOM. Specific UV Absorbance (SUVA) values at 254 nm confirmed less aromaticity in deep fen samples relative to deep bog samples. These differences were attributed to either difference in vegetation and primary production and/or environmental factors that are rendering DOM less reactive in the bog sites and/or more reactive in the fen sites. This difference in the reactivity suggests that bogs and fens will behave differently upon global warming, with more CO<sub>2</sub> and CH<sub>4</sub> released from fens compared to bogs. This in turn will shift fens (and maybe bogs) from carbon sequestering to carbon emitting environments.

1- F. Parish, A.S., D. Charman, H. Joosten, T. Minayeva, M. Silvius, L. Stringer, Assessment on Peatlands, Biodiversity and climate change: Main report. Global Environment centre and Wetlands International : Kuala Lumpur/ Wageningen, 2008.

2- Gorham, E., Northern Peatlands: Role in the Carbon Cycle and Probable Responses to Climatic Warming. Ecological Applications, 1991. 1(2): p. 182-195.

3- Khalil, A.K., Atmospheric Methane: Its Role In The Global Environment. Springer,Berlin, 2000.

4- Khalil, M.A.K., Non-CO<sub>2</sub> greenhouse gases in the atmosphere. Annual Review of Energy and the Environment, 1999. 24: p. 645-661.

5- J. P. Chanton, P.H.G., L. S. Chasar, D. J. Burdige, M. E. Hines, D. I. Siegel, L. B. Tremblay, and W. T. Cooper,

Radiocarbon evidence for the importance of surface vegetation on fermentation and methanogenesis in contrasting types of boreal peatlands. *GLOBAL BIOGEOCHEMICAL CYCLES*, 2008.