



Reactive and Refractory Components of Organic Matter in Peat Soils and their Relation to Climate Change

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The growth of northern peatlands during the Holocene created a globally important source and sink for greenhouse gases. However, the response of these large carbon reservoirs to global warming remains uncertain. Different models predict that future warming could alter the balance of peatlands by either increasing the rate of carbon sequestration or accelerating greenhouse gas emissions. We have therefore begun a multi-disciplinary study of soil (SOM) and soil porewater (DOM) organic matter in the Glacial Lake Agassiz Peatlands (GLAP) in northern Minnesota, USA, with the goal of developing a multiphase groundwater flow model that incorporates solute transport, organic matter reactivity and peat accumulation.

In this presentation we will describe the results of experiments designed to identify the differences in reactive and refractory SOM and DOM pools from two distinctly different peatland geofoms; bogs and fens. Raised bogs develop over sites that support local recharge mounds that drive surface waters downward into the deeper peat. Bogs thus have acidic surface waters with low concentrations of inorganic solutes. In contrast, fens develop where mineral solutes are transported upward to the peat surface. Bogs tend to develop over sand and gravel deposits, whereas fens are generally underlain by silty or clayey sediments.

We utilize a variety of analytical techniques to determine the bulk characteristics and molecular composition of solid- and solution-phase organic matter, including stable and radiocarbon isotope analyses, solid and solution state ^{13}C and ^{31}P NMR spectroscopy, UV-visible and fluorescence optical spectroscopy, and ultrahigh resolution mass spectrometry. Initial results of radiocarbon measurements indicated that DOM formation and evolution was different in fens and bogs [1]. DOM in sedge-dominated fens appears to be quite reactive, with most respiration products (CH_4 and CO_2) derived from the DOM pool. DOM in Sphagnum-dominated bogs, however, is much less reactive, and the respiration products have a significant solid phase signature.

Molecular-level analyses of porewater DOM by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) confirmed the radiocarbon results. Approximately 80% of the molecular composition observed in the bog surface DOM was preserved throughout the peat profile, and this qualitative stability of molecular composition was accompanied by a quantitative increase in DOC with depth. In contrast, the composition of DOM in the fen was significantly different at depth with little change in DOC levels. The ultrahigh resolution mass spectrometry also revealed that the preserved DOM in the bog peat was characterized by high aromaticity indices [2], suggesting that aromaticity may play a role in the reactivity of DOM in peatlands through expression or suppression of phenol oxidase enzymes. Because optical spectroscopy techniques like absorption and 3-D excitation emission fluorescence spectroscopy (EEMS) are sensitive to the aromatic content of bulk DOM, we are now correlating these optical measurements with molecular level FT-ICR MS analyses in an effort to develop surrogate molecular analyses from these bulk techniques [3].

Recent characterizations of solid phase peat material by ^{13}C NMR are now being combined with these porewater DOM analyses in our development of a comprehensive model of organic matter reactivity in peatlands that we believe will provide better estimates of the response of these important carbon reservoirs to climate change.

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2. D'Andrilli, J.; Chanton, J. P.; Glaser, P. H.; Cooper, W. T., Characterization of Dissolved Organic in Northern Peatland Soil Porewaters by Ultrahigh Resolution Mass Spectrometry. *Organic Geochemistry* 2010, 41, 791-799.
3. D'andrilli, J.; Tfaily, M. M.; Corbett, J. E.; Chanton, J. P.; Glaser, P. A.; Cooper, W. T., Optical Properties and

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