



Elemental composition and optical properties reveal changes in dissolved organic matter along a permafrost thaw chronosequence in a subarctic peatland

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Abstract

The fate of carbon stored in permafrost-zone peatlands represents a significant uncertainty in global climate modeling. Given that the breakdown of dissolved organic matter (DOM) is often a major pathway for decomposition in peatlands, knowledge of DOM reactivity under different permafrost regimes is critical for determining future climate feedbacks. To explore the effects of permafrost thaw and resultant plant succession on DOM reactivity, we used a combination of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), UV/Vis absorbance, and excitation-emission matrix spectroscopy (EEMS) to examine the DOM elemental composition and optical properties of 27 pore water samples gathered from various sites along a permafrost thaw sequence in Stordalen Mire, a thawing subarctic peatland in northern Sweden. The presence of dense *Sphagnum* moss, a feature that is dominant in the intermediate thaw stages, appeared to be the main driver of variation in DOM elemental composition and optical properties at Stordalen. Specifically, DOM from sites with *Sphagnum* had greater aromaticity, higher average molecular weights, and greater O/C, consistent with a higher abundance of phenolic compounds that likely inhibit decomposition. These compounds are released by *Sphagnum* and may accumulate due to inhibition of phenol oxidase activity by the acidic pH at these sites. In contrast, sites without *Sphagnum*, specifically fully-thawed rich fens, had more saturated, more reduced compounds, which were high in N and S. Optical properties at rich fens indicated the presence of microbially-derived DOM, consistent with the higher decomposition rates previously measured at these sites. These results indicate that *Sphagnum* acts as an inhibitor of rapid decomposition and CH₄ release in thawing subarctic peatlands, consistent with lower rates of CO₂ and CH₄ production previously observed at these sites. However, this inhibitory effect may disappear if *Sphagnum*-dominated bogs transition to more waterlogged rich fens that contain very little to no living

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Sphagnum. Release of this inhibition allows for higher levels of microbial activity and potentially greater CH₄ release, as has been observed in these fen sites.

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1. INTRODUCTION

1.1. Decomposition in northern peatlands

Boreal and subarctic peatlands store between 270 and 455 Pg of carbon (Gorham, 1991; Turunen et al., 2002), of which ~277 Pg is in the permafrost zone (Schuur et al., 2008). This carbon has an uncertain fate as permafrost thaws due to continuing warming (Schuur et al., 2008). Although the Arctic is currently a net sink for carbon dioxide (CO₂), sequestering up to 0.8 Pg C/year mostly due to boreal forest growth, it is a net source of methane (CH₄) with annual emissions of 32–112 Tg CH₄/year, mostly from wetlands and lakes (Walter et al., 2007; McGuire et al., 2009; Thornton et al., 2015). Since CH₄ results in 25–33 times the radiative forcing of CO₂ (per kg of gas) on a 100-year timescale (Forster et al., 2007; Shindell et al., 2009), the response of CH₄ production to warming and permafrost thaw represents a major potential climate feedback. Net CH₄ and CO₂ balances in thawing permafrost peatlands depend on plant production, which determines net autotrophic CO₂ uptake, and belowground decomposition, which determines heterotrophic CH₄ and CO₂ release. Belowground decomposition rates and pathways depend on inputs and reactivity of fresh plant litter and thawed permafrost carbon, soil water saturation (which controls belowground oxygen availability and aboveground plant species), and microbial metabolic pathways. The responses of these factors, and thus CH₄ and CO₂ emissions, to a warming climate remain uncertain. In this study, we focus on the effects of permafrost thaw and associated vegetation change on peatland organic matter chemistry.

1.2. Controls on DOM composition and lability

Anaerobic decomposition in peatlands is typically fueled by dissolved organic matter (DOM) rather than solid peat (Chanton et al., 2008). According to the size-reactivity model (Alperin et al., 1994; Amon and Benner, 1996; Burdige and Gardner, 1998), the first step in DOM decomposition is the degradation of high molecular weight macromolecules (HMW-DOM), defined as either >1000 or >3000 Da, into either monomeric or polymeric low molecular weight DOM (mLMW-DOM or pLMW-DOM). mLMW-DOM is more labile and can be rapidly degraded into CO₂ or used in methanogenesis (Conrad, 1999), while pLMW-DOM is more refractory and often accumulates. The reactivity of peatland DOM is thus an important control on both overall decomposition rates and the proportion of carbon released as CH₄.

Inputs from aboveground plants and belowground thawing permafrost (Ward and Cory, 2015) determine the

initial composition and lability (defined here as the potential for rapid decomposition) of raw DOM that enters peat pore water. The main compounds that plants introduce to the DOM pool—either via direct input or via release from solid-phase peat—include carbohydrates, proteins, lipids, lignin-derived compounds, tannins and other phenolics, and other miscellaneous compounds such as chlorophyll (Kögel-Knabner, 2002; Kalbitz et al., 2003b). Microbial activity can then change DOM composition by several processes including preferential mineralization of more labile DOM compounds, alteration of existing compounds, or assimilation into microbial biomass. Compounds that are usually enriched as others are degraded include lignin, humic acids, other aromatics, lipids, and alkyls with double bonds (Harvey et al., 1995; Glatzel et al., 2003; Kalbitz et al., 2003a, 2003b; Lorenz et al., 2007). Lignin in particular can only be degraded aerobically (Kirk and Farrell, 1987), and thus should accumulate in anaerobic peatlands.

DOM structure can influence decomposition not only directly via its reactivity, but also indirectly via reactions of specific DOM molecules. For example, humic substances and quinones can act as electron acceptors in anaerobic respiration, which due to more favorable energy yields outcompetes methanogenesis (Lovley et al., 1996; Cervantes et al., 2000; Heitmann et al., 2007; Keller and Bridgman, 2007; Blodau and Deppe, 2012; Bridgman et al., 2013). Phenolic compounds can also inhibit hydrolase enzymes and thereby suppress decomposition (Freeman et al., 2001, 2004).

Compared to other plant groups, litter from *Sphagnum* mosses decomposes unusually slowly. This slow decomposition is caused both directly by *Sphagnum* litter's recalcitrance, and indirectly by the inhibitory activity of specific compounds that also slow the decomposition of organic matter from other sources (Verhoeven and Toth, 1995). The main component of *Sphagnum* that contributes to its tanning properties (i.e., preservation of animal tissues) is the polysaccharide sphagnan (Painter, 1991), which is unusual for its reactive carboxylic acid groups contained within uronic acid monomers. These acids can form complexes with proteins, including those found in *Sphagnum* litter, to form recalcitrant humic substances via abiotic Maillard reactions (Painter, 1983, 1991). Enzyme activity necessary for biodegradation is also suppressed, both by complexation of enzymes with sphagnan (Painter, 1991), and by enzyme-inhibiting phenolics such as tannin-like compounds and sphagnum acid (van Breemen, 1995; Verhoeven and Toth, 1995; Verhoeven and Liefveld, 1997; Freeman et al., 2004). Experiments and field observations indicate that humic substances from *Sphagnum* inhibit methanogenesis, not only by competition as terminal electron acceptors, but also by possible direct toxicity to methanogens

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