

Dissolved Organic Carbon in Alaskan Boreal Forest: Sources, Chemical Characteristics, and Biodegradability

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ABSTRACT

The fate of terrestrially-derived dissolved organic carbon (DOC) is important to carbon (C) cycling in both terrestrial and aquatic environments, and recent evidence suggests that climate warming is influencing DOC dynamics in northern ecosystems. To understand what determines the fate of terrestrial DOC, it is essential to quantify the chemical nature and potential biodegradability of this DOC. We examined DOC chemical characteristics and biodegradability collected from soil pore waters and dominant vegetation species in four boreal black spruce forest sites in Alaska spanning a range of hydrologic regimes and permafrost extents (Well Drained, Moderately Well Drained, Poorly Drained, and Thermokarst Wetlands). DOC chemistry was characterized using fractionation, UV-Vis absorbance, and fluorescence measurements. Potential biodegradability was assessed by incubating the samples and measuring CO₂ production over 1 month. Soil pore water DOC from all sites was dominated by hydrophobic acids and was highly aromatic, whereas the chemical composition of vegetation leachate DOC varied significantly with species. There was no seasonal variability in soil

pore water DOC chemical characteristics or biodegradability; however, DOC collected from the Poorly Drained site was significantly less biodegradable than DOC from the other three sites (6% loss vs. 13–15% loss). The biodegradability of vegetation-derived DOC ranged from 10 to 90% loss, and was strongly correlated with hydrophilic DOC content. Vegetation such as *Sphagnum* moss and feathermosses yielded DOC that was quickly metabolized and respired. In contrast, the DOC leached from vegetation such as black spruce was moderately recalcitrant. Changes in DOC chemical characteristics that occurred during microbial metabolism of DOC were quantified using fractionation and fluorescence. The chemical characteristics and biodegradability of DOC in soil pore waters were most similar to the moderately recalcitrant vegetation leachates, and to the microbially altered DOC from all vegetation leachates.

Key words: dissolved organic carbon; decomposition; fluorescence; boreal forest; Alaska; black spruce; thermokarst.

INTRODUCTION

Dissolved organic carbon (DOC) cycling in northern terrestrial ecosystems, especially in areas affected by permafrost, is of particular interest in light

of changing climate at northern latitudes. The large amounts of organic carbon (C) in biomass and soils, combined with relatively slow decomposition rates, provides a potentially large DOC source, while permafrost prevents deep percolation into soils so DOC can be efficiently transported to surface waters. Changes in temperature and permafrost depths are likely impacting DOC production, processing, and transport in northern terrestrial ecosystems (Frey and Smith 2005; Striegl and others 2005). Warmer temperatures may be stimulating DOC production and/or consumption rates by influencing microbial activity, and thawing permafrost is likely altering hydrologic flow paths, leading to increased residence time of DOC in soils. To understand the mechanisms that underlie this potentially important C flux in high-latitude ecosystems, it is essential to: (1) know the chemical characteristics of the terrestrially-derived DOC, (2) quantify the potential biodegradability of the DOC, and (3) understand environmental controls on DOC chemistry and biodegradability.

DOC is a complex mixture of low and high molecular weight compounds that originates from vegetation, litter, soil leachates, plant root exudates, and microbial enzymes and biomass (Thurman 1985; Guggenberger and Zech 1994). DOC pools and fluxes in terrestrial ecosystems may be small compared to other terrestrial C pools and fluxes (Neff and Asner 2001; Moore 2003), but these pools and fluxes have important roles in both terrestrial and aquatic C cycles. DOC is a substrate for microbial activity (McArthur and others 1985; Amon and Benner 1996), it can be a readily stabilized form of C through sorption to mineral soils (McDowell and Wood Neff and Asner 2001), and it serves as a link between terrestrial and aquatic systems (Dalva and Moore 1991; Schiff and others 1998; Cole and others 2007). Microbial metabolism of DOC is affected by environmental conditions such as temperature (Christ and David 1996)

and oxygen availability (Bastviken and others 2004), and by the chemical structure of DOC molecules (Qualls and Haines 1992). The fluxes of terrestrially-derived DOC within and between soils and aquatic systems are highly dependent on the source strength and the amount of water moving through soils to surface waters (Hope and others 1994; Aitkenhead and McDowell as well as on the amount of microbial metabolism and sorption the DOC undergoes during transport (Kawahigashi and others 2004).

To increase our understanding of terrestrial DOC cycling in northern ecosystems, we characterized the chemical nature and the potential biodegrad-

ability of DOC collected from terrestrial sources in interior Alaska. We focused on black spruce [*Picea mariana* Mill.) B.S.P.] forest, which constitutes a major ecosystem type in the North American boreal forest (Van Cleve and Dyrness 1988; Hall and others 1997). We chose black spruce systems because they are most commonly found on permafrost soils, but also exist in areas without permafrost; they have large amounts of soil organic C (SOC) and, thus, are a potentially large DOC source; and they are found in areas with soils that range from poorly to well drained. Their common association with permafrost makes many poorly drained black spruce forests particularly vulnerable to effects of climate warming, as permafrost thaw can cause changes in drainage conditions (Osterkamp and others 2000; Camill and others 2001; Wickland and others 2006) and increase the amount of SOC in the active layer as it deepens. Current and future climate warming may increase soil biological activity and decomposition (Shaver and others 1992; Oechel and others 1993; Goulden and others 1998), and potentially increase DOC release from peatlands (Frey and Smith 2005), depending on hydrologic connectivity with surface waters (Striegl and others 2005).

Groundcover vegetation species and tree productivity in black spruce systems are influenced by drainage conditions and permafrost. In well drained systems, trees are more productive and light penetration through the canopy is limited, creating ideal conditions for feathermosses and lichens to dominate the understory vegetation (Bisbee and others 2001). In poorly drained systems the trees are slow growing and sparse, and *Sphagnum* mosses thrive in the high light conditions when moisture is not limiting (Bisbee and others 2001). Moderately drained systems have intermediate tree productivity and the understory is dominated by feathermosses. To represent the current range of conditions in which black spruce systems exist, we chose three sites in central Alaska that included a well drained forest without permafrost, a moderately drained forest having permafrost, and a poorly drained forest having permafrost. Within the poorly drained site there are several thermokarst collapse wetlands that have formed due to localized permafrost thaw.

We collected DOC from soil pore waters several times annually during multiple years to capture seasonal and site variability of DOC chemical characteristics and biodegradability. We also leached DOC from dominant vegetation for chemical characterization and biodegradability. Our objectives were to: (1) compare the chemical charac-

teristics of DOC from black spruce forest sites having differences in permafrost, drainage, and vegetation cover, (2) quantify the potential biodegradability of DOC from a range of black spruce forest soils and vegetation, and (3) examine the influence of DOC chemical characteristics on potential biodegradability.

SITE DESCRIPTION

The study sites are located in central Alaska (Figure 1) in regions underlain by discontinuous permafrost. The sites are all populated by black spruce, but vary in drainage, permafrost depth, organic layer thickness, stand density, and dominant groundcover vegetation (Table 1). Two sites are located in the Donnelly Flats area near Delta Junction, AK ($63^{\circ}53'N$, $145^{\circ}44'W$) and two sites are in the Tanana River floodplain near Fairbanks, AK ($64^{\circ}42'N$, $148^{\circ}19'W$). Soils in the Donnelly flats area are mainly derived from Donnelly moraine and wind-blown loess (O'Neill 2000), and are underlain by deposits of sand and gravel. A "Well Drained" site and a "Moderately Well Drained" site are located here in mature black spruce forest (80-100 years-old) (Marries and others 2001, 2004). In early spring, water collects in the surface soils on top of the seasonal ice layer. As the seasonal ice layer thaws, water drains into deeper soils by early June at the Well Drained site, whereas the presence of permafrost prevents water from completely draining at the Moderately Well Drained site. The

"Poorly Drained" site near Fairbanks is a mature black spruce stand (up to 130 years-old). Permafrost and underlying alluvial material prevent vertical movement of water, and the water table is within 35-40 cm of the surface during the entire snow-free season. Isolated thermokarst features have formed within the Poorly Drained site where permafrost has thawed ("Thermokarst Wetlands" site). In these areas the ground surface is 0.5-1 m lower than the surrounding forest there is standing water in many places, and there are standing dead black spruce and tamarack trees. No permafrost is present to a depth of at least 2.2 m in the Thermokarst Wetlands (see Wickland and others for detailed site description).

METHODS

Soil Pore Water Collection and Analyses

Soil pore water samples were collected within transects ranging from 40 to 100 m in length (one transect at Poorly Drained, two transects each at Moderately Well Drained and Well Drained). Five to ten sampling locations were distributed among each transect spaced 10-20 m apart. In addition, there were five sampling locations distributed within the Thermokarst Wetlands site. The depth of available water varied with site and season, as the water table was most often located immediately above the ice layer. In addition, local spatial heterogeneity of the water table at each site resulted in varying sample collection locations within the

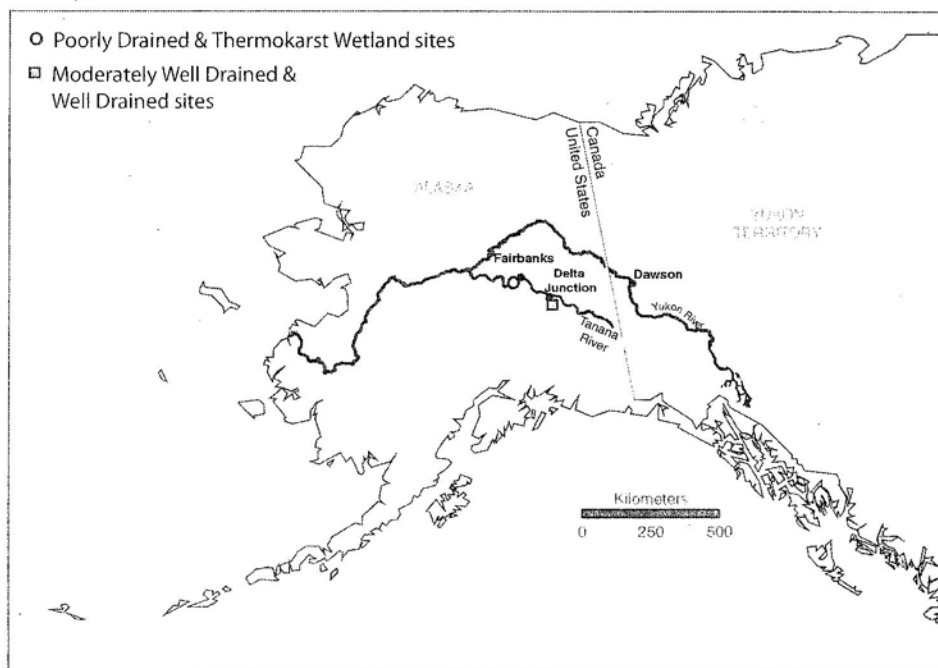


Figure 1. Map of study site locations.

Table 1. Site Characteristics

Site	Well Drained	Moderately Well Drained	Poorly Drained	Thermokarst Wetlands
Permafrost depth (cm)	No permafrost	43 (range: 37–55)	41 (range: 36–43)	>220
Mean O layer thickness (cm)	10.5	20	90	90+
Stand density (trees ha ⁻¹)	7053 ¹	5505 ²	2626	0
Moss cover (%)	64	87	~90	~95
Dominant Moss species (%) ³	HS: 91	HS: 54, AS: 22	SS: ~40, HS: ~40, PS: ~20	SS: 100
Lichen cover (%)	28	10	~2	0
Other vegetation	<i>Arctostaphylos</i> sp., <i>Ledum</i> sp., <i>Vaccinium</i> sp., scattered <i>Betula papyrifera</i>	<i>Arctostaphylos</i> sp., <i>Ledum</i> sp., <i>Vaccinium</i> sp.	<i>Eriophorum</i> sp., <i>Betula nana</i> , <i>Ledum</i> sp., <i>Vaccinium</i> sp.	<i>Carex</i> sp., <i>Eriophorum</i> sp.

Moss cover, lichen cover, and O layer thickness for WD and MD are from Manies and others 2003

¹Manies and others 2003

²Manies, unpublished data

³HS=*Hylocomium* sp., AS=*Aulacomium* sp., SS=*Sphagnum* sp., PS=*Pleurozium* sp.

transects during the study. A stainless steel probe (3 mm i.d.) slotted at the bottom 2 cm was inserted into the soil and water was drawn through the probe using a peristaltic pump attached to the end of the probe. Samples ranging in volume from 1 to 2 L were filtered in the field through Gelman AquaPrep 600TM capsule filters (0.45 µm) into pre-baked amber glass bottles with Teflon-lined caps (the first 200 mL of pore water were used to rinse the filters and discarded). The samples were kept on ice during transport to the lab and refrigerated until analysis for DOC concentration, UV absorbance, fluorescence, and DOC fractionation.

Soil pore water samples were collected during the following time periods:

Well Drained = July 2003, April and May 2004, and May 2005, ranging from 0.5 to 17 cm depth;

Moderately Well Drained = September 2002, May–October 2003, May–September 2004, and May 2005, ranging from 0.5 to 34 cm depth;

Poorly Drained = July–September 2002 and 2003, April–September 2004, and May 2005, ranging from 2 to 43 cm depth;

Thermokarst Wetlands = July–September 2002 and 2003, and March–September 2004, ranging from 6 to 80 cm depth.

Vegetation Leachates

We collected samples of representative vegetation from each site for leaching, including *P. mariana* needles (brown needles still on trees) and bark and twigs from the Well Drained and Poorly

Drained sites; *Hylocomium splendens* (Hedw.) B.S.G. (stair-step moss) and *Pleurorium schreberii* (Brid.) Mitt. (red-stemmed leathermoss) from the Moderately Well Drained site (live, clipped; hereafter referred to as "mixed feathermoss"); *Sphagnum angustifolium* (Russow) C. Jens (live, clipped) and *Eriophorum angustifolium* Honck. (live, clipped) from the Thermokarst Wetlands; and *Betula nana* L. leaves (senesced leaves still on branches) from the Poorly Drained site. We also collected *Betula papyrifera* Marsh. leaves (senesced, recently dropped) from a stand next to the Poorly Drained site, as this tree species is commonly found near black spruce forest. Soluble organic carbon was obtained by leaching air-dried vegetation. Ten to fifty grams of vegetation (dry weight) was combined with 5–9 L of 0.001 N NaHCO₃ solution in 9 L clear pyrex jugs covered with foil. The NaHCO₃ was used to buffer pH and to mimic ionic strength of natural systems. The samples were aerated continuously using fish tank pumps and sintered glass tubes to prevent anoxia. The vegetation samples were leached for 7–14 days, during which the solutions were periodically sampled for DOC concentration, UV absorbance, fluorescence, and DOC fractionation. Replicate *Sphagnum* and feathermoss-mix vegetation samples were subjected to 3-month long leaching periods to examine changes in leachate DOC chemical characteristics with lime. The volumes removed during sampling (50–500 mL) were replaced with an equal volume of dilute NaHCO₃ solution. Samples were immediately filtered through 0.45-µm Supor syringe fil-

ters or 0.45- μm capsule filters depending on sample volume.

DOC Analyses

Pore water samples were analyzed for DOC concentration within 2 weeks of collection, and vegetation leachate samples were analyzed within one day of collection using an O.I. Analytical Model 700 TOC Analyzer via the platinum catalyzed persulfate wet oxidation method (Aiken and others 1992). The instrument was calibrated using a minimum of live standards spanning the range of sample concentrations, and standards and samples were run in duplicate (instrument std. dev. $\pm 0.2 \text{ mg C L}^{-1}$). Samples were diluted with deionized (DI) water by weight prior to DOC analysis to fall within the optimum range of the TOC analyzer ($\leq 30 \text{ mg C L}^{-1}$).

UV-Vis Absorption Analyses

Samples were analyzed for UV-Vis absorption using a Hewlett-Packard Model 8453 photo-diode array spectrophotometer ($\lambda = 200\text{--}800 \text{ nm}$) and a 1-cm path-length quartz cell. DI water was used as an instrument blank. Samples were diluted by weight with DI to be within the range of the instrument. Results are reported for absorption at $\lambda = 254 \text{ nm}$, the wavelength associated with aromatic compounds (Chin and others 1994). The standard deviation for a UV measurement at 254 nm is $\pm 0.002 \text{ AU}$. Specific UV absorbance (SUVA) of DOC gives an "average" molar absorptivity for all the molecules contributing to the DOC in a sample, and it has been used as a measure of DOC aromaticity (Chin and others 1994; Weishaar and others 2003). SUVA was determined by dividing UV-Vis absorbance at $\lambda = 254 \text{ nm}$ by DOC concentration, where each variable was measured at the same dilution factor. SUVA is reported in units of $\text{L mg C}^{-1} \text{ m}^{-1}$, with a standard deviation of $\pm 0.1 \text{ L mg C}^{-1} \text{ m}^{-1}$.

DOM Fluorescence

To further characterize the optically active portion of the dissolved organic matter (DOM), we measured 3-dimensional fluorescence of a subset of soil pore waters and vegetation leachates using a Jobin-Yvon Horiba Fluoromax-3TM fluorometer. These 3-D fluorescence intensities are referred to as Excitation-Emission Matrices (EEMs). Before analysis, an aliquot of each sample was allowed to warm to room temperature and diluted, when necessary, to remain within the range of the detector. UV-Vis was measured after dilution, as

above. EEMs were collected over an excitation range of 240–450 nm every 5 nm, and an emission range of 300–600 nm every 2 nm. A series of corrections were made to the EEMs to ensure that they were comparable among samples. DI water EEMs, which served as blanks, were collected daily and subtracted from each sample EEM. The blank-subtracted EEMs were then corrected for instrument biases using instrument-specific excitation and emission corrections files provided by the manufacturer. The EEMs were then Raman-normalized using the area under the Raman scatter peak (350 nm excitation wavelength) obtained from the corresponding DI water blank. We then corrected EEMs for inner filter effects using the UV-Vis absorbance spectra. This correction accounts for the absorption of excitation and emission light by the sample (Ohno 2002). The resulting corrected EEMs were plotted using MatLab with 30 contour lines, after normalizing fluorescence intensities to DOC concentration. The location of maximum fluorescence intensity (F_{max}) for each EEM was determined on regions unaffected by first- and second-order Rayleigh scattering (Ingle and Crouch 1988).

Two indices based on fluorescence spectra, the fluorescence index (FI) and the humification index (HIX), were determined from the EEMs. The fluorescence index is calculated as the ratio of the intensities at excitation (ex) and emission (em) wavelengths $\text{ex}370/\text{em}450$ and $\text{ex}370/\text{em}500$, and has been used to distinguish between microbially-derived ($\text{FI} = 1.7\text{--}2.0$) and terrestrially-derived ($\text{FI} < 1.4$) aquatic fulvic acids (McKnight and others 2001). The humification index is based on the suggestion that as decomposition, or humification, of fluorescing molecules proceeds, their emission spectra will shift towards longer wavelengths due to lower molecular H:C ratios (Zsolnay and others 1999). Therefore the sum of fluorescence intensities at long wavelengths can be compared to the intensities at shorter wavelengths to quantify the relative degree of humification. We calculated the humification index (HIX) from the DOC normalized fluorescence values as:

$$\text{HIX} = \sum I_{434 \rightarrow 480} / \left(\sum I_{300 \rightarrow 344} + \sum I_{434 \rightarrow 480} \right) \quad (1)$$

where $\sum I_{x \rightarrow y}$ is the sum of the fluorescence intensity at emission wavelengths $x \rightarrow y \text{ nm}$ at $\text{ex} 255 \text{ nm}$ (Ohno 2002). The HIX values range from 0

to 1, with higher values indicating an increasing degree of humification (Ohno 2002).

Parallel factor analysis (PARAFAC), a statistical modeling technique, was applied to the corrected EEMS to identify fluorescing components according to their unique excitation and emission patterns (Stedmon and others 2003; Cory and McKnight 2005). We quantified the relative contribution of thirteen different fluorescing components previously identified by Cory and McKnight (2005). Seven of these components (Q1-Q3, SQ1-SQ3 and HQ) are identified as quinone-like molecules, which vary in redox state and degree of conjugation. Tyrosine and tryptophan are identified as protein-like fluorophores, and the remaining four components are not associated with any particular molecule class (Cory and McKnight

DOC Fractionation

We used a resin-based method of DOC fractionation as a further means to characterize DOC chemistry. Soil pore water and vegetation leachate samples were chromatographically separated into five different fractions (hydrophobic acids, hydrophobic neutrals, transphilic neutrals, hydrophilic organic matter, and transphilic acids) using Amberlite XAD-8 and XAD-4 resins (Aiken and others 1992). The resins preferentially sorb different classes of organic acids based on aqueous solubility of the solute, chemical composition of the resin, resin surface area, and resin pore size. The amount of organic matter within each fraction was calculated using the DOC concentration and the sample mass of each fraction, and are presented as percentages of total DOC. UV-Vis absorption was run on hydrophobic acids (HPOA), hydrophilic organic matter (HP1), and transphilic acid (TPIA) fractions. Fluorescence was run on HPOA and HPI fractions from soil pore water collected in May 2005. The fractions were brought to neutral pH prior to fluorescence analysis using NaOH. A select number of samples were fractionated in duplicate, and the average values are presented. The standard deviation for the mass percentages of the fractionation analysis was $\pm 2\%$.

DOC Incubations

Potential DOC biodegradation was determined by incubating samples in sealed serum bottles at 22°C and measuring CO₂ production in the headspace over 28–31 days. Vegetation leachates were subsampled after 1 week of leaching for incubation. All samples were diluted to approximately 10 mg C L⁻¹ with DI water to prevent excessive microbial growth, and 50 mL aliquots were dispensed into 100 mL amber glass serum bottles (12 replicate

bottles per sample). An inoculant was prepared by mixing soil from each site with DI water, filtering a portion of the solution through a 1.6 µm glass fiber filter, and sequentially diluting the filtrate for a 10⁻³ serial dilution. One mL of dilute soil solution was added to each serum bottle. The DOC content of the dilute soil solution was below detection limits. One-eighth of a pre-baked (400°C for 4 h) glass fiber filter was added to each bottle to provide a surface for microbial establishment, and the bottles were sealed using butyl rubber stoppers. Within 2 h of sealing the serum bottles, we analyzed CO₂ in the equilibrated headspace of the serum bottles by withdrawing 0.5-mL aliquots of headspace (four reps per bottle) and injecting them into a nitrogen carrier stream passing through a Licor 6252 infrared CO₂ analyzer. The mean of the four injections was used to calculate headspace CO₂ concentration. Calibration curves were created using a minimum of three standards. On the first and last days of the incubations, three replicate bottles per sample were acidified with 2 mL 42.5%, H₃PO₄ and the headspace was analyzed for dissolved inorganic carbon (DIC) on the Licor CO₂ analyzer to ensure that all carbonate species were accounted for. The remaining replicate serum bottles were analyzed for headspace CO₂ concentration on Days 1, 3, 5, 7, 14, 21, and 28. The volume of headspace removed for analysis was replaced by an equal volume of N₂ after each sampling. Between analyses the bottles were placed upside-down on a shaker set at 100 rpm and covered with foil. On days 14 and 28 three replicate bottles per sample were opened and analyzed for DOC concentration, SUVA, and fluorescence after headspace analysis. We calculated dissolved CO₂ concentrations (headspace + aqueous) from the lab analyses and known CO₂ equilibrium constants (Plummer and Busenberg 1982) adjusted for ambient temperature and pressure (Striegl and others 2001).

Total CO₂ production over the incubation period was quantified as the difference between initial and final DIC concentrations, as this accounts for any changes in pH during the incubation, which would alter the ratio of dissolved versus gaseous CO₂. The change in DIC was assumed to originate completely from respiration of DOC, thus equaling DOC consumption. Biodegradation is expressed as % DOC mineralized (mg C-DIC produced/initial mg C-DOC).

The decomposition constants for each DOC sample were determined from the time series of cumulative DIC production, which we calculated by multiplying the CO₂ concentrations by the ratio

of total change in DIC: total change in CO_2 , assuming a constant pH (Kawahigashi and others 2004). We fitted a single exponential model (Eq. 2) and a double exponential model (Eq. 3) to the incubation results assuming one or two distinct DOC pools (Kalbitz and others 2003):

$$\text{Mineralized DOC (\% of initial DOC)} = \frac{100 * (1 - e^{-k_1 t})}{100} \quad (2)$$

$$\text{Mineralized DOC (\% of initial DOC)} = \frac{(100 - a) * (1 - e^{-k_2 t}) + a * (1 - e^{-k_1 t})}{100} \quad (3)$$

where t = time (days), k_1 = decomposition rate constant of "stable" DOC (slowly mineralizable DOC pool, day^{-1}), a = the portion of the total DOC pool that is stable (%), k_2 = decomposition rate constant of "labile" DOC (rapidly mineralizable DOC pool, day^{-1}). The curves were fitted using a least-squares regression (Levenberg-Marquardt method) in Statistica 7.0. We fitted both models to all sample incubations and determined which model best described each sample.

Statistical Analyses

We used repeated-measures ANOVA followed by Unique N HSD post-hoc analyses ($p < 0.05$; Statistica 7.0) where appropriate to test for significant differences in soil pore water DOC chemical characteristics and DOC incubation results between sites (p values are reported when significant). We partitioned the samples into seasons, designated "early" (March-May), "middle" (June-August),

and "late" (September-October) prior to statistical analyses. This allowed us to test for site by season effects, and to compare the Well Drained site, where soil pore water was present only during the early season, with the other sites. Two-factor ANOVA without replication was used to test PARAFAC results for significant differences between samples ($p < 0.05$).

RESULTS

Soil Pore Water DOC Concentrations and Chemical Characteristics

Soil pore water DOC concentrations and fractions were not significantly different between sites or seasons, so we present the mean values here (Table 2). Although spatial and temporal variability were insignificant, general trends among the sites were evident. DOC concentrations tended to be greatest at the wettest sites (Poorly Drained and Thermokarst Wetlands) and lowest at the Well Drained site. The SUVA values were high at all sites, indicating high aromatic content. The dominant DOC fraction at all sites was HPOA, accounting for more than 50% of the total DOC. The next largest fractions were HPI and TPIA, whereas the neutral fraction (hydrophobic plus transphilic neutrals) was consistently the smallest fraction at all sites.

We measured fluorescence on whole water DOC and on the HPOA and HPI fractions from one sample date (May 2005) for Well Drained, Moderately Well Drained, and Poorly Drained. The fluorescence signatures of samples from each site were very similar, and we show one example in Figure 2. (Moderately Well Drained, whole water DOC). The whole waters and DOC fractions all displayed

Table 2. Chemical Characteristics of DOC Collected from Soil Pore Waters

Site	Well Drained		Moderately Well Drained		Poorly Drained		Thermokarst Wetlands	
	Mean (SE)	<i>n</i>	Mean (SE)	<i>n</i>	Mean (SE)	<i>n</i>	Mean (SE)	<i>n</i>
WW DOC (mg C L^{-1})	55.1 (8.9)	6	67.5 (6.4)	15	76.3 (6.6)	12	91.8 (12.9)	12
WW DOC SUVA	3.8 (0.15)	6	4.2 (0.15)	14	4.5 (0.18)	12	4.0 (0.06)	12
HPOA (%)	56.2 (1.8)	6	51.9 (1.8)	15	55.9 (1.0)	12	59.3 (1.2)	12
HPOA SUVA	4.3 (0.30)	6	4.5 (0.12)	15	4.5 (0.14)	12	4.4 (0.11)	12
HPI (%)	17.8 (0.98)	6	21.6 (1.2)	13	16.4 (0.84)	12	14.4 (0.90)	12
HPI SUVA	1.9 (0.47)	6	2.3 (0.29)	12	3.2 (0.59)	7	3.5 (0.24)	10
TPIA (%)	15.2 (1.3)	6	16.8 (0.88)	15	16.4 (0.64)	12	15.8 (0.77)	12
TPIA SUVA	3.2 (0.27)	4	3.3 (0.11)	13	3.4 (0.09)	10	3.2 (0.09)	12
HPON+TPIN (%)	8.5 (3.20)	4	9.7 (1.6)	13	11.3 (0.84)	12	8.6 (2.1)	7

WW = whole water; HPOA = Hydrophobic acids; HPI = Hydrophilic organic matter; TPIA = Transphilic acids; HPON = Hydrophobic neutrals; TPIN = transphilic neutrals; SUVA = specific UV absorbance ($\text{l. mg C}^{-1} \text{ m}^{-1}$)

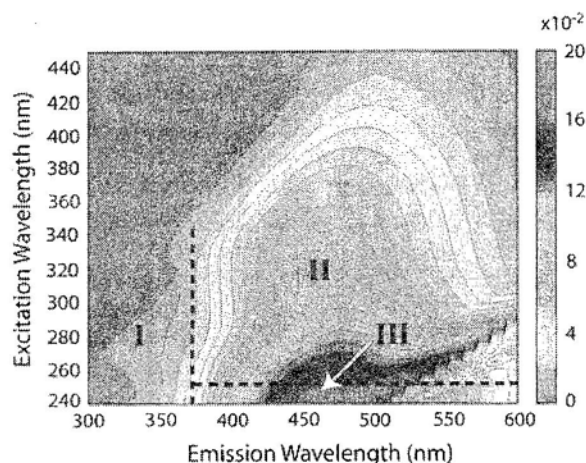


Figure 2. Fluorescence of soil pore water DOC from the moderately well drained site, 5/11/2005. The color bar to the right indicates fluorescence intensity, which has been normalized to DOC concentration. The dashed lines and roman numerals indicate regions that correspond to protein-like (I), humic acid-like (II), and fulvic acid-like fluorophores (Chen and others 2003).

maximum fluorescence intensities (F_{max}) in a region that is associated with fulvic acid fluorophores ($ex < 250/em440-504$; Stedmon and Markager 2005) (Table 3). PARAFAC analyses reveal similar trends in the dominant fluorescing components of the DOC in each sample (Table 3). The dominant fluorophore in the whole water DOC and HPOA fraction samples was Component 4, identified as a hydroquinone (HQ) by Cory and McKnight (2005), whereas Component 2, a terrestrially-derived quinone (Q2; Cory and McKnight 2005), was the greatest contributor to the HPI fractions. There is no statistical difference in the relative abundance of the fluorophores for the whole water DOC or the DOC fractions between sites.

The FI values for the soil pore water DOC samples range from 1.14 to 1.51 (Table 3), and are consistently lower for the whole water samples and HPOA fractions than the HPI fractions. The HIX values of the samples from the different sites are relatively similar (Table 3) and suggest that overall the DOC is highly humified. The HPI fractions from each site have consistently lower HIX values than the HPOA fractions, although differences were not statistically significant, possibly due to the small sample number.

Vegetation Leachate DOC Yields and Chemical Characteristics

In contrast to the soil pore waters, the vegetation leachates had large ranges in DOC yields (mg C

mg^{-1} litter dry wt) and DOC chemical characteristics (Table 4). *Betula papyrifera* leaves yielded the highest amount of DOC, whereas the lowest DOC yields were from the mixed feathermoss and *P. mariana* bark and twigs. In addition to differences in the magnitude of DOC yields, there were differences in the timing of maximum DOC yields (Table 4 Figure 3A). *P. mariana* and *E. angustifolium* litter leached increasing amounts of DOC throughout the leaching period, whereas DOC concentrations of the two moss and *B. papyrifera* leachates actually decreased after about 24 h (Figure 3A). SUVA values varied widely (Table 4), but all the vegetation leachates were less aromatic than soil pore water DOC (Table 2). There was a large range in the relative amounts of DOC fractions among the leachates (Table 4, Figure 3B), although all the leachates had higher % HPI and lower % HPOA than the soil pore water DOC.

Fluorescent properties of leachate DOC varied in intensity and in dominant regions (Table 4, Figures 4, 5). The *P. mariana* needles and *B. papyrifera* leaves leachates had the greatest F_{max} , whereas the *Sphagnum* leachate had the lowest. The *P. mariana* bark and twigs and the *E. angustifolium* leachates had F_{max} values in the same region as the soil pore waters F_{max} values. All of the other leachates had F_{max} values at $ex280/em310-350$, which is a region characterized by the protein-like fluorophores tryptophan and tyrosine (Coble 1996; Baker 2002; Jaffe and others 2004).

The relative proportions of the different DOC fractions were dynamic during the course of leaching, particularly the HPOA and HPI fractions. The ratio of HPOA:HPI increased with time to varying degrees in all the leachates (Figure 3B), but for different reasons depending on the vegetation. Shifts in HPOA:HPI were attributable to net increases in HPOA in *P. mariana* vegetation leachates, and to net decreases in HPI in the moss leachate, and the *B. papyrifera* leachate. The increases in HPOA:HPI in the *E. angustifolium* and *B. nana* leachates were due to roughly equal net increases in HPOA and net decreases in HPI over time.

During the longer-term leaching of *Sphagnum* and mixed feathermoss, there were distinct changes in DOC fluorescence intensities and regions (Figure 5). Quantifiable changes in fluorescing components, as identified by PARAFAC, and the FI and HIX values over time in the leachates indicate prominent shifts in the DOC chemical characteristics (Table 5). After 24 h of leaching Component 8, which corresponds to tryptophan (Cory and McKnight 2005) was the most abundant fluoro-

Table 3. Fluorescence Properties and PARAFAC Analyses of Soil Pore Water DOC

	Well Drained, 5 cm, 5/11/2005			Moderately Well Drained, 11 cm, 5/11/2005			Poorly Drained, 17 cm, 5/6/2005		
	Whole water	HPOA	HPI	Whole water	HPOA	HPI	Whole water	HPOA	HPI
$F_{\max}$	0.16 (240/450)	0.42 (240/452)	0.020 (240/432)	0.16 (240/456)	0.47 (240/458)	0.0063 (240/436)	0.16 (240/448)	0.32 (240/454)	0.0072 (240/444)
FI	1.27	1.17	1.49	1.27	1.14	1.45	1.23	1.20	1.51
HIX	0.94	0.94	0.77	0.96	0.96	0.84	0.95	0.95	0.85
%C1	10	13	12	10	12	14	11	13	14
%C2	17	17	21	17	17	20	18	17	20
%C3	3	2	9	2	1	6	3	2	7
%C4	26	24	11	26	28	13	23	22	13
%C5	10	9	3	11	11	3	9	9	3
%C6	7	10	3	9	11	6	9	11	5
%C7	7	4	5	6	4	5	5	3	6
%C8	0	1	4	0	0	2	0	1	3
%C9	3	1	2	2	0	1	2	1	2
%C10	4	5	7	3	3	7	4	5	7
%C11	6	7	6	6	6	9	7	8	8
%C12	5	6	11	4	4	9	6	6	8
%C13	3	2	6	3	2	6	2	2	3

$F_{\max}$ is the maximum fluorescence intensity normalized to DOC concentration, excitation and emission wavelengths follow in parentheses

FI = fluorescence index; HIX = humification index

The fluorescent components correspond to the following fluorophores as identified by Cory and McKnight (2005): C2 = Quinone 2, C4 = Hydroquinone, C5 = Semiquinone 1, C7 = Semiquinone 2, C8 = Tryptophan, C9 = Semiquinone 3, C11 = Quinone 1, C12 = Quinone 3, C13 = Tyrosine

The chemical structures of C1, C3, C6, and C10 are currently unidentified.

The component values correspond to the relative percentage of the total fluorescence.

Table 4. Chemical Characteristics of DOC from Vegetation Leachates

Vegetation Type	<i>Picea mariana</i> needles	<i>P. mariana</i> bark and twigs	<i>Sphagnum</i> <i>angustifolium</i>	Feathermoss mix	<i>Eriophorum</i> <i>angustifolium</i>	<i>Betula nana</i> leaves	<i>B. papyrifera</i> leaves
DOC yield	0.014	0.006	0.052	0.004	0.018	0.021	0.073
WW DOC SUVA	0.8	1.8	0.4	1.7	1.6	2.3	2.2
HPOA (%)	19	42	8	27	32	45	27
HPOA SUVA	2.6	3.6	3.1	3.2	3.5	3.5	4.1
HPI (%)	52	32	73	48	43	34	51
HPI SUVA	0.1	0.3	0.1	0.6	0.3	0.4	0.3
TPIA (%)	10	6	6	9	7	9	6
TPIA SUVA	1.5	1.6	0.8	2.0	1.4	1.4	1.3
HPON+TPIN (%)	19	20	13	16	18	12	16
$F_{\max}$	0.17 (280/314)	0.077 (240/440)	0.031 (280/346)	0.066 (280/342)	0.11 (240/446)	-	0.16 (280/310)

All analyses were done on DOC samples collected after 24 h of leaching, except for *E. angustifolium* and *B. papyrifera* leaves which were collected after 48 h of leaching. DOC yield, mg C mg⁻¹ litter dry wt.
 WW = whole water; HPOA = hydrophobic acids; HPI = hydrophilic organic matter; TPJA = transphilic acids; HPON = hydrophobic neutrals; TPIN = transphilic neutrals; SUVA = specific UV absorbance (L mg C⁻¹ m⁻¹).
 $F_{\max}$ is the maximum fluorescence intensity normalized to DOC concentration, excitation and emission wavelengths follow in parentheses.

phore in both leachates. After 3 months, the relative contribution of tryptophan decreased by 83–97 %. The other amino acid-like fluorophore, Component 13 or tyrosine, also decreased in relative abundance in both leachates with time. The initial rates of disappearance of tryptophan and tyrosine (24–194 h) were greater in the *Sphagnum* leachate than the feathermoss leachate. Component 4 (hydroquinone) was the dominant fluorophore at 194 h and 3 months. The components that increased the most in relative contribution to fluorescence were Components 7 and 9 (semiquinones) in both leachates, and Component 6 (unidentified) in the feathermoss and Component 12 (a quinone) in the *Sphagnum* leachates. Concurrent with these changes, the FI and HIX values increased over time (Table 5).

DOC Incubations of Soil Pore Water and Vegetation Leachates

In contrast to the soil pore water DOC chemical characteristics, DOC biodegradability exhibited noticeable trends both among sites and, in some cases, with season. The DOC collected from the Poorly Drained site was the least biodegradable, followed by the Well Drained site and Thermokarst Wetlands, whereas DOC from the Moderately Well Drained site was the most biodegradable when considering % mineralized DOC (Table 6). We present the means of the incubation results here. DOC decomposition was best described by a single pool model for all soil pore waters. The decomposition constants (k_l) of the soil pore waters followed a similar pattern as the % mineralized, with Poorly Drained DOC having the slowest k_l , followed by Well Drained, Thermokarst Wetlands, and Moderately Well Drained DOC. The half-life of DOC is almost twice as long for the Poorly Drained site than for the Well Drained and Thermokarst Wetlands sites, and more than 2.5 times that for the Moderately Well Drained site. When we compared samples based on season, the half-life of Poorly Drained-DOC was significantly longer than Moderately Well Drained-DOC during the middle and late seasons ($p < 0.01$ and $p < 0.05$, respectively). In addition, the half-life of Poorly Drained-DOC was significantly longer than Thermokarst Wetlands-DOC during the middle season ($p < 0.001$). Seasonal variation in DOC biodegradability was significant only at the Poorly Drained site, where DOC half-life was approximately twice as long during the middle season as during the early and late seasons ($p < 0.05$).

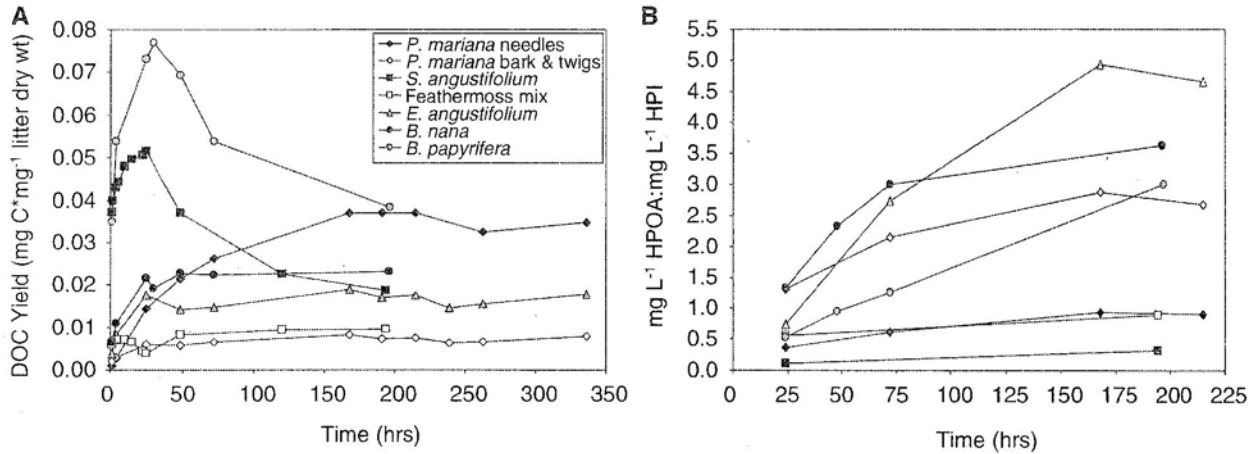


Figure 3. **A** DOC yields during vegetation leaching. **B** Change in ratios of hydrophobic acids to hydrophilic organic matter (HPOA:HPI) during vegetation leaching.

The vegetation leachates DOC had a wide range in potential biodegradability, ranging from about 11% mineralization for *P. mariana* leachates to about 90% mineralization for moss leachates (Table 6). When calculating DOC biodegradation, we included any net decreases in DOC concentration that we measured during the first week of leaching where appropriate (see Figure 3A). DOC decomposition was best described by a single pool model for all leachates except *Sphagnum* and *B. papyrifera*, which were

best described using a two pool model. *Sphagnum* DOC had the fastest decomposition constants for the labile and stable DOC pools, followed closely by mixed feathermoss DOC for the stable pool. The *P. mariana* leachates had the slowest decomposition constants, and were similar to those calculated for soil pore water DOC.

Potential DOC biodegradability of all soil pore waters and vegetation leachates combined was positively associated with initial % HPI content (Figure 6, $r^2 = 0.82$).

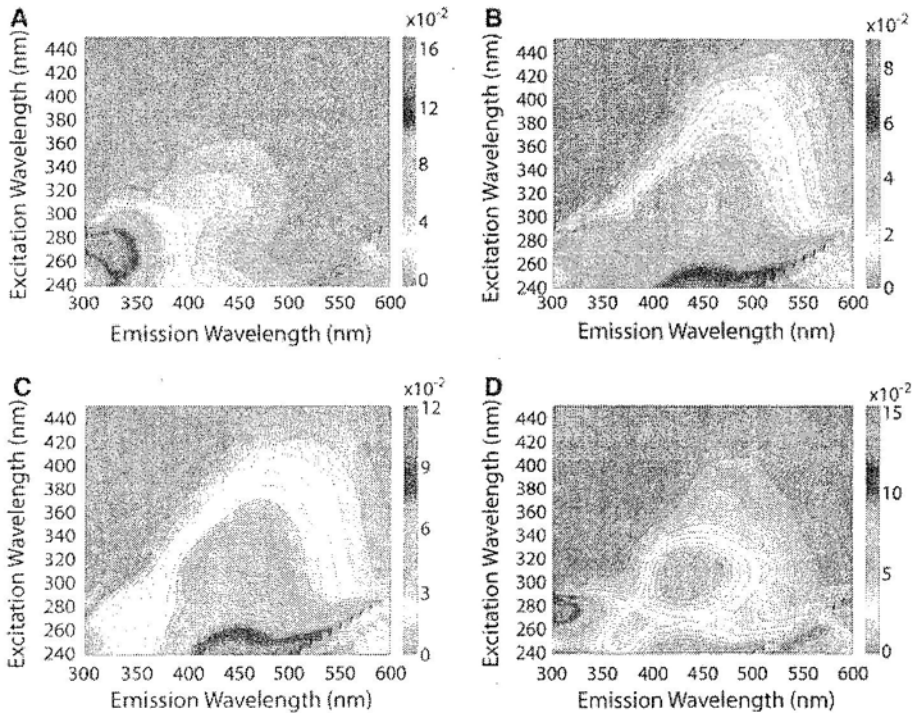


Figure 4. Fluorescence of vegetation leachate DOC after 24–48 h of leaching: **A** *Picea mariana* needles (24 h), **B** *P. mariana* bark and twigs (24 h), **C** *Eriophorum angustifolium* (48 h), **D** *Betula papyrifera* leaves (48 h). The color bar to the right indicates fluorescence intensity, which has been normalized to DOC concentration. See Figure 5 (A1, B1) for moss leachate DOC fluorescence.

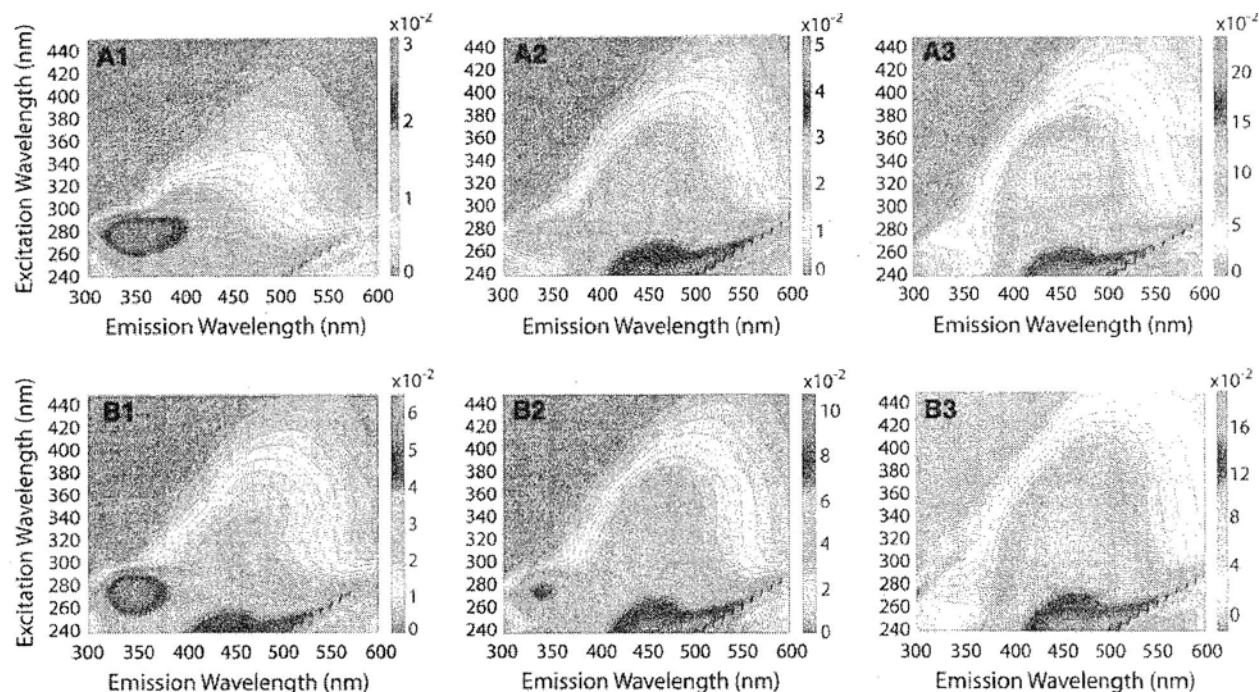


Figure 5. Change in fluorescence of moss leachate DOC over time: *Sphagnum angustifolium* at 24 h (A1), 194 h (A2), and 3 months (A3); Feathermoss mix at 24 h (B1), 194 h (B2), and 3 months (B3). The color bar to the right indicates fluorescence intensity, which has been normalized to DOC concentration.

Potential biodegradability was negatively associated with % HPOA, but to a lesser degree ($r^2 = 0.50$; not shown). The variability in soil pore

water DOC biodegradability alone was not significantly correlated with % HPI, % HPOA, or any other measured DOC chemistry parameter.

Table 5. Fluorescence Properties and PARAFAC Analyses of Moss Leachate DOC over Time

Time	<i>Sphagnum angustifolium</i>			Feathermoss mix		
	24 h	194 h	3 months	24 h	194 h	3 months
FI	1.14	1.26	1.38	1.17	1.30	1.38
HIX	0.61	0.83	0.89	0.68	0.79	0.90
%C1	5	10	11	7	9	10
%C2	9	14	17	15	17	19
%C3	7	3	4	2	2	3
%C4	13	22	22	14	18	19
%C5	4	8	7	6	6	9
%C6	4	5	4	2	2	5
%C7	2	4	7	5	7	9
%C8	29	4	1	18	9	3
%C9	1	2	4	1	2	4
%C10	7	9	8	5	6	7
%C11	3	5	5	6	6	6
%C12	1	6	4	6	5	5
%C13	15	9	5	12	11	3

FI = fluorescence index; HIX = humification index.

The fluorescent components correspond to the following fluorophores as identified by Cory and McKnight (2005): C2=Quinone 2, C4=Hydroquinone, C5=Semi-quinone 1, C7=Semi-quinone 2, C8=Tryptophan, C9=Semi-quinone 3, C11=Quinone 1, C12=Quinone 3, C13=Tyrosine.

The chemical structures of C1, C3, C6, and C10 are currently unidentified.

The component values correspond to the relative percentage of the total fluorescence.

Table 6. DOC Incubation Results

Sample	Mineralized DOC (%)	% Labile DOC	% Stable DOC	k ₂ (day ⁻¹)	k ₁ (day ⁻¹)	Half-life Labile	Half-life Stable
Well Drained							
Mean	13.4	0	100	–	0.00478	–	179
std error	5.8				0.00140		40
n	4				4		4
Moderately Well Drained							
Mean	15.3	0	100	–	0.00619	–	122
std error	1.6				0.00078		13
n	7				7		7
Poorly Drained							
Mean	6.6	0	100	–	0.00259	–	327
std error	1.3				0.00045		65
n	7				7		7
Thermokarst Wetlands							
Mean	13.4	0	100	–	0.00553	–	167
std error	2.6				0.00105		38
n	7				7		7
<i>P. mariana</i> needles	11.4	0	100	–	0.00440	–	158
<i>P. mariana</i> bark and twigs	10.9	0	100	–	0.00384	–	180
<i>Sphagnum angustifolium</i>	93.0	31.5	68.5	0.6332	0.05840	1.1	12
Feathermoss mix	89.0	0	100	–	0.05548	–	12
<i>E. angustifolium</i>	21.9	0	100	–	0.00898	–	77
<i>B. papyrifera</i> leaves	59.8	49.8	50.2	0.4316	0.00800	1.6	87

Mineralized DOC is % of total DOC.

k₁ and k₂ are decomposition constants derived from equations 2 and 3.

Half-life values are in days.

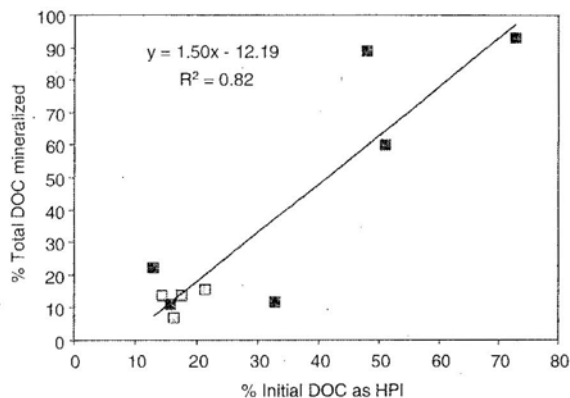


Figure 6. Initial percent hydrophilic organic matter (% HPI) in soil pore water DOC and vegetation leachate DOC versus percent total DOC mineralized during one month incubations. Gray squares, soil pore waters (means), black squares, vegetation leachates. The line represents the linear regression of all points.

DISCUSSION

DOC collected from black spruce forest soils ranging in drainage and permafrost regime was dominated by hydrophobic compounds and was

generally slow to degrade, whereas DOC leached from representative vegetation contained potentially large amounts of hydrophilic compounds and ranged from slow to fast biodegradability. Soil pore water DOC chemistry was not reflective of vegetation leachate DOC chemistry probably because the highly biodegradable compounds were quickly consumed and respired as CO₂ and/or CH₄, leaving the more recalcitrant compounds to accumulate in the soil solution (van Hees and others 2005). Forest soils characterized by poor drainage and shallow permafrost contained the least labile pore water DOC, suggesting that the large DOC pools in these systems have undergone significant microbial processing, and that relatively recalcitrant DOC accumulates as a result of slow hydrologic transport out of the system.

Soil Pore Water DOC Chemical Characteristics and Biodegradability

Soil pore water DOC concentrations were generally highest in the wettest sites (Thermokarst Wetlands > Poorly Drained > Moderately Well Drained > Well Drained), which is likely a result of

differences in organic soil layer thickness, water availability, redox potential, and water residence times. Organic layer thickness increases by almost tenfold from the Well Drained to the Thermokarst Wetlands sites, which has two implications for DOC concentrations. First, there is a much larger potential DOC source in the sites that have more soil organic C (Hope and others 1997). Second, sites with thicker O horizons have comparatively deep mineral soil horizons, so pore water DOC must be transported further to sorb to mineral soils. Shallow permafrost further isolates DOC from mineral soils, particularly at the Poorly Drained site, by blocking vertical transport. Differences in water availability among the sites may affect DOC concentrations by influencing DOC production (Christ and David 1996), and by increasing the potential for OC compound dissolution. Free soil pore water is present at varying depths during the entire snow-free season at the Thermokarst Wetlands and Poorly Drained sites, and is often present at the Moderately Well Drained site. However, free soil pore water is rarely present at the Well Drained site except during spring snowmelt before the seasonal ice layer disappears. Finally, poor drainage conditions likely result in longer residence times of water, and thus of DOC, at the Thermokarst Wetlands and Poorly Drained sites. Hongve (1999) suggested that high DOC concentrations found in poorly drained peat are due primarily to long water retention times.

Soil pore water DOC collected from all the sites was highly aromatic and dominated by the HPOA fraction (Table 2), which is consistent with other studies of soil pore waters (Guggenberger and Zech 1994; Cronan and Aiken 1985; McKnight and others 1985; Qualls and Haines 1991; Michaelson and others 1998; Smolander and Kitunen 2002). Fluorescence analyses further highlight the similarity in DOC chemical characteristics among the sites (Table 3). Fluorescence analyses of the DOC fractions indicate that there may be differences in sources and degree of humification of the different fractions (McKnight and others 2001; Ohno 2002). In particular, the FI and HIX values suggest that in soil pore waters the HPOA fraction is strongly derived from terrestrial plant sources and has undergone extensive microbial processing, whereas the HPI fraction is a mixture of terrestrially- and microbially-derived compounds and is relatively less humified. Comparison of the HIX values of the HPI fractions from the three sites suggest that this fraction is more degraded in Poorly Drained-DOC.

The range in decomposition rate constants (kl) of soil pore water DOC was similar to values mea-

sured for DOC from other terrestrial ecosystems (Kalbitz and others 2003; McDowell and others 2006). The relatively low potential biodegradability of soil pore water DOC is consistent with the generally low hydrophilic content, as that is regarded as the most biodegradable fraction (Qualls and Haines 1992; Jandl and Sollins 1997; Qualls 2005). Among the sites, Poorly Drained-DOC was the least biodegradable, and had a significantly longer half-life than Moderately Well Drained- and Thermokarst Wetlands-DOC. The differences in biodegradability are likely due to a combination of DOC residence time (that is, age of DOC), extent of prior microbial processing, and of source material. Vegetation may account for much of the difference in DOC biodegradability between the Poorly Drained and Thermokarst Wetlands sites (Table 1). The primary vegetation at the Thermokarst Wetlands site is *Sphagnum* moss, a source of highly labile DOC as shown in this study. The Poorly Drained site has comparatively less *Sphagnum* moss, and it has more black spruce trees, which are a source of more recalcitrant DOC (this study). Low oxygen availability at the Thermokarst Wetland site may also serve to slow in situ decomposition (Bastviken and others 2004), resulting in the "preservation" of more labile DOC compounds. The Well Drained site has the highest density of black spruce trees and the least moss cover (Table 1), and thus potentially the least labile DOC sources. However, the smaller DOC pool at the Well Drained site is transient as the soils drain quickly after spring thaw, so there may not be the opportunity to accumulate more recalcitrant DOC in soils at this site.

Vegetation Leachate DOC Chemical Characteristics and Biodegradability

Soluble OC yields from various boreal forest vegetation species ranged from less than 1 to 7%, of dry litter mass, although these yields are conservative as some DOC was likely lost to respiration, especially from the highly biodegradable DOC leachates. These values are similar in magnitude to DOC yields measured from a wide range of vegetation from very different ecosystems, including subalpine and tropical plant species (Cleveland and others 2004). The relatively narrow range in DOC yields that we measured from the various vegetation types is in striking contrast to the very broad range in potential biodegradability of this DOC, which spanned from approximately 10 to 90%, DOC loss over one month. The variability in potential DOC biodegradation was highly correlated with the relative amounts of hydrophilic DOC in the vegeta-

lion leachates (Figure 6). Qualls (2005) more narrowly defined hydrophilic neutrals as the most labile DOC fraction, and hydrophilic acids as the least labile. We did not separate the hydrophilic fraction into neutrals and acids (the fraction we call HPI includes both), and this may explain why some leachates, such as *P. mariana* needles, had a large HPI fraction but a low potential biodegradability (33% DOC as HPI at the start of the incubation, 11% total DOC mineralized). Presumably, the HPI fraction from *P. mariana* needles was predominantly composed of HPI-acids. This may be the case for the soil pore water HPI DOC as well.

The high potential biodegradability of DOC leached from the mosses is opposite of what we expected, based on low decomposition rates reported for both *Sphagnum* moss and *Hylocomium splendens* (Hobbie 1996; Aerts and others 1999). Slow *Sphagnum* decomposition rates have been attributed to low concentrations of nutrients, high concentrations of decay-resistant compounds, and the release of decay inhibitors (Painter 1991; Johnson and Damman 1993; Verhoeven and Toth 1995; Aerts and others 1999). However, our results demonstrate that DOC leached from some *Sphagnum* and feather mosses is highly biodegradable, and results from other studies provide supporting evidence of this. Moore and Dalva (2001) measured moderately high rates of CO₂ production during incubation of fresh *Sphagnum fuscum* and *Sphagnum magellanicum* moss under saturated conditions. It is possible that DOC leached from the *Sphagnum* fueled this respiration. Carlton and Read (1991) found that *Pleurozium schreberi* leachate contained sufficient nutrients to support growth of mycorrhizal fungi in pure culture. Therefore, some mosses contain very labile soluble C compounds, while at the same time have recalcitrant structural components. Whether this is the case for most moss species needs to be investigated further.

Transformation of DOC Chemistry by Microbial Metabolism

The changes in the HPOA:HPI ratios of the vegetation leachates (Figure 3B) and the moss leachate fluorescence (Figure 5) demonstrate that as DOC undergoes microbial processing certain compounds are selectively removed while other compounds remain, increasing in relative abundance. Specifically, the labile HPI fraction was metabolized and decreased in absolute abundance whereas the HPOA fraction became relatively enriched. In terms of tile fluorescent components, the protein-like components were preferentially metabolized while

certain quinone- and semiquinone-like components increased in relative abundance. Over time, the distinct chemical signatures of the fresh vegetation leachates became more similar to each other, and to the chemical characteristics of DOC in the soil pore waters.

The transformation of DOC by microbial metabolism may in part explain the absence of significant site-dependent and seasonal variability in soil pore water DOC chemical characteristics, and explain the distinct differences between vegetation leachates and soil pore water DOC properties (Figure 7). For example, mosses may contribute significant amounts of DOC to the forest floor (Wilson and Coxson 1999; Moore 2003), but the chemical signature of fresh moss-derived DOC was absent from soil pore waters because much of this DOC is highly labile and disappears on the order of days. Although much of the moss-derived DOC is mineralized quickly, the microbially altered DOC remaining in the leachate resembles the chemical character of soil pore water DOC. The chemical character of the soil pore water DOC also resembles *P. mariana* bark and twigs leachate DOC, although this type of biomass is relatively less abundant in these sites and has less direct contact with soils than the mosses. Other sources of DOC, including plant root exudates and microbial enzymes and biomass (Thurman 1985; Guggenberger and Zech 1994), likely contribute to soil pore water DOC chemical characteristics as well.

CONCLUSIONS

Boreal black spruce forest soils generally contained relatively recalcitrant DOC in their pore waters, although this was not due to the lack of labile DOC source material. *Sphagnum* mosses and feathermosses, which often form continuous groundcover on the forest floor, leached DOC that is characterized by high hydrophilic DOC content and high potential biodegradability. Most of the moss-derived DOC can be respired on the order of days, leaving behind more recalcitrant DOC that has not been consumed, and DOC from other vegetation, to accumulate in soil pore waters. The chemical nature of DOC from different vegetation species, rather than differences in the rate of DOC supply, dictates the fate of plant-derived DOC in soils. Drainage condition, which varies with permafrost depth, appears to be an important influence on both the size of the DOC pool and of the extent of accumulation of more recalcitrant DOC compounds. The biodegradation of plant and litter-derived DOC may be a significant source of heterotrophic respiration in surface soils of

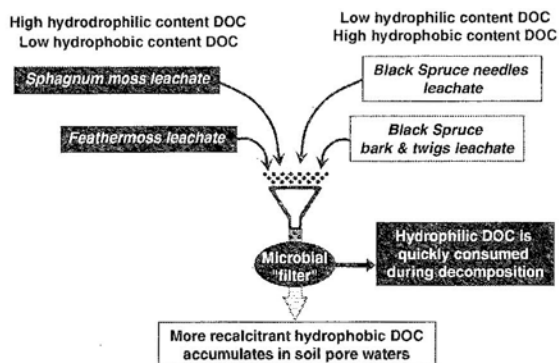


Figure 7. Conceptual illustration of changes in DOC chemical characteristics as a result of microbial metabolism in boreal black spruce forest soils. Vegetation and litter leachates of varying DOC chemical character leach into the soil environment, where they undergo microbial processing. Labile hydrophilic compounds in the DOC mixture are quickly metabolized and respired, while more recalcitrant hydrophobic acids and DOC compounds altered by microbial metabolism remain in the soil pore waters and may accumulate over time.

black spruce forests and Sphagnum-dominated wetlands, as has been suggested for other terrestrial ecosystems (Jandl and Sollins 1997; Chasar and others 2000; van Hees and others 2005).

Based on the results of this study, we suggest that there are at least two mechanisms through which climate change at northern latitudes may be influencing the chemical characteristics and cycling of terrestrially-derived DOC: shifts in vegetation distributions and changes in water residence times. Shifting vegetation distributions at local scales, such as those resulting from thermokarst wetland formation, and regional scales, such as increasing shrub abundance in the arctic tundra (Sturm and others 2005), may be changing DOC chemical characteristics through the introduction of new types of plant-derived DOC. It may be difficult, however, to detect these chemical changes in situ due to changes in the DOC chemical character that occur during microbial metabolism. Further studies of plant-derived DOC leachate chemical characteristics and biodegradability will be instrumental in determining the effects of vegetation distribution shifts. Changes in water residence times across the landscape as a result of permafrost thaw may be having significant impact on the chemical nature and biodegradability of DOC transported to aquatic systems. Increased water residence times allows greater opportunity for microbial metabolism of DOC in soils, whereas decreased residence times likely results in the transport of more labile DOC to surface waters.

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